THE ORGANOMETALLIC CHEMISTRY OF TITANIUM AND ZIRCONIUM

by

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Academic Qualifications of the Submitter

Honours B.Sc. (Sydney), 1950

M.Sc. (Sydney), 1952

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Since 1954 I have been employed on research at C.S.I.R.O., Melbourne.

[redacted]

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FOREWORD

The work described in this submission formed part of a programme of investigation of the organometallic chemistry of metals of economic importance to Australia and was initiated by the submitter, Peter C. Wailes. Papers 1,2,4 and 5 resulted from a collaboration with A. F. Reid of the Division of Mineral Chemistry, C.S.I.R.O. while the remaining work was carried out in the Division of Organic Chemistry and later the Division of Applied Chemistry, C.S.I.R.O., either personally or under my supervision, and is based on original ideas. As senior author I have checked the results, written the papers and developed any theme they may contain. Publication 34 is a review of fifty-three pages incorporating much of my own work and was written at the request of the editors of Advances in Organometallic Chemistry.

Although ineligible for consideration in this submission several papers published in the last twelve months[35-42] are included in an Appendix for reference purposes and to show how the work is being developed. In addition a book now in press[43] illustrates the perspective of this work relative to that of others.

The Organometallic Chemistry of Titanium and Zirconium.

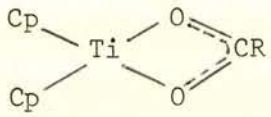
Introduction

The organometallic chemistry of titanium and zirconium has developed rapidly since the 1950's when the first compounds were prepared; namely, phenyltitanium triisopropoxide[S1] and bis(cyclopentadienyl)-titanium dihalides[S2]. Work in this area has no doubt been encouraged by the activity of these metal derivatives in Ziegler-Natta catalysis and in nitrogen fixation.

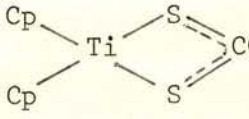
By far the major part of this work deals with the cyclopentadienyl derivatives since the stability imparted by this unique ligand has allowed the isolation of numerous organotitanium and organozirconium compounds. The papers included in this submission cover firstly, new methods for preparing cyclopentadienyl derivatives (including those of titanium and zirconium), either from lower-valent halides or by employing magnesium cyclopentadienide in solution or in the molten state[2,4,5]. The last method allows the use of anhydrous metal fluorides as starting materials which no other method will allow. Two patents were filed covering the preparation and use of magnesium cyclopentadienide[6,7]. The remainder of the papers describe the use of cyclopentadienyltitanium (and zirconium) halides as starting materials for the synthesis of a wide range of new derivatives containing titanium and zirconium in oxidation states of 4,3 and 2.

The preparation of bis(cyclopentadienyl)titanium(III) chloride in quantity for the first time[2] led to a study of its magnetic properties and a comparison with those of $TiCl_3$, $CpTiCl_2$ and $Cp_2Ti(\underline{h}^2\text{-}C_5H_5)$[14]. More recently all of the halides, Cp_2TiX, where X = F, Cl, Br or I, have been synthesised and compared[38]. These compounds were found to be dimeric with bridging halogens, so that the series offers a unique opportunity to study the effect of the availability of orbitals of the bridging halide atom on metal-metal interaction in dimeric systems.

$(Cp_2TiCl)_2$ dissolves readily in air-free water to give a bright blue solution with the molar conductance of a 1:1 electrolyte solution. The Cp_2Ti^+ ion can be precipitated by a great variety of anions giving extremely air-sensitive and highly coloured titanium(III) derivatives. The carboxylates[11], thiocarboxylates[13], dithiocarbamates[17,24] and xanthates[25] are unusual in that the bidentate ligands do not bridge but form four-membered rings with the titanium atom leading to monomeric, volatile compounds; eg. the carboxylates



, and xanthates,



.

The green sulphate, $Cp_2TiO_2SO_2TiCp_2$, contains two such four-membered rings[15]. In all of these compounds the magnetic moments show the spin-only value (1.73 BM/Ti), independent of temperature.

Antiferromagnetic behaviour was noted in the case of the carbonate, $(Cp_2Ti)_2CO_3$[15], the tetraphenylborate, $(Cp_2Ti.BPh_4 3H_2O)_2$[18] and the pseudohalides, Cp_2TiX, where X = CN, NCS or NCSe[10,43]. In each case the compound is polymeric so that exchange occurs via bridging groups.

Reaction of $(Cp_2TiCl)_2$ with sodium tin triphenyl or lithium germanium triphenyl led to the first titanium-metal bonded compounds[12], $Cp_2TiMPh_3.THF$, where M = Sn or Ge, and the titanium(IV) derivatives, $Cp_2Ti(Cl)MPh_3$. In addition, $(Cp_2TiCl)_2$ was found to undergo oxidative addition reactions in that it split disulphides giving thiolato derivatives[8], $Cp_2Ti(Cl)SR$, and reacted with HN_3 to give $(Cp_2TiCl)_2NH$ with liberation of nitrogen[27].

Convenient new methods for the synthesis of monocyclopentadienyl dihalides, $CpTiX_2$, where X = Cl, Br or I, were developed using the readily available titanium(IV) halides, $CpTiX_3$, as starting materials[28,31]. Previous to this work only the chloride, $CpTiCl_2$ had been made[S3]. An investigation of the physical and chemical properties of the halides and other derivatives of mono(cyclopentadienyl)titanium(III) compounds was then carried out[31,35,39-42]. The behaviour of these compounds is closer to that of $TiCl_3$ than to that of $(Cp_2TiCl)_2$. The halides, $CpTiX_2$, are polymeric but the magnetic interaction between neighbouring titanium atoms is weak. Conductivity and spectral data indicate that the titanium is probably octahedral in such compounds, and indeed, the isolation of complexes of type $(CpTiL_5)^{2+}.2BPh_4^-$, where L is CH_3CN or pyridine, supports this contention.

In contrast almost all of the accompanying data on bis(cyclopentadienyl)titanium(III) compounds indicate that the Cp_2Ti^{III} moiety adopts a pseudotetrahedral stereochemistry. Throughout all of this work involving titanium(III) the magnetic and spectroscopic properties of all compounds have been recorded. The visible spectra of almost all of the forty-six new bis(cyclopentadienyl)titanium(III) compounds described are characterized by three bands at 10-11, 13-14 and 16-17 kK, probably ascribable to d-d transitions, but the symmetry is so low that it is doubtful if any meaningful conclusions can be reached from such data at this time.

Although the chemical behaviour of zirconium is similar to that of titanium in many respects, a study of the organometallic chemistry of these metals has brought out many differences. Much of this distinction, including the relative inefficiency of zirconium derivatives in Ziegler-Natta catalysis, is probably due to the difficulty in reduction of compounds of zirconium compared with those of titanium. Thus while metal alkyls and hydrides reduce titanium(IV) to titanium(III), these reagents with zirconium derivatives form alkyl and hydrido derivatives without a drop in oxidation number of the metal.

It was found in these laboratories in 1969 that several new zirconium hydrides could be prepared from aluminium hydrides and cyclopentadienylzirconium halides[21,22]. The products were $Cp_2Zr(H)Cl$, $Cp_2Zr(H)AlH_4$, $Cp_2Zr(H)CH_3$ and $(Cp_2ZrH)_2O.Cp_2ZrH_2$. A convenient synthesis of the known dihydride, Cp_2ZrH_2, was also developed. All of these compounds are polymerized through bridging hydrido groups leading to absorption in the infra-red around 1300-1500 cm^{-1}, instead of 2000 cm^{-1} as is found in

terminal M-H complexes. The assignment of these bands was strengthened by comparison with the deuterido analogues of all of the compounds.

Despite their insolubility the zirconium hydrides are active hydrogenation catalysts for olefins and acetylenes[37]. Under milder conditions addition of Zr-H across carbon-carbon multiple bonds occurs forming new alkyl and alkenyl zirconium derivatives[29]. The hydrides will also reduce organic carbonyl groups[23] and form soluble bimetallic complexes with aluminium derivatives[22], an example of which is the compound from Cp_2ZrH_2 and trimethylaluminium which contains both Zr-H-Zr and Zr-H-Al moieties[36].

Synthesis of lower-valent zirconium species has been possible using strong reducing agents such as complexes of sodium with naphthalene or 2,2'-bipyridyl[30], while another approach utilizes the instability of the alkyl derivatives of zirconium. Thus $Cp_2Zr(CH_3)_2$ in petrol at 110° can be hydrogenated to $[Cp_2Zr(CH_3)]_2$[33].

Alkyl derivatives of titanium and zirconium were found to react readily with sulphur dioxide and nitric oxide[32,33], the incoming ligand inserting between one of the alkyl groups and the metal to form sulphinates and N-nitrosohydroxylamine derivatives respectively. In the case of zirconium, insertion between the metal and one of the cyclopentadienyl groups was observed for the first time. The more basic the other groups attached to zirconium, the more labile the cyclopentadienyl ligands become.

The sensitivity to moisture and/or to oxygen has meant that all of the work described in the papers submitted has been carried out

in an inert atmosphere, either in a nitrogen-filled glove-box or in a stream of purified argon. All analytical procedures were accomplished similarly. In collaboration with the Australian Microanalytical Service, a technique was developed for analysis of air-sensitive materials for carbon, hydrogen and nitrogen. A weighed pellet of the substance is sealed in an aluminium capsule in a glove-box and the whole capsule is then burned in a combustion tube.

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The characterisation of solid cyclopentadienyl metal compounds by their near infra-red reflection spectra

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(*Received* 31 *December* 1963)

Abstract—A simple technique has been developed for obtaining reflection spectra from solids and the near infra-red combination spectra of a number of cyclopentadienyl compounds have been recorded. The method makes possible the spectral identification of the cyclopentadienyl ring structure in reactive solid compounds and complements proton magnetic resonance and infra-red transmission spectra characterizations. The combination spectra above 3800 cm^{-1} are similar and characteristic of a C_5H_5 ring bonded with five-fold symmetry to a metal atom, and with, as a particular feature, a single sharp CH stretching overtone at 6100–6200 cm^{-1}. The spectra of the solids are compared with near infra-red solution spectra obtained for ferrocene and $C_5H_5TiCl_3$; the combination spectrum of ferrocene is assigned from its known fundamentals.

Introduction

The near infra-red combination and overtone spectra of cyclopentadienyl compounds have not previously been reported, except in part for solid ferrocene [1]. This region of the spectrum offers a convenient alternative to the examination of the often reactive cyclopentadienyl compounds in the 600–4000 cm^{-1} region.

In the present work the near infra-red solution spectra of ferrocene and $C_5H_5TiCl_3$ and the reflection spectra of a large number of solid cyclopentadienyl metal compounds with one to four rings per molecule, or with various halogens or other groups also attached to the metal, have been recorded and found to show striking similarity.

The fundamental infra-red spectra of cyclopentadienyl metal compounds also show marked similarities, and have been discussed by a number of authors [2–7]. The fundamental spectra are largely derived from the vibrations of the C_5H_5 moiety, but ring–metal vibrational frequencies in the 100–800 cm^{-1} region [1, 6] also contribute. The near infra-red spectra are due to combinations of the fundamental frequencies. Their great similarity above 3800 cm^{-1} is shown to be characteristic

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of a C_5H_5 ring bonded with five-fold symmetry to a metal atom. The near infra-red spectra of ferrocene both in solution and as the solid are examined in detail and the combination bands are assigned.

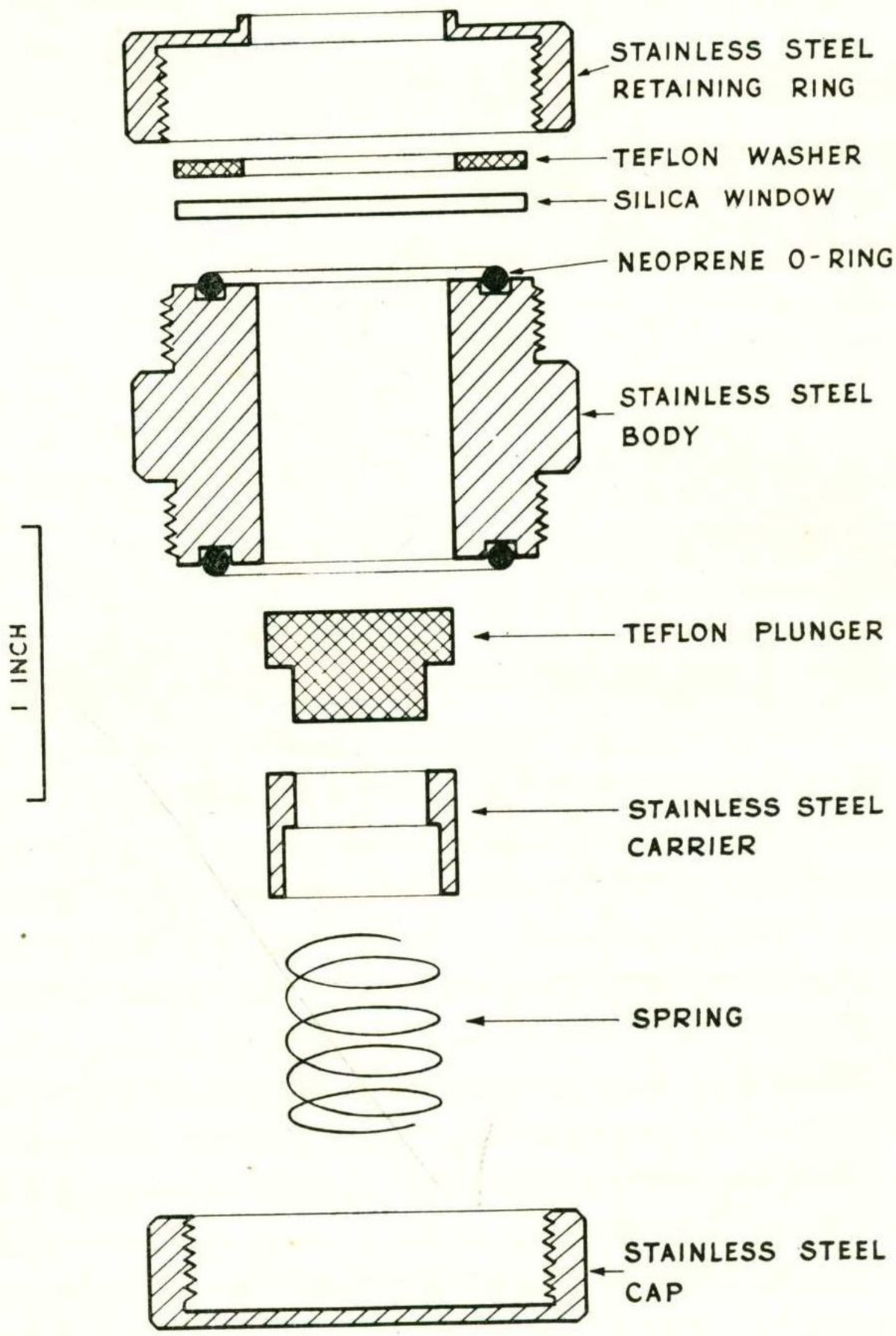


Fig. 1. Sample cell for use with Beckman DK–2A Reflectance housing.

Experimental

Cyclopentadienyl compounds

Most of the cyclopentadienyl compounds studied were made by standard methods [3, 4] and were usually purified by vacuum sublimation. Air sensitive compounds were transferred in vacuum or in an argon filled dry box. Titanium and zirconium compounds were made by methods following those of Sloan and Barber [8] and Gorsich [9], and by methods to be described elsewhere. The compound $[(C_5H_5)_2ZrCl]_2$ was prepared by the action [10] of aniline on $(C_5H_5)_2ZrCl_2$,

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and $(C_5H_5)_2TiCl$ by the action [11] of zinc dust on $(C_5H_5)_2TiCl_2$ at 275°C. The tetracyclopentadienyls of thorium [12] and uranium [13] were prepared by a method yet to be published. The uranium compound was found to sublime at 200–220°C, contrary to an earlier report [13]. X-ray powder photographs showed the thorium and uranium compounds to be isomorphous.

The method of LIPPINCOTT and NELSON [6] was used to prepare *d*-ferrocene. Two successive equilibrations of a 10:1 weight ratio of $Ca(OD)_2$ and ferrocene in sealed and evacuated tubes at 320°C gave better than 80 per cent exchange, sufficient to allow the major *d*-ferrocene bands to be distinguished from those of ferrocene; the spectra of 50 per cent and 65 per cent exchanged materials were also recorded. The relative intensities of the CH stretching overtone band at 6120 cm^{-1}, and of the CD band at 4570 cm^{-1}, were used to determine the extent of exchange. Use of the solid obviates recovery of the labelled compound from solution.

Spectra

The spectra of the solid compounds from 3600–30,000 cm^{-1} were obtained as diffuse reflectance spectra, using a Beckman DK–2A recording spectrophotometer fitted with a reflectance attachment. A blank plate covered with magnesium oxide was used as reference. Samples were pressed against a silica window by means of a spring-loaded "Teflon" plunger in a metal cell sealed with neoprene *o*-rings (Fig. 1). For reactive samples the cell was loaded in a dry box. In most cases crystals of 0·05 to 0·5 mm dimensions were simply crushed against the window; more intense spectra, with no significant shifts in peak positions, were obtained by this means rather than by use of finely ground powder. A sample weight of 100 mg was usually taken, but 5–10 mg were sufficient to give an identifiable spectrum, even with the "Teflon" backing only partially covered. From Fig. 3, it can be seen that the reflection spectrum of solid ferrocene is approximately as intense as that of a 0·1 M solution in carbon tetrachloride with a 10 cm path. The spectra of compounds in carbon tetrachloride solution were recorded from 3000–10,000 cm^{-1} with a Beckman DK–2 spectrophotometer using silica cells, and below 4000 cm^{-1} with a Perkin–Elmer model 21 machine, using sodium chloride optics and cells.

The method of measurement of reflection spectra discussed here is applicable also to the ultra-violet and visible regions and can be used with advantage for those solids exhibiting characteristic solid state spectra. All of the solid cyclopentadienyl compounds were found to absorb strongly and continuously in the ultra-violet. A number of the compounds exhibited electronic transition bands in the visible and near infra-red and these in some cases—e.g. $(C_5H_5)_2Co$ and $(C_5H_5)_4U$—overlapped with the C_5H_5 spectra.

RESULTS AND DISCUSSIONS

The near infra-red spectra of a number of cyclopentadienyl metal compounds are shown in Fig. 2, and that of ferrocene in Fig. 3(c). The near infra-red solution spectra of ferrocene and $C_5H_5TiCl_3$ are shown in Figs. 3 and 4. In Table 1 are listed

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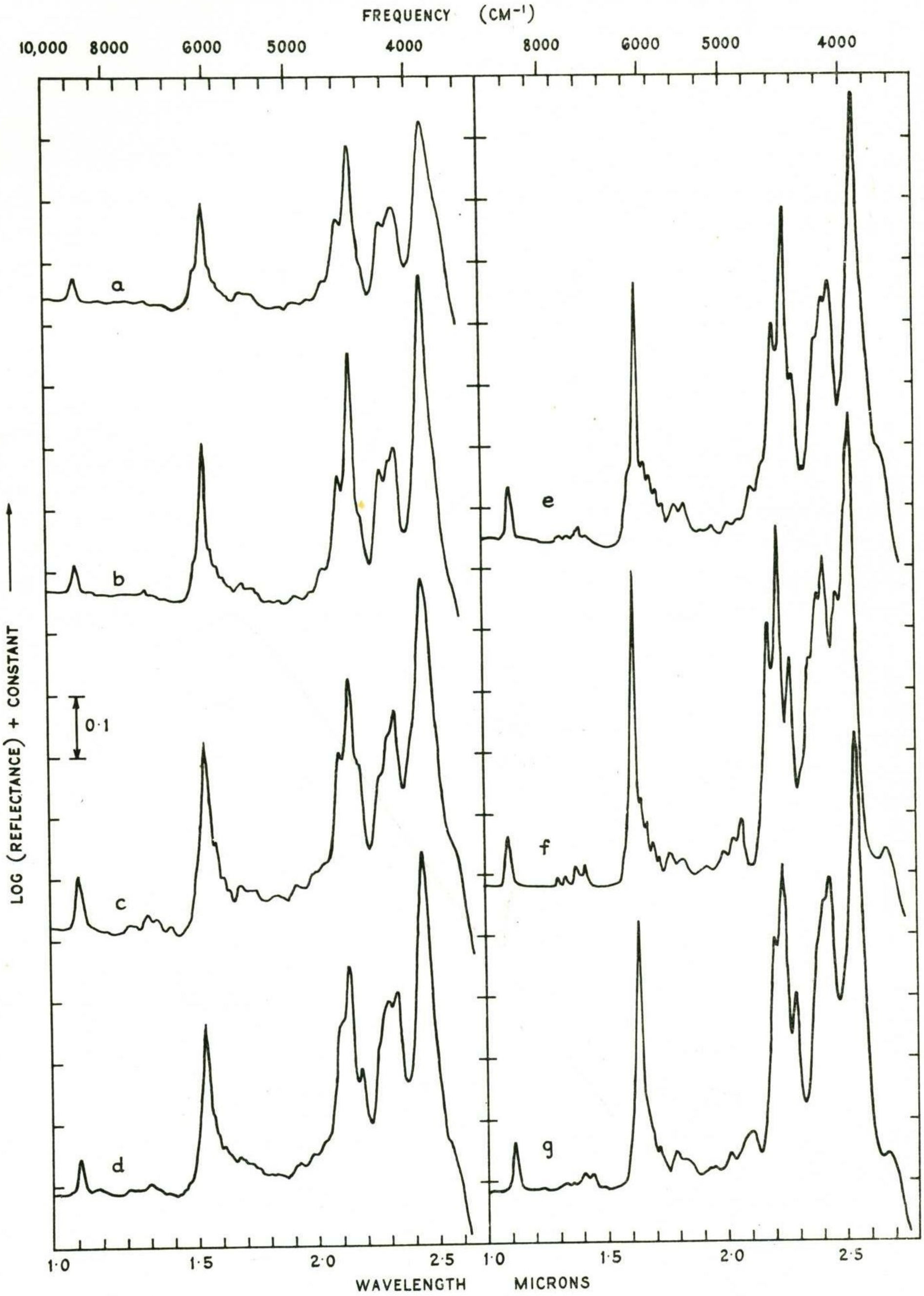


Fig. 2. Near infra-red reflection spectra of representative solid cyclopentadienyl compounds.

(a) C_5H_5Tl
(b) $(C_5H_5)_2Pb$
(c) $(C_5H_5)_3Sc$
(d) $(C_5H_5)_4Th$
(e) $(C_5H_5)_2Mg$
(f) $C_5H_5TiCl_3$
(g) $(C_5H_5)_2ZrCl_2$

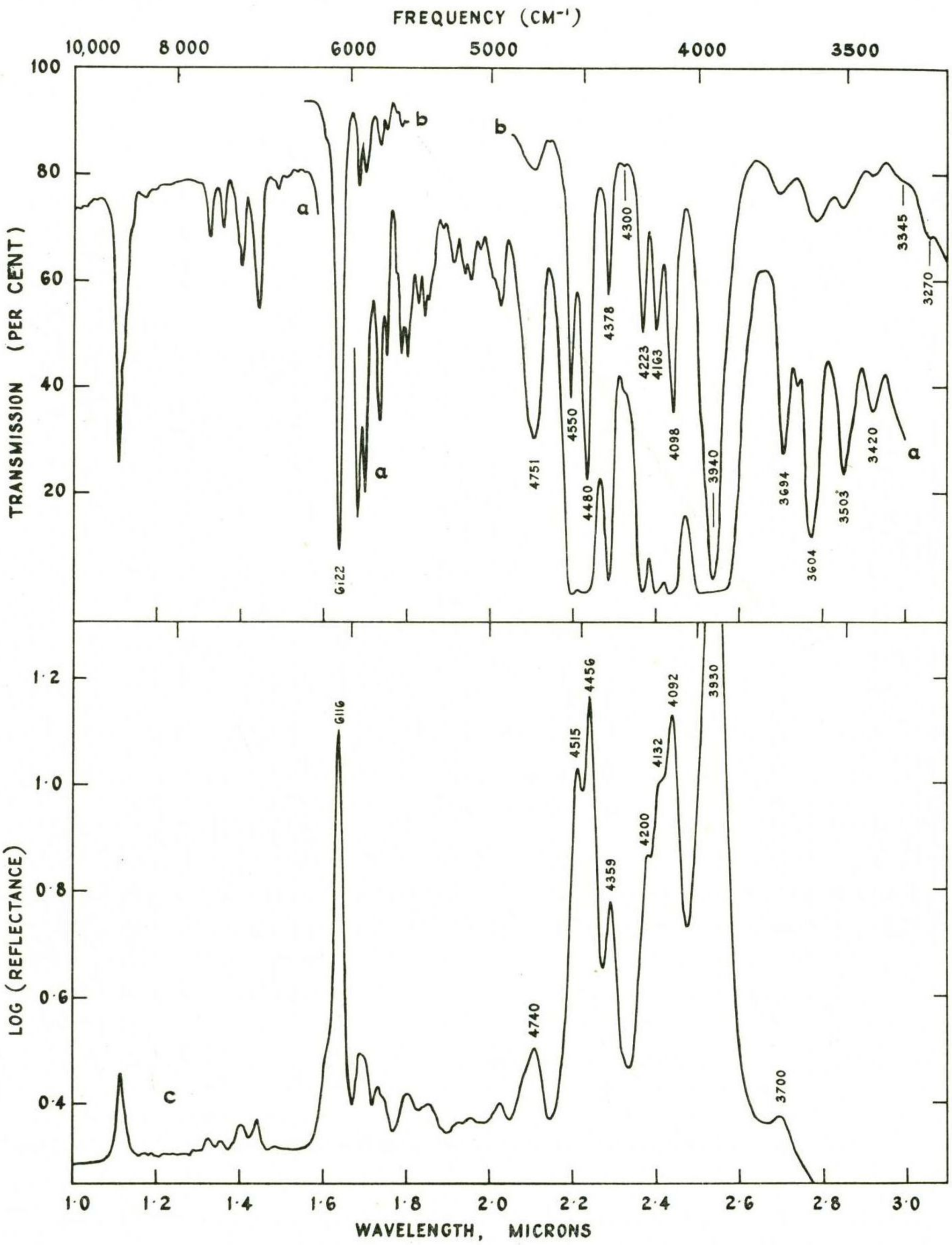


Fig. 3. Near infra-red spectra of ferrocene.

(a) 0·3M in CCl_4, 100 mm (b) 0·3M in CCl_4, 10 mm

(c) solid reflection spectrum

the positions of the binary combination bands above 3800 cm^{-1} for the range of compounds studied. The spectra of all of the compounds examined are extremely similar and the equivalence of the five H atom positions in the C_5H_5 ring results in a single sharp CH stretching overtone at 6100–6200 cm^{-1}. The near infra-red spectrum of liquid or of gaseous cyclopentadiene has a complex CH overtone band structure, as have the spectra of molecules containing C_5H_5 rings *sigma*-bonded through a single C atom and thus retaining the diene structure of the ring.

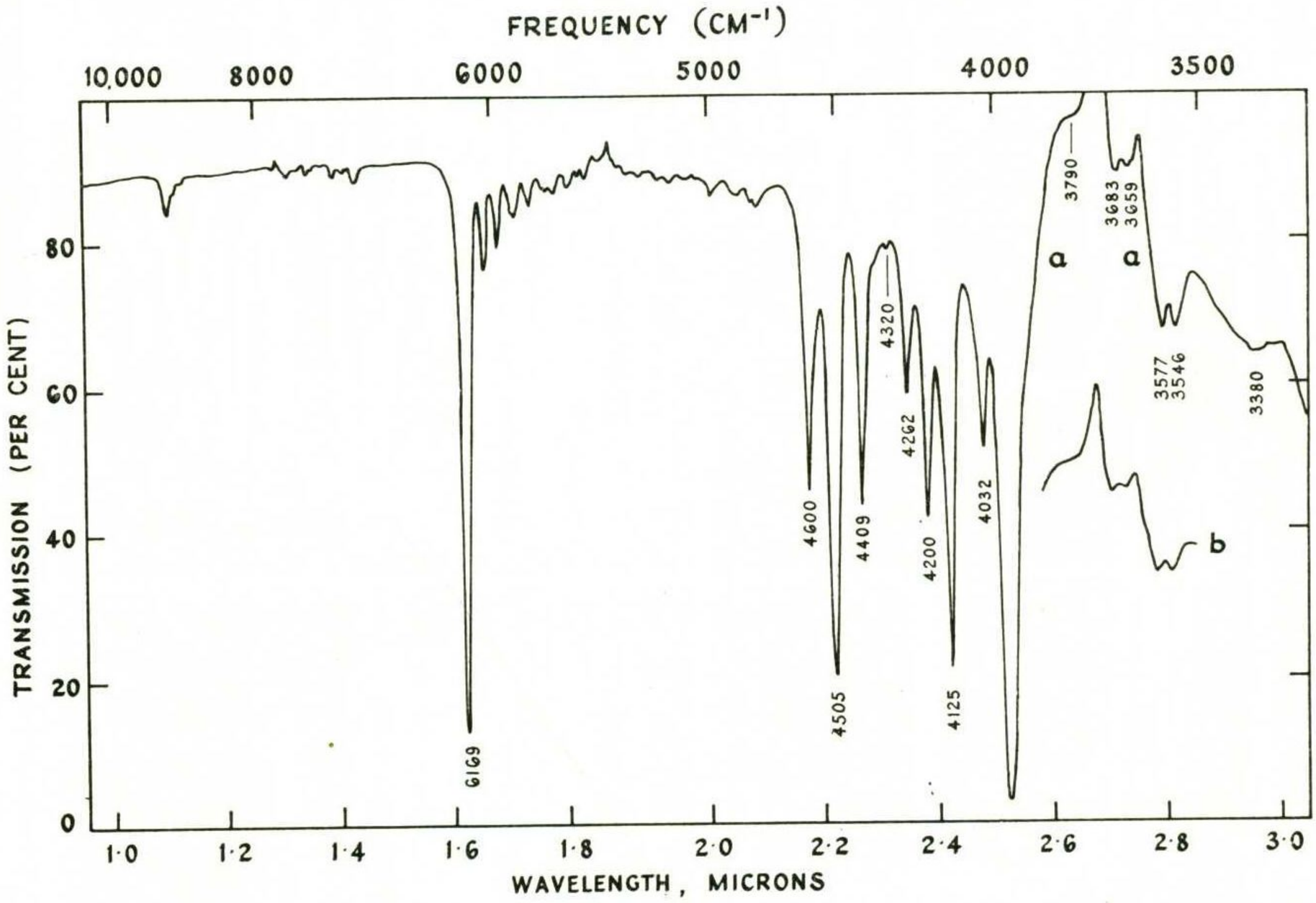


Fig. 4. Near infra-red spectrum of $C_5H_5TiCl_3$, 0·04M in CCl_4, 100 mm path.
(a) 0–100 % transmission (b) 0–200 % transmission

Apart from the CH stretching frequencies the highest fundamental frequency in the spectra of cyclopentadienyl metal compounds is [6] approximately 1580 cm^{-1} (Table 2). Thus, all binary combination bands above 3200 cm^{-1} contain a contribution from the CH stretching frequency 3100 cm^{-1} and, with the exception of the CH stretching overtone at 6100 cm^{-1}, all bands above 4600 cm^{-1} are due to ternary combinations.

The four strongest bands in the fundamental spectra [1–7], are at 820, 1010, 1430 and 3100 cm^{-1}, ascribable respectively to CH out-of-plane bending, CH in-plane bending, CC stretching and CH stretching. The binary combination bands containing these frequencies, i.e. those at 3930, 4100, 4450 and 6100 cm^{-1} (see Table 1 and Figs. 2 and 3), are observed to be the strongest combination bands.

The fundamental spectra of cyclopentadienyl metal compounds will differ in the region below 800 cm^{-1}, where ring–metal frequencies occur. As a consequence the combination spectra in the 3200–3800 cm^{-1} region will show marked differences, as can be seen for example between the solution spectra of $C_5H_5TiCl_3$ (Fig. 4) and of ferrocene (Fig. 3).

Characterisation of compounds

The close similarities evident in Table 1 and Figs. 2, 3 and 4 show that the combination spectrum resulting from the vibrational modes of the C_5H_5 ring is insensitive to the electron density distribution in the bond between the metal atom and ring, or to the overall symmetry of the molecule.

Halogens or carbonyl groups attached to the metal atom are seen not to affect the C_5H_5 binary combination spectrum in the 3800–4700 cm^{-1} region. The fundamental frequencies of carbonyl [14], nitrosyl [15] or thiocyanate [15] groups all occur

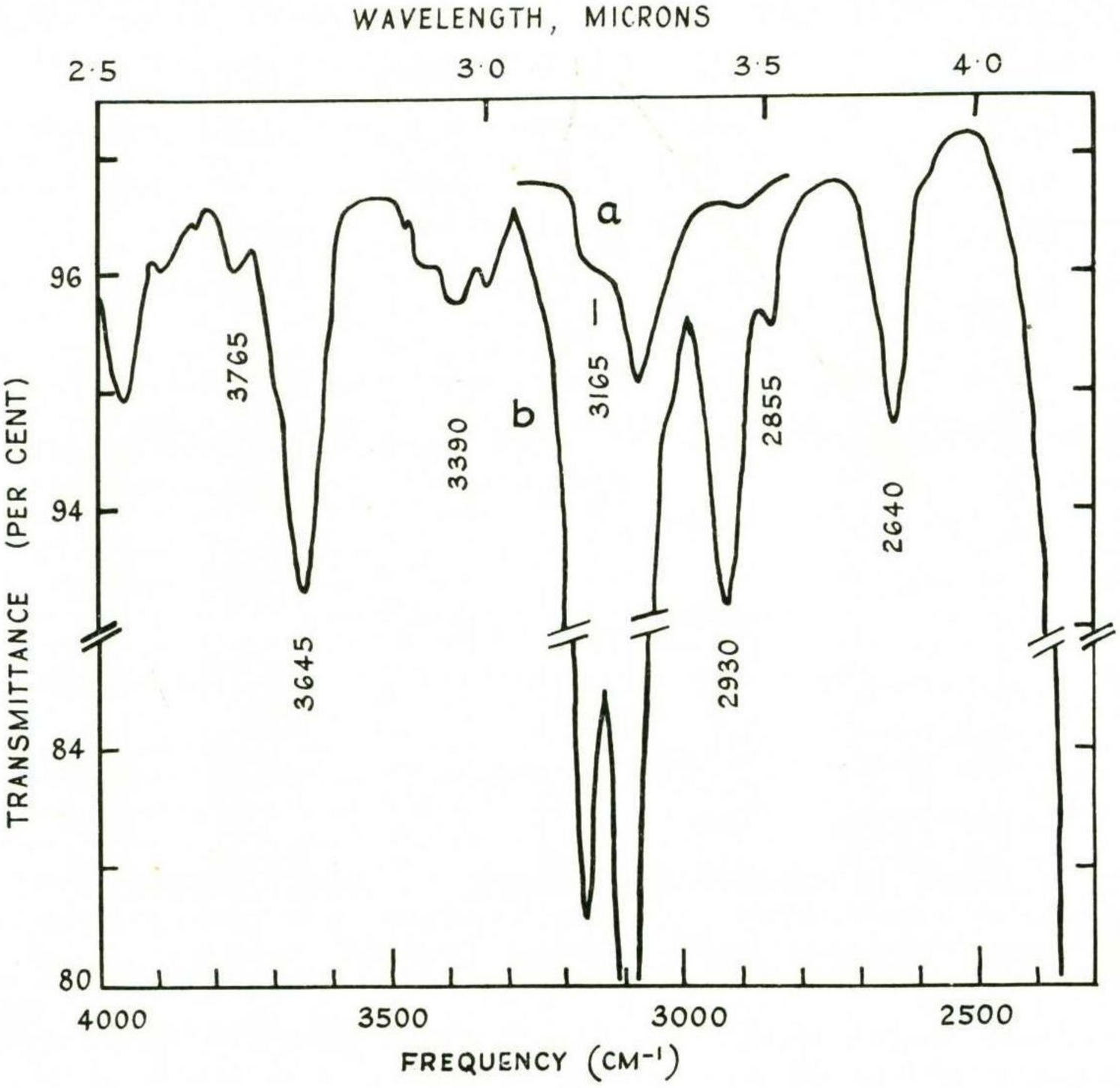


Fig. 5. Infra-red spectrum of deutero-ferrocene, 0·4M in CCl_4, 1 mm path.

in the 1700–2200 cm^{-1} region; cyclopentadienyl compounds, which contain these groups bonded to the central metal atom, still show in their spectra the typical cyclopentadienyl fundamental bands [15] and thus will be expected to show the characteristic binary bands listed in Table 1, though possibly with some interference.

The spectrum of $(C_5H_5)_2Pb$ (Fig. 2b) confirms that this compound, although having a dipole moment and therefore non-parallel rings, contains C_5H_5 rings bonded with five-fold symmetry, as is also evidenced by its NMR and fundamental infra-red spectra [2]. The combination spectrum of $(C_5H_5)_4Th$ (Fig. 2d) and the isomorphism of the compound with $(C_5H_5)_4U$ show that in both compounds all of the rings are bonded with five-fold symmetry.

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[14] F. A. Cotton, A. D. Liehr and G. Wilkinson, *J. Inorg. Nuclear Chem.* **1,** 175 (1955).
[15] T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.* **2,** 38 (1956).

The compound "$C_{10}H_9ZrCl$" reported by Samuel and Setton [10] shows a combination spectrum indistinguishable from that of $(C_5H_5)_2ZrCl_2$ (Fig. 2g) and hence contains unaltered C_5H_5 rings π-bonded to the zirconium atom; its formulation should therefore be $[(C_5H_5)_2ZrCl]_n$, where $n = 1$ or 2. This compound will be the subject of a later publication.

Table 1. Frequencies of binary combination bands of solid cyclopentadienyl metal compounds

Compound	Ferrocene assignment $\nu_1+\nu_9$	$\nu_8+\nu_{27}$	$\nu_1+\nu_{18}$	$\nu_8+\nu_{25}$	$\nu_1+\nu_{10}$	$\nu_5+\nu_{12}$	$\nu_1+\nu_{20}$	$\nu_8+\nu_{26}$	$\nu_1+\nu_8$
$(C_5H_5)_2Fe$	3930	a	4092	4132	4200	4359	4456	4515	6116
C_5H_5Tl	3913	a	4100	b	4198	4357 sh	4434	4530	6127
$(C_5H_5)_2Mg$	3938	a	4098	4130	4189	4363	4435	4529	6098
$(C_5H_5)_2V$	3916	a	4098	b	b	4348 sh	4427	4509	6070
$(C_5H_5)Cr$*	3922	a	4080	b	b	4353	4450	4515	6091
$(C_5H_5)_2Mn$	3906	a	4090	4149	4210	4348	4425	4515	6070
$C_5H_5Mn(Co)_3$†	3937	a	4120	b	b	4386	4484	4552	6135
$(C_5H_5)_2Co$*	3916	a	4090	b	4184 sh	4348 sh	4425	4520	6098
$(C_5H_5)_2Ni$	3922	a	4103	4141 sh	4202 sh	4367 sh	4444	4541	6130
$(C_5H_5)_2Pb$	3917	a	4098	4132	4202	4351	4434	4546	6091
$C_5H_5TiCl_3$	3942	4035	4127	4176	4232	4386	4472	4556	6135
$C_5H_5TiCl_3$ in CCl_4	(3960)	(4032)	(4125)	(4200)	(4262)	(4409)	(4505)	(4600)	(6169)
$(C_5H_5)_2TiCl$	3950	4026 sh	4132	4172	4237	4386	4490	4566	6155
$(C_5H_5)_2TiCl_2$	3951	4032 sh	4132	b	4220 sh	4386	4484	4560	6152
$C_5H_5ZrCl_3$	3952	4032	4132	4165 sh	4233 sh	4386	4484	4574	6154
$C_5H_5ZrBr_3$	3953	4040	4137	4167 sh	4246 sh	4386	4490	4572	6162
$C_5H_5ZrI_3$‡	3932	4040 sh	4130	b	b	4369	4480	4545	6135
$[(C_5H_5)_2ZrCl]_2$	3942	4030 sh	4130	4167 sh	4228 sh	4386	4480	4562	6132
$(C_5H_5)_2ZrCl_2$	3930	a	4115	4149 sh	4202 sh	4372	4466	4545	6116
$(C_5H_5)_2ZrBr_2$	3932	a	4118	4167 sh	4219 sh	4367	4466	4545	6127
$(C_5H_5)_2ZrI_2$	3926	a	4110	b	b	4357	4463	4525	6104
$(C_5H_5)_3Sc$	3918	3990 sh	4110	4149	4219	4382	4458	4549	6090
$(C_5H_5)_3Nd$	3922	a	4106	4140	4202	4367 sh	4454	4545	6098
$(C_5H_5)_4Th$	3937	a	4110	4175	4224 sh	4376	4478	4545	6135
$(C_5H_5)_4U$§	(3870)							(4464)	(6200)
Frequency range	47	50	57	46	57	39	66	62	90

a = Masked in 3930 cm^{-1} band. b = Not accurately resolved.

* Broad electronic transition band.

† Additional bands at 5138, 5068, 4016 and 3860 cm^{-1} arise from the CO fundamental frequencies.

‡ Poorly resolved spectrum.

§ Complex electronic bands from 4000–20,000 cm^{-1}; observed bands are combined with near co-incident electronic bands.

The mono-ring titanium and zirconium trihalide compounds are distinguished from the di-ring compounds and from all the other compounds examined by the resolution of a band at 4030–4040 cm^{-1} (Figs. 1 and 4) assignable to the combination $\nu_8 + \nu_{27}$. In the fundamental spectrum of all of the titanium and zirconium compounds there is a band attributable to this vibration at 935 cm^{-1}, rather than at 885 cm^{-1}, as in ferrocene [6]. Only in the spectra of mono-ring compounds is the binary combination band resolved however, although a weak shoulder is evident in the spectra of derivatives of some other metals (Table 1).

Assignment of the Combination Spectra

The vibrational assignment of the ferrocene fundamental spectrum given by Lippincott and Nelson [6] shows that, assuming a D_{5d} symmetry (the staggered

ring molecular structure) there are eight vibrational symmetry species, of which only two are infra-red active and three Raman active. However, combination of the symmetry species by the rules given by WILSON, DECIUS and CROSS [16] show that ten combinations are infra-red active and that all assigned fundamental frequencies whether active or inactive enter at least once into the combination frequencies (Table 3). A similar result is obtained if D_{5h} symmetry is considered i.e. that for an isolated C_5H_5 planar ring or an "eclipsed sandwich" di-cyclopentadienyl metal

Table 2. Observed fundamental vibrational frequencies of ferrocene, after LIPPINCOTT and NELSON [5] and WILSON *et al.* [6] with relative intensities estimated from the spectra in Refs. [1, 5 and 6]

Vibrational mode	Frequency number	Frequency		Approximate relative intensities solid
		Vapour or solution	Solid	
Ring metal ring bending	$22(E_{1u})$	170		5
Sym. ring metal stretch	$4(A_{1g})$	303		5
Sym. ring tilt	$16(E_{1g})$	388		1
Antisym. ring metal stretch	$11(A_{2u})$	478	488	10
Antisym. ring tilt	$21(E_{1u})$	492	488	10
Ring distortion ($\perp$)	$28(E_{2g})$		488	10
Ring deformation ($\perp$)	$34(E_{2u})$		569	1
CH bending ($\perp$)	$2(A_{1g})$, $9(A_{2u})$, $14(E_{1g})$	811	820	10
CH bending ($\perp$)	$19(E_{1u})$	834	855	6
Ring distortion and deformation ($\parallel$)	$27(E_{2g})$, $33(E_{2u})$		885	4
CH bending ($\parallel$)	$13(E_{1g})$, $18(E_{1u})$	1010, 1002	1005	10
CH bending ($\perp$)	$25(E_{2g})$, $31(E_{2u})$	1050	1055*	
Sym. and antisym. ring breathing	$3(A_{1g})$, $10(A_{2u})$	1105, 1108	1110	6
CH bending ($\parallel$)	$24(E_{2g})$, $30(E_{2u})$	1178	1189	2
CH bending ($\parallel$)	$5(A_{1u})$, $7(A_{2g})$		1257	5
Sym. and antisym. CC stretch	$15(E_{1g})$, $20(E_{1u})$	1408, 1411	1410	10
CC Stretch	$26(E_{2g})$, $32(E_{2u})$	1560	1580	1
CH Stretching	$17(E_{1u})$	3075	3077	5
CH Stretching	$8(A_{2u})$, $12(E_{1g})$, $23(E_{2g})$	3085	3103	10
CH Stretching	$1(A_{1g})$	3099	3103	10
CH Stretching	$29(E_{2u})$		3159	3

* Split into the frequencies 1052, 1062 and 1049, 1060 cm^{-1} for particular orientations of the crystal [1].

structure. The values of the frequencies to be assigned are almost identical for both cases, owing [6] to the low degree of coupling of the vibrational modes of the two rings. Similar considerations apply for most other overall molecular symmetries in which a C_5H_5 ring can be placed.

Ferrocene binary combination assignments

The fundamental frequencies of absorption for ferrocene in solution or as a vapour [5], and for the crystal [1], are collected for convenience in Table 2, together with an approximate estimate of relative intensities for the spectra of the solid, derived from the spectra given by WINTER *et al.* [1] and by WILKINSON, COTTON and BIRMINGHAM [5] for a single crystal in transmitted non-polarized light.

In the molecular fundamental spectrum and therefore in the combination spectrum only the symmetry species A_{2u} and E_{1u} are infra-red active. The calculated values given in Table 3 are either the strongest allowed combination (italicized in

[16] E. B. WILSON, J. C. DECIUS and P. C. CROSS, *Molecular Vibrations*, p. 331, McGraw-Hill, New York (1955).

the first or second column) or the average of combinations of comparable strength. The calculated values for the combination bands in the spectrum of the solid are within 2–30 cm^{-1} of those calculated for the molecule, and are not included in Table 3.

The band at 3930 cm^{-1}, by far the most intense in all the compounds studied, is seen from Table 3 and Fig. 3 to contain a large number of contributing combinations,

Table 3. Binary combination frequencies (Fig. 3) and assignments of ferrocene and *d*-ferrocene

Binary combination		Ferrocene			*d*-Ferrocene		
A_{2u}	E_{1u}	Calc.	Observed		Calc.	Observed	
			CCl_4 Solution	Solid		CCl_4 Solution	Solid
22 + 12	*22* + *1*, 22 + 23	3269	3273	3250* 3270†			
4 + 8	4 + 17	3383	3345	—	2645	2640	—
16 + 17	16 + 29	3504	3420	3500†			
11 + 1	11 + 23	3577	3503				
		3563	3484 sh				
21 + 12	*21* + *1*, 21 + 23	3591	3604	3585†			
28 + 29	*28* + *8*, 28 + 17	3585					
34 + 23	34 + 12	3654	3694	3700 3670†	2880	2855	
2 + 8, *9* + *1*	2 + 17, 9 + 23	3910			2972		
14 + 17	14 + 29		3940	3930		2930	
19 + 12	*19* + *1*, 19 + 23	3933		3922‡	2997		
27 + 29	*27* + *8*, 27 + 17	3965			2994		
33 + 23	33 + 12						
13 + 17, 18 + 12	13 + 29, *18* + *1*	4101	4098	4092 4078‡	3102	(masked)	
18 + 22							
25 + 29, 31 + 23	*25* + *8*, 25 + 17	4135	4163	4132 4132‡	3202	3165	
	31 + 12						
3 + 8, *10* + *1*	3 + 17, 10 + 23	4207	4223	4200 4196‡	3387	3342	
24 + 29, 30 + 23	24 + 17, 30 + 12	4263	4300	—	3399	3390	
	24 + *8*						
	5 + *12*, 7 + 29	4342	4378	4359 4338‡	3445§	3440	
15 + 17, 20 + 12	15 + 29, *20* + *1*	4510	4480	4456 4440‡	3599	3645	3650
26 + 29, 32 + 23	*26* + *8*, 26 + 17	4645	4550	4515 4509‡	3894	3890 3765	3830 3760
	32 + 12						
1 + *8*, 12 + 17	1 + 17, 8 + 23	6184	6122	6116	4680	4602	4572
23 + 29	12 + 29, 17 + 23					4519 4568	

* Taken from single crystal ferrocene in Ref. [5].
† Approximate values from Fig. 5, Ref. [1].
‡ Table 8, Ref. [1].
§ Estimated from CH (||) to CD (||) frequency ratio [6] of 1·30.

though even in solution it could not be resolved into separate bands at any concentration. The band at 1257 cm^{-1} in the fundamental spectrum of ferrocene [1, 5, 6] is noticeably more intense than the 1189 cm^{-1} band, also due to CH in-plane bending, and only in the solution spectra of ferrocene and $C_5H_5TiCl_3$ is the 4300 cm^{-1} combination band observed (Figs. 3 and 4). (In the mono-ring titanium and zirconium compounds $C_5H_5TiCl_3$, $C_5H_5ZrCl_3$ and $C_5H_5ZrBr_3$, where in effect the single ring spectrum is in evidence, the fundamental band at 1261–1264 cm^{-1} is in each case markedly stronger than that at 1180 cm^{-1}.)

The next band, that at 4456 cm^{-1} in the solid, is the third most intense in the combination spectrum, and in sequence is assigned to the coincident combinations containing the strong 1410 cm^{-1} symmetrical and antisymmetrical CC stretching modes. The band at 4515 cm^{-1}, assigned to $\nu_8 + \nu_{26}$ shows the largest shift observed in the combination spectrum, but its sequential identity is confirmed by the position of the next band at 4740 cm^{-1} assignable to the relatively strong ternary combination $\nu_2 + \nu_2 + \nu_8$.

The final binary combination band, and perhaps the most characteristic one for cyclopentadienyl compounds, is the single sharp CH stretching overtone at 6116 cm^{-1}, confirmation that the five H atom positions are identical.

WINTER *et al.* [1] suggest that the band observed by them at 4440 cm^{-1} is due to the combination $\nu_{12} + \nu_{22} + \nu_{30}$. This is unlikely for a number of reasons. Firstly, the strongest assignable ternary combinations, $\nu_2 + \nu_2 + \nu_8$, are weaker than the binary bands in the 3900–4600 cm^{-1} region, and it is unlikely that a combination involving three unlike modes will be stronger than these: secondly, both of the binary combinations $\nu_1 + \nu_{22}$ and $\nu_{12} + \nu_{30}$ are weak; finally, this assignment does not take into account the fundamental CC stretch vibration at 1580 cm^{-1}, ν_{22}, and thus ignores what should be the final binary combination below 6120 cm^{-1}.

d-ferrocene

Although some residual CH bands were evident at approximately 80 per cent exchange, the major CD bands were easily distinguished from them (Fig. 4), except for $\nu_1 + \nu_{18}$ which is masked by the residual CH stretching fundamental. The observable bands corresponding to the three other strongest CH bands, $\nu_1 + \nu_9$, $\nu_1 + \nu_{20}$ and $\nu_1 + \nu_8$ are the strongest in the CD combination spectrum, and their shifts to the calculated positions confirm their assignments. The calculated shifts were also observed for the other bands whose positions are listed in Table 3. In the region between 3700 and 3900 cm^{-1}, in which the combination $\nu_8 + \nu_{26}$ should appear, two bands in fact do so.

The relative decreases in intensity of the CH combination bands with increasing deuterium exchange also help to confirm their assignments; the binary combinations at 3928 and 4132 cm^{-1} containing CH out-of-plane bending contributions decrease proportionally to one another and to the CH stretching overtone, while the bands at 4100 and 4350 cm^{-1} contain CH in-plane bending modes and decrease together and much more rapidly than the 3928 and 4132 cm^{-1} bands. The band at 4456 cm^{-1} decreases at a rate approximately proportional to that of the CH stretching overtone band, further indicating that it contains a CC stretching contribution and not a CH in plane bending contribution.

Ternary combination bands

With the exception of the CH overtone at 6116 cm^{-1} all bands above 4600 cm^{-1} are due to ternary combinations. A large number of the ternary bands can be readily assigned (Table 4); in general the strongest bands are those containing twice a given fundamental frequency combined with a CH stretching frequency. In the region above 6200 cm^{-1} the bands are repeating the pattern of the binary combinations, but with an additional CH stretching frequency in the combination. In the spectra

Table 4. Ternary combination frequencies of ferrocene (Fig. 3)

Representative ternary combinations	Sum of fundamental frequencies	Observed frequency	
		CCl_4 Solution	Solid
2 + 2 + 8, 1 + 2 + 19	4707–4869	4751, 4783 sh	4740, 4790 sh
8 + 19 + 19, 1 + 27 + 33			
1 + 9 + 13, 1 + 13 + 19	4920–4980	4938, 4963 sh	4950, 4975 sh
8 + 3 + 27		4985 sh	
8 + 13 + 13, 1 + 18 + 25	5105, 5159, 5185	5063, 5123, 5157	5115, 5180
8 + 25 + 25			
1 + 3 + 25	5254	5233	
3 + 3 + 8, 1 + 10 + 10	5295, 5315	5280, 5305	
17 + 24 + 24, 8 + 24 + 24	5431–5515	5373 sh, 5400	5450
24 + 24 + 29		5429, 5473	
7 + 7 + 8, 1 + 5 + 7	5599, 5613	5600, 5631	5545–5585
5 + 12 + 15, 1 + 5 + 15	5750, 5764	5714, 5777	5714 sh, 5780
1 + 1 — 11, 1 + 17 — 16	5720, 5782		
15 + 15 + 17, 1 + 20 + 20	5891, 5921	5892, 5916	5890 sh, 5917
1 + 4 + 8	6487	6430	
1 + 17 + 16	6562	6515	
1 + 1 + 11	6676	6623	
1 + 12 + 34	6753	6702	6735
1 + 1 + 9	7009	6930	6935
1 + 1 + 18	7200	7134	7123
1 + 8 + 25	7234	7169 sh	
1 + 1 + 10	7306	7220 sh	
1 + 5 + 12	7441	7369	7380
1 + 1 + 20	7609	7547	7547
1 + 1 + 8	9283	9033	8970

of partially deuterated solid ferrocene the bands assigned as containing CH in-plane bending frequencies decrease rapidly with increase in deuterium content in the compound, while those containing out-of-plane bending or symmetrical–antisymmetrical CC stretch frequencies decrease more slowly, as for the corresponding binary combination bands.

Acknowledgment—The authors are greatly indebted to Dr. N. S. Ham for his helpful discussions and advice.

SYNTHESES AND PROPERTIES OF DI(CYCLOPENTADIENYL)TITANIUM(III) CHLORIDE

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Summary

Di(cyclopentadienyl)titanium(III) chloride has been prepared in high yield by addition of tetrahydrofuran to dry mixtures of titanium trichloride and di(cyclopentadienyl)magnesium in stoicheiometric or excess amounts. Reaction of titanium tetrachloride with excess di(cyclopentadienyl)magnesium also yielded $(C_5H_5)_2TiCl$ in moderate yield. Some properties of the compound are given, including solid state and aqueous spectra. Magnetic measurements show the compound to have one unpaired electron per titanium atom.

Introduction

Di(cyclopentadienyl)titanium chloride has previously been made by reduction of di(cyclopentadienyl)titanium dichloride with zinc dust, lithium aluminium hydride, and other reductants,[1,2] by the reaction of a solution of cyclopentadienyl sodium with a suspension of titanium trichloride in tetrahydrofuran,[3] and by the action of hydrogen chloride on di(cyclopentadienyl)titanium(III) borohydride, $(C_5H_5)_2TiBH_4$.[4] The compound has been shown to be dimeric,[3] but few other properties have been reported.

In the present paper a convenient synthesis of the compound is described, and electronic and near infrared spectra for the solid and its aqueous solution are presented, together with magnetic and other properties.

Attempts to produce $C_5H_5TiCl_2$ (cf.[5]) from $C_5H_5TiCl_3$ and from $TiCl_3$ were found to give apparent mixtures of $C_5H_5TiCl_2$ and $(C_5H_5)_2TiCl$.

Results and Discussion

(*a*) *Syntheses of Di(cyclopentadienyl)titanium Chloride*

Including the presently described syntheses, di(cyclopentadienyl)titanium chloride has now been made directly from the intermediates $TiCl_4$, $(C_5H_5)_2TiCl_2$,[1] $(C_5H_5)_2TiBH_4$,[4] and $TiCl_3$.[3] Of these preparations the present reaction of titanium trichloride with di(cyclopentadienyl)magnesium, carried out by addition of tetrahydrofuran to a dry mixture of the reactants, is particularly convenient and gives

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[1] Birmingham, J. M., Fischer, A. K., and Wilkinson, G., *Naturwissenschaften*, 1955, **42**, 96.
[2] Giddings, S. A., *Inorg. Chem.*, 1964, **3**, 684.
[3] Natta, G., Dall'asta, G., Mazzanti, G., Gianni, U., and Cesca, S., *Angew. Chem.*, 1959, **71**, 205.
[4] Nöth, H., and Hartwimmer, R., *Chem. Ber.*, 1960, **93**, 2246.
[5] Bartlett, P. D., and Seidel, B., *J. Amer. Chem. Soc.*, 1961, **83**, 581.

yields close to 80% of theoretical. Titanium trichloride is commercially available, and di(cyclopentadienyl)magnesium is easily made by the method of Barber[6] and modifications of it.[7]

Although tri(cyclopentadienyl)titanium has been prepared[8] by the reaction of di(cyclopentadienyl)titanium dichloride with cyclopentadienyl sodium in solution at 125°, it was found here that when di(cyclopentadienyl)magnesium is used introduction of two rings is the limit of substitution on titanium(III) or titanium(IV) even at 140°.

Reaction of the correct stoicheiometric amounts of titanium tetrachloride can of course be used to prepare the titanium(IV) compounds $C_5H_5TiCl_3$[9,10] and $(C_5H_5)_2TiCl_2$.[9,10,11] Reaction of excess di(cyclopentadienyl)magnesium with $TiCl_4$ to give di(cyclopentadienyl)titanium(III) chloride parallels that of cyclopentadienyl sodium with di(cyclopentadienyl)titanium dichloride and is analogous to the preparations of ferrocene, di(cyclopentadienyl)vanadium, and di(cyclopentadienyl)-chromium by, respectively, the reactions of $FeCl_3$, VCl_3, and $CrCl_3$ with the cyclopentadienyl derivatives of sodium or magnesium. However, the tetra(cyclopentadienyl) derivatives of thorium,[12] uranium,[13] and zirconium[7] can be prepared from the corresponding tetrachlorides without reduction taking place.

(*b*) *Properties of Di(cyclopentadienyl)titanium Chloride*

Di(cyclopentadienyl)titanium chloride has been reported as a green crystalline compound,[1] having a melting point of 279–281°,[3] and shown to exist as a dimer in benzene solution.[3] It dissolves in water[1] to give a green solution containing $(C_5H_5)_2Ti^+$ ions, as demonstrated by the formation of picrates and other salts.[1]

In the present work the compound was obtained as a green, or more frequently violet-brown crystalline solid, melting at 282–283°. Products from reaction of $(C_5H_5)_2TiCl_2$ with zinc in a sealed tube, and from titanium trichloride or titanium tetrachloride reactions all gave identical X-ray powder photographs and showed identical visible and near infrared spectra whether green or violet-brown in appearance. The colour appeared to depend on degree of subdivision and on the degree of separation of individual crystals.

The magnetic susceptibility of the compound at room temperature was found to be 1·56 B.M. per titanium atom. The small reduction from the value expected for one unpaired electron (1·72 B.M.) is probably due to interaction between pairs of titanium atoms linked by chlorine bridges in the dimeric molecule. As a result of its paramagnetism the compound, in deuteriochloroform solution, was found to give a broad weak n.m.r. band centred at δ 6·5 p.p.m. instead of the sharp peak in this region observed for diamagnetic π-bonded cyclopentadienyl compounds.[9] The near infrared

[6] Barber, W. A., *Inorg. Synth.*, 1960, **6**, 27.
[7] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.* (in press).
[8] Fischer, E. O., and Löchner, A., *Z. Naturf.*, 1960, **15b**, 266.
[9] Reid, A. F., and Wailes, P. C., *J. Organometallic Chem.*, 1964 (in press).
[10] Sloan, C. L., and Barber, W. A., *J. Amer. Chem. Soc.*, 1959, **81**, 1364.
[11] Wilkinson, G. W., and Birmingham, J. M., *J. Amer. Chem. Soc.*, 1954, **76**, 4281.
[12] Fischer, E. O., and Treiber, A., *Z. Naturf.*, 1962, **17b**, 275.
[13] Fischer, E. O., and Hristidu, Y., *Z. Naturf.*, 1962, **17b**, 276.

spectrum of the solid compound (Fig. 1) is however characteristic[14] of C_5H_5 rings bonded with fivefold symmetry (i.e. "π-bonded") to the metal atom, displaying in particular a single sharp CH stretching overtone at 6154 cm^{-1} resulting from the equivalence of the hydrogen atom positions. In the near infrared spectrum of a solution of the compound in water the CH stretching overtone at 6170 cm^{-1} and several of the CH and CC vibrational combination bands due to the C_5H_5 ring could be observed (Fig. 1) providing direct spectral evidence that the nature of the bonding of the C_5H_5 rings to titanium is unchanged in the $(C_5H_5)_2Ti^+$(aq) ion.

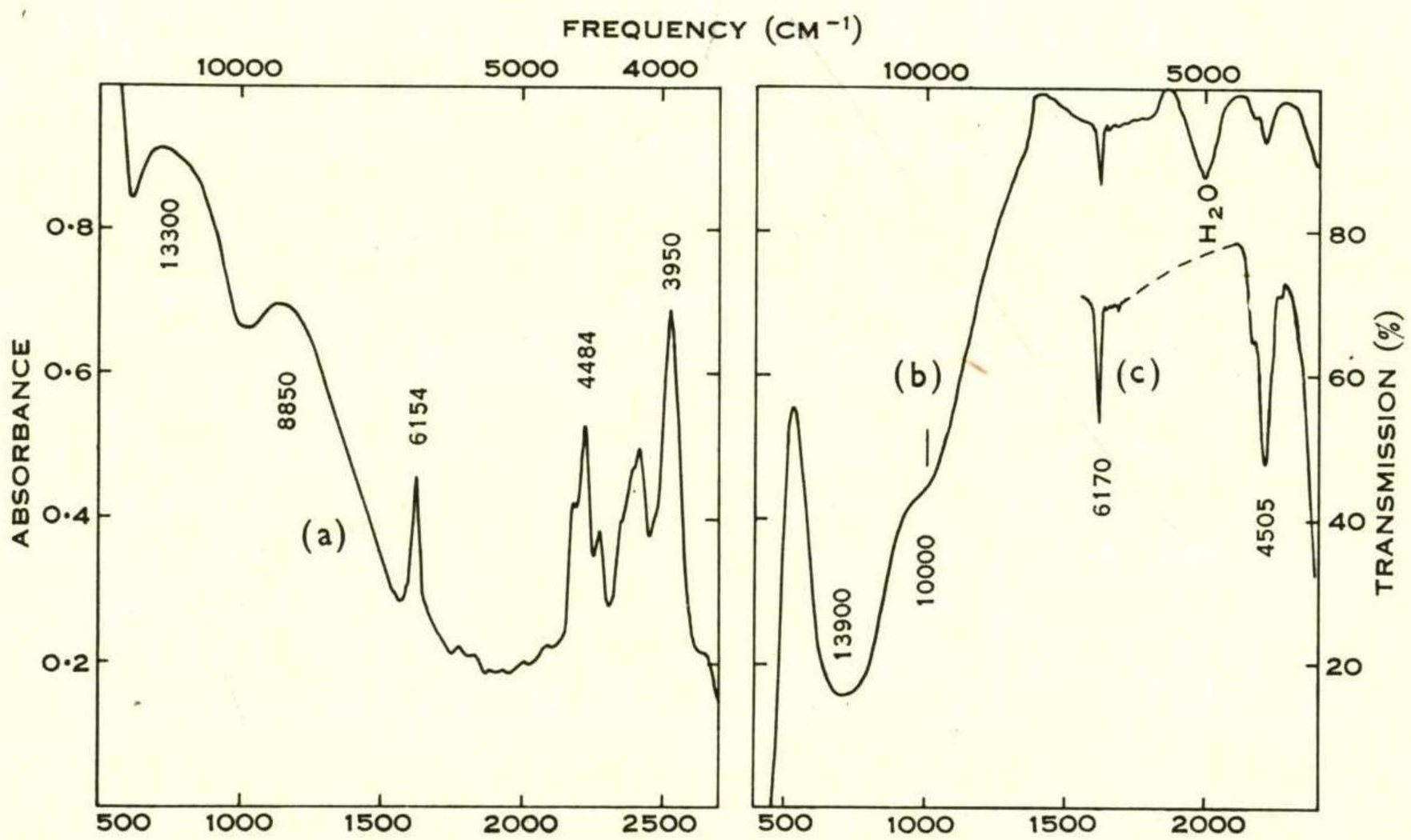


Fig. 1.—(*a*) Electronic and vibrational combination spectrum of solid $(C_5H_5)_2TiCl$, diffuse reflection. (*b*) $(C_5H_5)_2Ti^+$, 0·80M solution of $(C_5H_5)_2TiCl$ in air-free water, 2 mm cell. (*c*) Vibrational combination bands amplified; arbitrary scale.

The solid state spectrum also shows electronic transition bands, Figure 1 and Table 1, very similar to those observed for *d–d* transitions in $TiCl_3$[15] and $TiCl_3$ complexes.[16,17] The molecular complex $TiCl_3$,2dioxan for example[16] has a main peak at 14,800 cm^{-1} and a shoulder at 12,800 cm^{-1}, while α-$TiCl_3$[15] has a main *d–d* peak at 13,800 and a shoulder at 12,000 cm^{-1}. The somewhat lower values observed for di(cyclopentadienyl)titanium chloride, 13,300 cm^{-1} and 8850 cm^{-1}, are consistent with the C_5H_5 ring having a lower ligand field strength than a chlorine atom, and therefore producing a lower overall orbital splitting. While the bond angles about the Ti atom in the, presumably chlorine bridged, dimeric species are probably tetrahedral, the overall symmetry will not be cubic, and so far removed from octahedral that assignments on an octahedral basis are meaningless. This is borne out by the very large band splitting, 4450 cm^{-1}.

[14] Reid, A. F., Scaife, D. E., and Wailes, P. C., *Spectrochim. Acta.*, 1964 (in press).
[15] Clark, R. J. H., *J. Chem. Soc.*, 1964, 417.
[16] Clark, R. J. H., Lewis, J., Machin, D. J., and Nyholm, R. S., *J. Chem. Soc.*, 1963, 379.
[17] Fowles, G. W. A., Hoodless, R. A., and Walton, R. A., *J. Chem. Soc.*, 1963, 5873.

The visible and near infrared spectrum of $(C_5H_5)_2Ti^+$ ion is shown in Figure 1. The main peak at 13,900 cm^{-1} has $\epsilon_{max.}$ 5·5. Similar bands are observed in methanol, Table 1. When di(cyclopentadienyl)titanium dichloride in methanol/5% conc. hydrochloric acid solution is reduced,[1] the resulting green solution gives an additional weak spectral band at 19,200 cm^{-1}; a similar band has been observed for various of the solid $TiCl_3$ complexes.[17]

It is noteworthy that except for some reduction in band splitting, the spectrum of the $(C_5H_5)_2Ti^+$ ion in solution is little altered from that of solid $(C_5H_5)_2TiCl$, whereas when $TiCl_3$ is dissolved in water the main *d–d* adsorption peak shifts from 14,800 cm^{-1} to 20,100 cm^{-1}.[18] This strongly suggests that the $(C_5H_5)_2Ti^+$ ion is not solvated in water or methanol, and it seems probable that on ionization it adopts the configuration of the ferricinium ion $(C_5H_5)_2Fe^+$.

TABLE 1
ELECTRONIC SPECTRA OF $(C_5H_5)_2TiCl$ AND $(C_5H_5)_2Ti^+$

Compound or Ion	Solvent or State	Frequencies (cm^{-1})
$(C_5H_5)_2TiCl$	solid	13,300; 8,850
$(C_5H_5)_2Ti^+$	air-free water	13,900;* 10,000sh
$(C_5H_5)_2Ti^+$	methanol	14,100; 9,800sh
$(C_5H_5)_2Ti^+$†	methanol + 5% conc. HCl	13,700;‡ 10,000sh

* $\epsilon_{max.}$ 5·5.
† From $(C_5H_5)_2TiCl_2$ by reduction in solution.[1]
‡ Also a weak band at 19,200 cm^{-1}.

EXPERIMENTAL

(*a*) *General*

Manipulations of air-sensitive compounds were performed in an evacuable argon-filled dry box or in vacuum, and reactions were carried out under nitrogen as described elsewhere.[7]

(*b*) *Materials*

Titanium trichloride was made by the method of Groeneveld *et al.*[19] Titanium tetrachloride was purified by distillation from copper turnings. Cyclopentadienyltitanium trichloride was made by published methods.[9,10] Di(cyclopentadienyl)magnesium was prepared by the method of Barber.[6,7]

(*c*) *Reaction of Titanium Trichloride with Excess Di(cyclopentadienyl)magnesium*

In an attempt to replace all of the chlorine atoms on $TiCl_3$ with C_5H_5 rings $(C_5H_5)_2Mg$ (2·5 g, 16 mmoles) was placed with $TiCl_3$ (1·3 g, 8·4 mmoles) in a 50 ml flask and after addition of 15 ml of tetrahydrofuran the mixture was heated under reflux at 80° for 1 hr. After removal of solvent, unreacted $(C_5H_5)_2Mg$ was vacuum-sublimed from the reaction mixture at 120°, and the reaction product sublimed at 170°. A yield of 1·44 g of di(cyclopentadienyl)titanium chloride was obtained (78%) (Found: C, 56·2; Cl, 16·8; Ti, 22·0. Calc. for $C_{10}H_{10}ClTi$: C, 56·2; Cl, 16·7; Ti, 22·4%).

[18] Ilse, F. E., and Hartmann, H., *Z. phys. Chem.*, 1951. **197**, 239.
[19] Groenveld, W. L., Leger, G. P. M., Wolters, J., and Waterman, R., *Inorg. Synth.*, 1963, **7**, 45.

(*d*) *Reaction of Titanium Trichloride with 1 Mole of Di(cyclopentadienyl) magnesium*

$TiCl_3$ (10·0 g, 65 mmoles) was placed in a 100-ml flask with $(C_5H_5)_2Mg$ (10·0 g, 65 mmoles), and tetrahydrofuran (25 ml) was added to the cooled mixture, which was then heated under reflux at 80° for 1·5 hr. The product was directly sublimed from the green-brown reaction residue after removal of the solvent, a small amount of dark red oil collected at the start of sublimation being discarded. A yield of 11 g (79%) of $(C_5H_5)_2TiCl$ was obtained (Found: C, 55·6; Cl, 16·6; Ti, 22·4%).

(*e*) *Reaction of Titanium Tetrachloride with Excess Di(cyclopentadienyl)magnesium*

$TiCl_4$ (2·1 g, 10·6 mmoles) was added slowly to a stirred solution of $(C_5H_5)_2Mg$ (3·76 g, 24 mmoles) in tetrahydrofuran (15 ml). After being heated under reflux for 4 hr the solvent was removed, excess $(C_5H_5)_2Mg$ sublimed off at 120°, and the product sublimed in vacuum at 170°. The yield was 0·75 g (32%). The same product in similar yield was obtained when xylene was used as solvent at a reaction temperature of 140°. (Found: C, 54·8; Ti, 21·3%).

(*f*) *Characterization of Compounds*

(i) *N.m.r. spectra.*—N.m.r. spectra were obtained with a Varian A60 instrument. Samples were dissolved in deuteriochloroform, and tetramethylsilane was used as reference, δ 0·00 p.p.m.

(ii) *X-ray powder photographs.*—Samples for X-ray powder photographs were ground in a dry box and sealed in 0·5-mm Lindemann glass capillaries. Photographs were obtained with a Philips 114 mm camera.

(iii) *Melting points.*—Melting point samples were sealed in glass capillaries under argon. Temperatures given are uncorrected.

(iv) *Near infrared and visible spectra.*—The near infrared and visible spectra of the solid compounds were obtained as diffuse reflection spectra, as described elsewhere.[11] Solution spectra were obtained in transmission in the ordinary way.

(v) *Analyses.*—Analyses were performed by the Australian Microanalytical Service, Melbourne. Samples were pelleted in the dry-box and transferred in argon-filled tubes.

(vi) *Magnetic measurements.*—The Gouy method was used to measure the magnetic susceptibility of the powdered solid.

Acknowledgments

The authors are indebted to Dr. H. Gardner for the preparation of titanium trichloride, to Dr. G. Winter for magnetic measurements, to Mr. R. Coutts for experimental assistance, and to Dr. D. E. Scaife for helpful discussions.

CHARACTERIZATION OF BIS[CHLORIDODI(CYCLOPENTADIENYL)ZIRCONIUM] OXIDE, A COMPOUND CONTAINING THE Zr–O–Zr LINKAGE

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[*Manuscript received August* 24, 1964]

Summary

The previously reported reaction of dichloridodi(cyclopentadienyl)zirconium [$(C_5H_5)_2ZrCl_2$] with aniline or other bases has been shown to involve water as a reactant, with formation of the oxygen-bridged bis[chloridodi(cyclopentadienyl)-zirconium] oxide, $[(C_5H_5)_2ZrCl]_2O$, containing the linkage Zr–O–Zr. The compound is diamagnetic, stable to air and water, and can be sublimed in a vacuum at 200–220°. The crystals are monoclinic, with four molecules per unit cell. The structure was established by mass, infrared, near infrared, and proton magnetic resonance spectral examination, and by reaction of the compound with deuterium-labelled and tritium-labelled hydrogen chloride to regenerate unlabelled dichloridodi(cyclopentadienyl)-zirconium.

Introduction

Samuel and Setton[1,2] reported that the action of excess aniline or other amine on dichloridodi(cyclopentadienyl)zirconium (I) in chloroform or certain other organic solvents gave one mole of amine hydrochloride and a compound of unknown structure and of empirical formula "$C_{10}H_9ZrCl$". The dibromide corresponding to (I) reacted similarly. The new compounds reformed the starting dihalides with concentrated hydrochloric or hydrobromic acids.

It seemed unlikely to us that hydrogen could be lost readily from a π-bonded C_5H_5 ring on reaction with an amine and indeed the near infrared combination spectrum of "$C_{10}H_9ZrCl$" was virtually indistinguishable from that of (I), and possessed features solely characteristic of the π-bonded ring system.[3] The aromaticity and configuration of the C_5H_5 rings therefore appeared to be unchanged in the new compound, so that the source of the hydrogen atom liberated as hydrogen chloride came into question.

It has now been established, in particular by mass spectral evidence, that Samuel and Setton's compound is bis[chloridodi(cyclopentadienyl)zirconium] oxide (II).§

After this work was completed, a paper by Brainina, Freidlina, and Nesmeyanov appeared,[4] in which it was also suggested that Samuel and Setton's compound was the bridged oxide (II), and it was shown that adventitious water is required for the

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§ This compound could also be named dichlorido-μ-oxotetra(cyclopentadienyl)dizirconium. M. Cousins and M. L. H. Green, *J. Chem. Soc.*, 1964, 1567, have recently described a bridged cyclopentadienylmolybdenum oxide, $[C_5H_5MoO_2]_2O$, which they name tetraoxo-μ-oxodicyclopentadienyl-dimolybdenum.

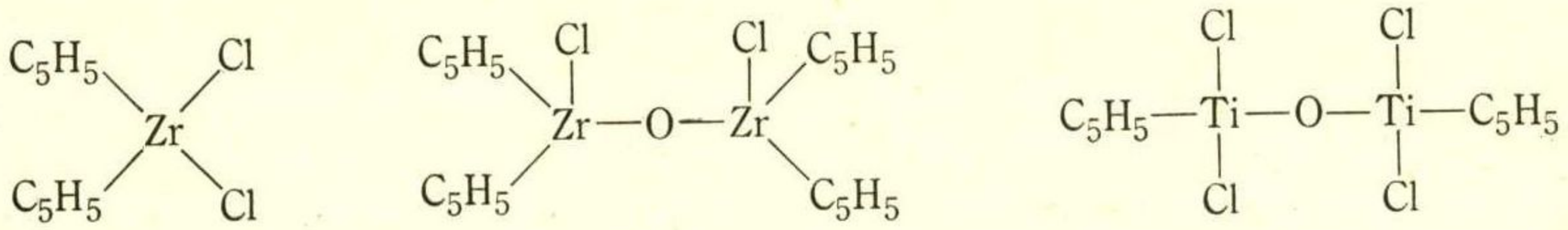
[1] Samuel, E., and Setton, R., *C. r. Hebd. Séanc. Acad. Sci.*, 1962, **254**, 308.

[2] Samuel, E., and Setton, R., *C. r. Hebd. Séanc. Acad. Sci.*, 1963, **256**, 443.

[3] Reid, A. F., Scaife, D. E., and Wailes, P. C., *Spectrochim. Acta*, 1964 (in press).

[4] Brainina, E. M., Freidlina, R. Kh., and Nesmeyanov, A. N., *Dokl. Akad. Nauk SSSR*, 1964, **154**, 1113.

formation of (II) from (I) in the presence of an organic amine. However, the characterization of (II) presented here is more complete than that of Brainina *et al.* who proposed structure (II) solely on the basis of molecular weight and preparation of the compound by hydrolysis both of dichloridodi(cyclopentadienyl)zirconium and chloridodi(cyclopentadienyl)ethoxyzirconium. Since (II) contains only 3·0% oxygen the analytical figures for the remaining elements do not distinguish between $C_{20}H_{20}Cl_2OZr_2$ and the formulae $C_{10}H_9ClZr$ or $C_{20}H_{20}Cl_2Zr_2$ suggested earlier.[1,2,3]



(I) (II) (III)

The compound bis[cyclopentadienyldichloridotitanium] oxide (III) has been reported, and characterized by X-ray analysis.[5,6] More recently, Giddings[7] has prepared the titanium analogue of (II) by oxidation of trivalent chloridodi(cyclopentadienyl)titanium (cf. Noth and Hartwimmer[8]).

Results and Discussion

(*a*) *Preparation of* (*II*) *from* (*I*), *and the Reverse Reaction*

Aniline, diethylamine, and hexamethylenetetramine in various aprotic organic solvents in flasks open to the atmosphere converted (I) into (II) in 40–90% yield. In a quantitative experiment using excess aniline in chloroform, it was established that the proton which appears as hydrogen chloride is not derived from the excess amine, since all the starting aniline was accounted for and no trace of an oxidation product of aniline could be detected. In reactions in which air was excluded, no reaction of (I) with either aniline or diethylamine was observed, both in the presence and absence of solvents. Concentrated hydrochloric acid converts (II), in solution in chloroform, into (I),[1,2] and the same reaction was found to occur very rapidly with anhydrous hydrogen chloride in various organic solvents. When the hydrogen chloride used was labelled with either deuterium or tritium no significant amount of the labelling isotope appeared in the product (I).*

(*b*) *Properties of* (*I*) *and* (*II*)

The diamagnetic starting material, (I), m.p. 248°, was monomeric in chloroform solution, and on titration with alkali was found to have an equivalent weight of 148 (calc. 145). The proton magnetic resonance spectrum showed a sharp singlet at δ

* When $(C_5H_5)_2ZrCl_2$ was treated with tritium chloride in toluene for 2 min at room temperature, the amount of exchange observed corresponded to replacement of 1 in 200 of the hydrogen atoms. This corresponds approximately to a half time of exchange of 24 hr at 25°. Deuterium or tritium labelling of $(C_5H_5)_2ZrCl_2$ by the use of DCl or tritiated HCl in toluene is thus feasible, and would probably be more rapid at higher temperatures.

[5] Corradini, P., and Allegra, G., *J. Amer. Chem. Soc.*, 1959, **81**, 5510.
[6] Allegra, G., Ganis, P., Porri, L., and Corradini, P., *Atti Accad. Naz. Lincei,* 1961, **30**, 44.
[7] Giddings, S. A., *Inorg. Chem.*, 1964, **3**, 684.
[8] Noth, H., and Hartwimmer, R., *Chem. Ber.*, 1960, **93**, 2246.

6·52 p.p.m. ($CHCl_3$ solution, tetramethylsilane as internal standard). The product (II) was found to sublime unchanged in a vacuum at 200–220°, after which purification it had m.p. 306–309°. Samuel and Setton[1,2] reported m.p. 300°, Brainina *et al.*[4] m.p. 270–280° (decomp.). The equivalent weight from alkali titration was 255–260 [formula (II) requires 265]. The compound was colourless, diamagnetic, non-conducting in chloroform solution, and the p.m.r. spectrum both at 60 Mc/s and at 100 Mc/s had a sharp singlet, δ 6·34 p.p.m. The disappearance of the peak at δ 6·52 p.p.m. and the appearance of a peak at δ 6·34 p.p.m. could be used to follow the conversion by limited amounts of hydrogen chloride of (II) into (I).

The above evidence suggests that (II) contains two $(C_5H_5)_2ZrCl$ units, with zirconium in the (4+) oxidation state, but the source and fate of the hydrogen atoms in the hydrogen chloride which takes part in the forward and back reactions is unexplained by a simple dimer formulation[3] such as $[(C_5H_5)_2ZrCl]_2$ which in any case would contain Zr^{III}.

The ultraviolet and visible spectra of both (I) and (II) in ethanol were almost identical, and were characteristic of compounds containing π-bonded cyclopentadienyl rings. No electronic transition bands due to the metal atoms were observed. The fundamental infrared spectra of (I) and (II) for the range 700–4000 cm^{-1} have been reported.[2] The very strong complex band at 750–775 cm^{-1} which occurs only in (II) seemed likely to be due to a metal–oxygen stretching frequency. The hydrolysis products of titanium alkoxides,[9,10] which contain the Ti–O–Ti linkage, show infrared absorption around 800 cm^{-1}, the bridged cyclopentadienyltitanium compound (III) shows a strong absorption band at 760 cm^{-1}, and the titanium analogue of (II) is reported[7] to show strong bands at 720 and 795 cm^{-1}.*

It is noteworthy that the near infrared combination spectra of (I) and (II) are virtually indistinguishable,[3] and in particular there is no combination band in the spectrum of (II) corresponding to the combination (3100+750), i.e. 3850 cm^{-1}. Thus the strong 750–775 cm^{-1} band in (II) (Zr–O stretch) is not coupling with the C–H vibrations in the C_5H_5 ring, which is further evidence that it is not a CH, CC, or ring-metal vibrational frequency.

The recognition of a Zr–O stretching frequency in (II) immediately suggested the bridged oxide structure, and this was fully confirmed by the mass spectrum (see below). Formula (II) implies that water is involved in the reaction [equation (1)], and this explains why the reaction proceeds in open flasks but not under conditions where water is rigorously excluded.

$$2(C_5H_5)_2ZrCl_2+2C_6H_5NH_2+H_2O \rightarrow [(C_5H_5)_2ZrCl]_2O+2C_6H_5NH_3Cl \qquad (1)$$

The regeneration of (I) from (II) with anhydrous hydrogen chloride, without introduction of hydrogen into (I), is explained by equation (2).

$$2[(C_5H_5)_2ZrCl]_2O+2HCl \rightarrow 2(C_5H_5)_2ZrCl_2+H_2O \qquad (2)$$

* A. Clearfield, *Rev. Pure Appl. Chem.*, 1964, **14**, 91, has recently given a useful discussion of the infrared evidence relating to possible Zr–O–Zr bonds in monoclinic zirconia, and certain oxyfluorides and isothiocyanates.

[9] Zeitler, V. A., and Brown, C. A., *J. Phys. Chem.*, 1957, **61**, 1174.

[10] Bradley, D. A., and Westlake, A. H., *Nature*, 1961, **191**, 273.

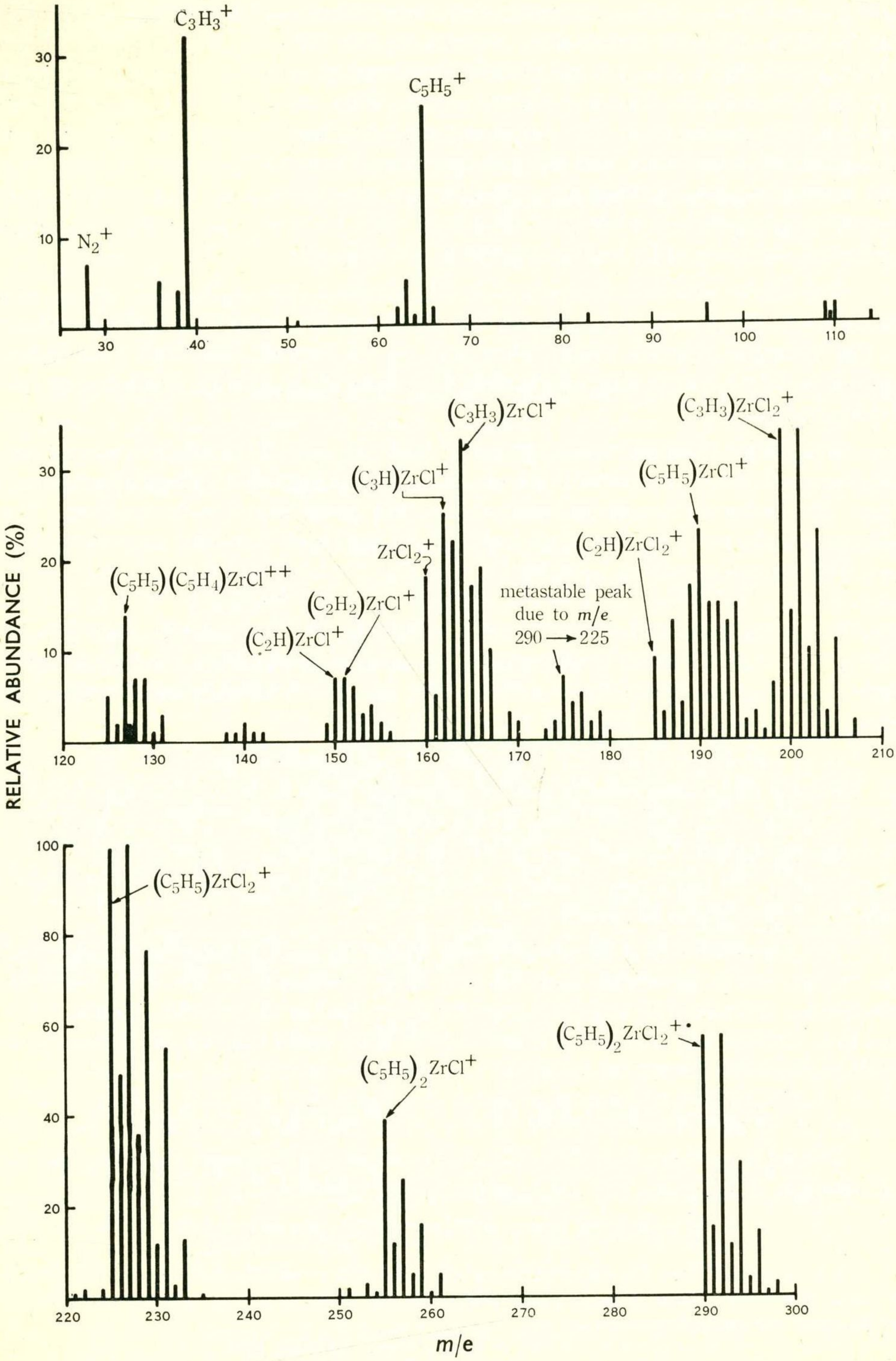


Fig. 1.—Mass spectrum of dichloridodi(cyclopentadienyl)zirconium, $(C_5H_5)_2ZrCl_2$.

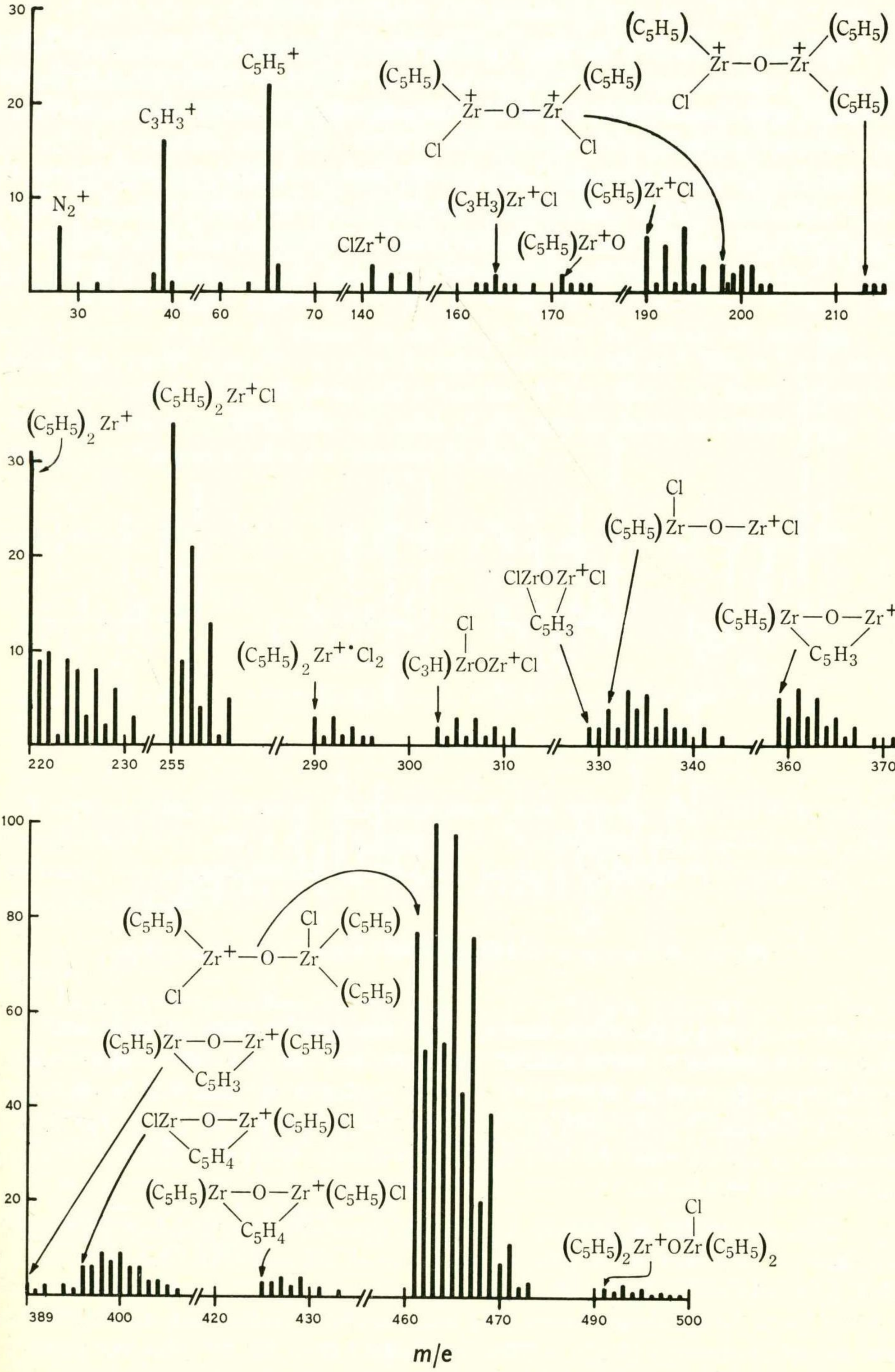


Fig. 2.—Mass spectrum of bis[chloridodi(cyclopentadienyl)zirconium] oxide, $(C_5H_5)_2Zr(Cl)OZr(Cl)(C_5H_5)_2$.

(c) *Mass Spectra of (I) and (II)*

For determination of the mass spectra, the compounds were introduced directly into the ion source of an Atlas CH4 spectrometer. The mass spectrum of (I) is shown in Figure 1 and that of (II) in Figure 2. Plausible structures for the principal ions are also shown in the figures.

Zirconium has four major isotopes, ^{90}Zr (51%), ^{91}Zr (11%), ^{92}Zr (17%), ^{94}Zr (17%), while chlorine has two isotopes ^{35}Cl (75%) and ^{37}Cl (25%). Consequently the mass peaks for a given chemical structure occur in groups characteristic of the isotope distributions of Zr and Cl atoms which they contain, the variations in C, H, and O

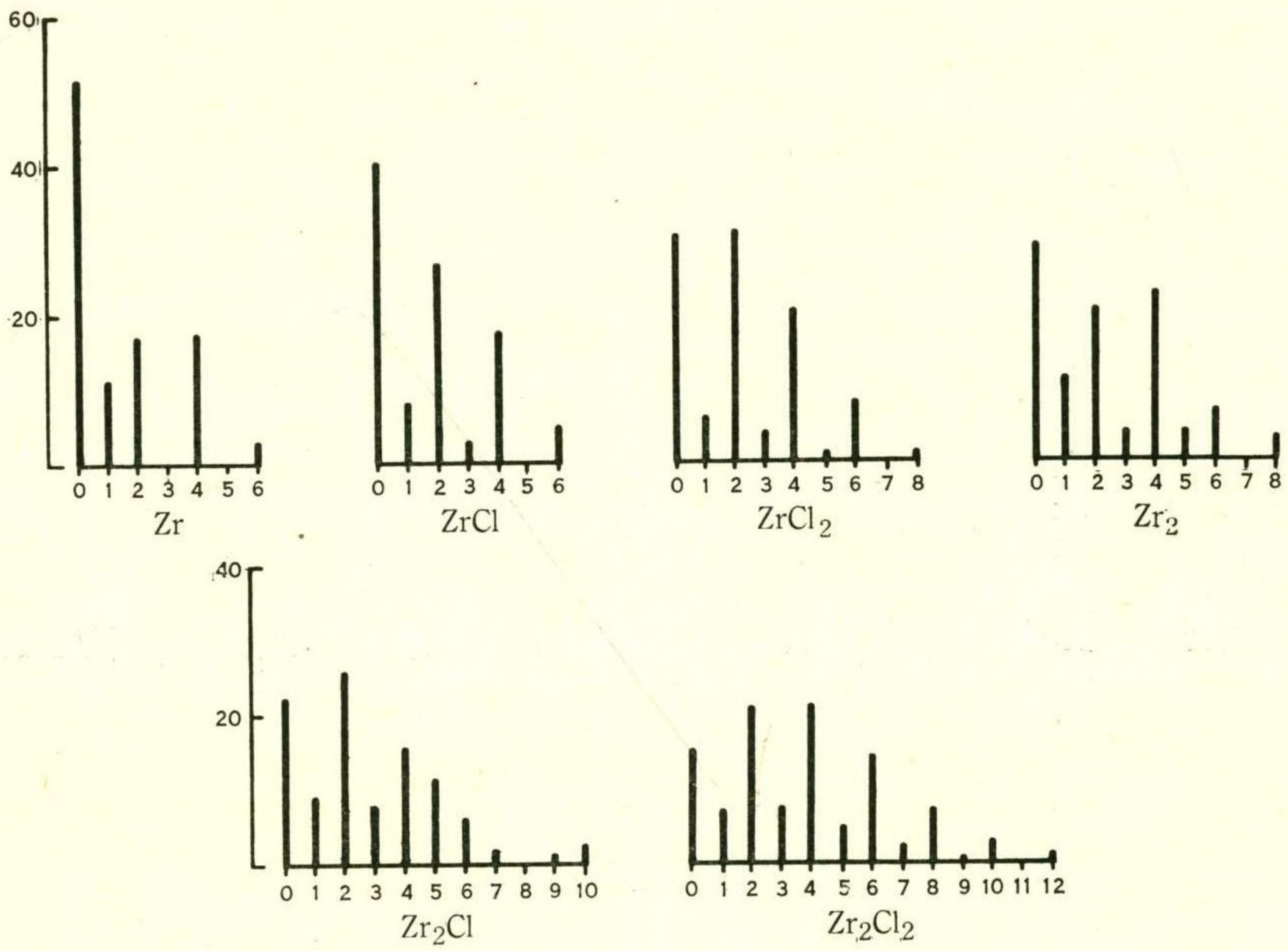


Fig. 3.—Isotopic mass distributions for various Zr/Cl combinations.

isotopes being negligible when compared to those of Zr and Cl. This enables the proposed structures to be confirmed both by observed mass and isotopic pattern. The isotopic patterns for the various Zr/Cl combinations, calculated by the method given in Biemann,[11] are shown in Figure 3. Each group of "isotopic mass peaks" is identified by the m/e value for the ion of lowest mass in that group, i.e. that containing only ^{90}Zr and ^{35}Cl atoms.

With a number of ions in the spectra the only plausible structures require trivalent or divalent zirconium, e.g. $[(C_5H_5)ZrCl]^+$, $[(C_5H_5)_2Zr]^+$, $[ZrCl_2]^+$, and $[(C_5H_5)(Cl)ZrOZrCl]^+$. In the latter ion, the resonance structure includes contributions in which both Zr atoms are formally trivalent and others in which one is tetravalent and the other divalent (Fig. 4). The new feature that arises in the mass spectra of

[11] Biemann, K., "Mass Spectrometry: Organic Chemical Applications." (McGraw-Hill: New York 1962.)

organic compounds containing transition metals[12] is that an ion $[M^n]^+$ in which the metal M is in valency state n, is equivalent to the radical ion $[M^{n-1}]^{+\cdot}$ in which the metal atom is now in valency state $n-1$.*

The mass spectrum of (I) is straightforward and the principal ions can all be explained by successive losses of cyclopentadienyl radicals or chlorine atoms from the molecular radical ion, with some disruption of the C_5H_5 rings to give fragments such as C_3H_3, C_3H, and C_2H attached to the zirconium atom. A suggested pathway of ionic reactions which accounts for virtually all the ions observed in the spectrum of (II) is shown in Figure 5. The mass spectrum contains numerous ions in which the Zr–O–Zr unit is clearly present, and the presence of two zirconium atoms in the molecule makes possible a number of novel structures for which no analogies are found in the spectrum of (I). In two of these ions (m/e 425 and 395) a C_5H_4 unit is shown as σ-bonded to one Zr atom and π-bonded to the other. In three further ions derived from these (m/e 389, 359, and 329) a C_5H_3 unit is shown as σ-bonded to both Zr atoms with formation of a five-membered ring.†

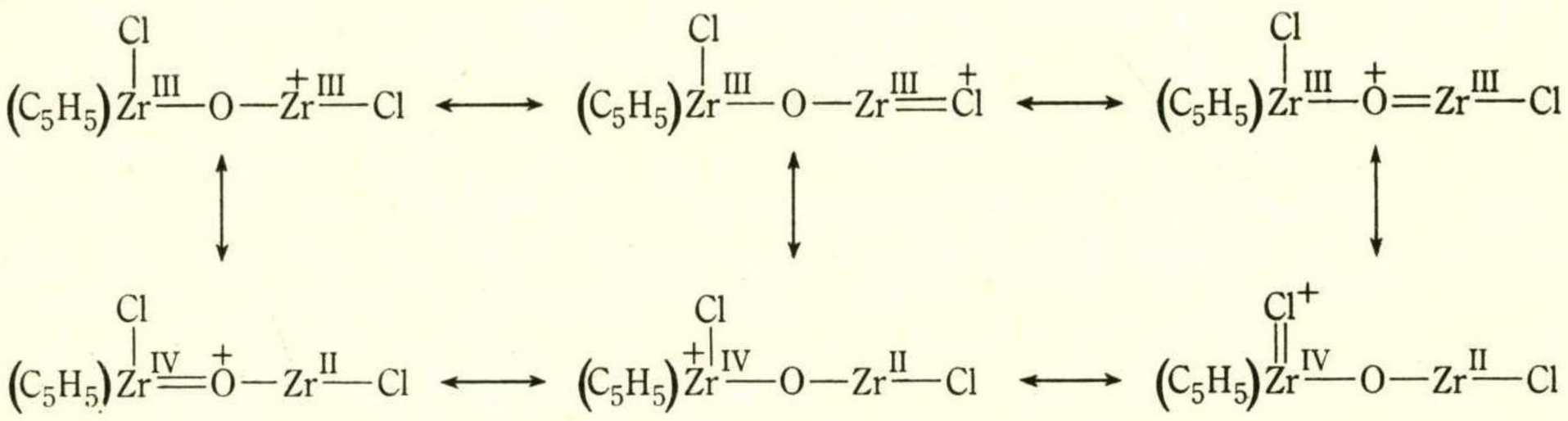


Fig. 4.—Resonance structures of ion m/e 331 in mass spectrum of (II).

Preliminary single crystal X-ray data show that the unit cell of (II) is monoclinic with a 13·75, b 7·80, and c 18·73 Å, β 94° 50′. The density, determined in a helium displacement apparatus, was found to be 1·70 g/cm³ at 25°. The unit cell thus contains four molecules.

Experimental

(a) *Reagents*

Dichloridodi(cyclopentadienyl)zirconium (I), m.p. 248°, was prepared by reaction of zirconium tetrachloride with di(cyclopentadienyl)magnesium in tetrahydrofuran solution.[14,15,16] Aniline and diethylamine were distilled before use and solvents were of analytical reagent grade.

Anhydrous hydrogen chloride was prepared by the action of water on phosphorus pentachloride, and dried by passage through a trap at −78°. Deuterium chloride was prepared similarly from D_2O and tritiated hydrogen chloride from water containing 1 mc/ml of T_2O.

* The $[\ ]^{+\cdot}$ symbolism which is used throughout this paper in the formulation of radical ions has been recently discussed elsewhere.[13]

† It can also be suggested that the entities C_5H_4 and C_5H_3 are cyclic structures which remain solely π-bonded to Zr atoms, for which the valency adjusts to balance the formal charge on the hydrocarbon ring.

[12] Shannon, J. S., and Swan, J. M., unpublished data.
[13] Shannon, J. S., *Proc. R. Aust. Chem. Inst.*, 1964, **31**, 323.
[14] Reid, A. F., and Wailes, P. C., *J. Organometallic Chem.*, 1964 (in press).
[15] Sloan, C. L. and Barber, W. A., *J. Amer. Chem. Soc.*, 1959, **81**, 1364.
[16] Reid, A. F., and Wailes, P. C., unpublished data.

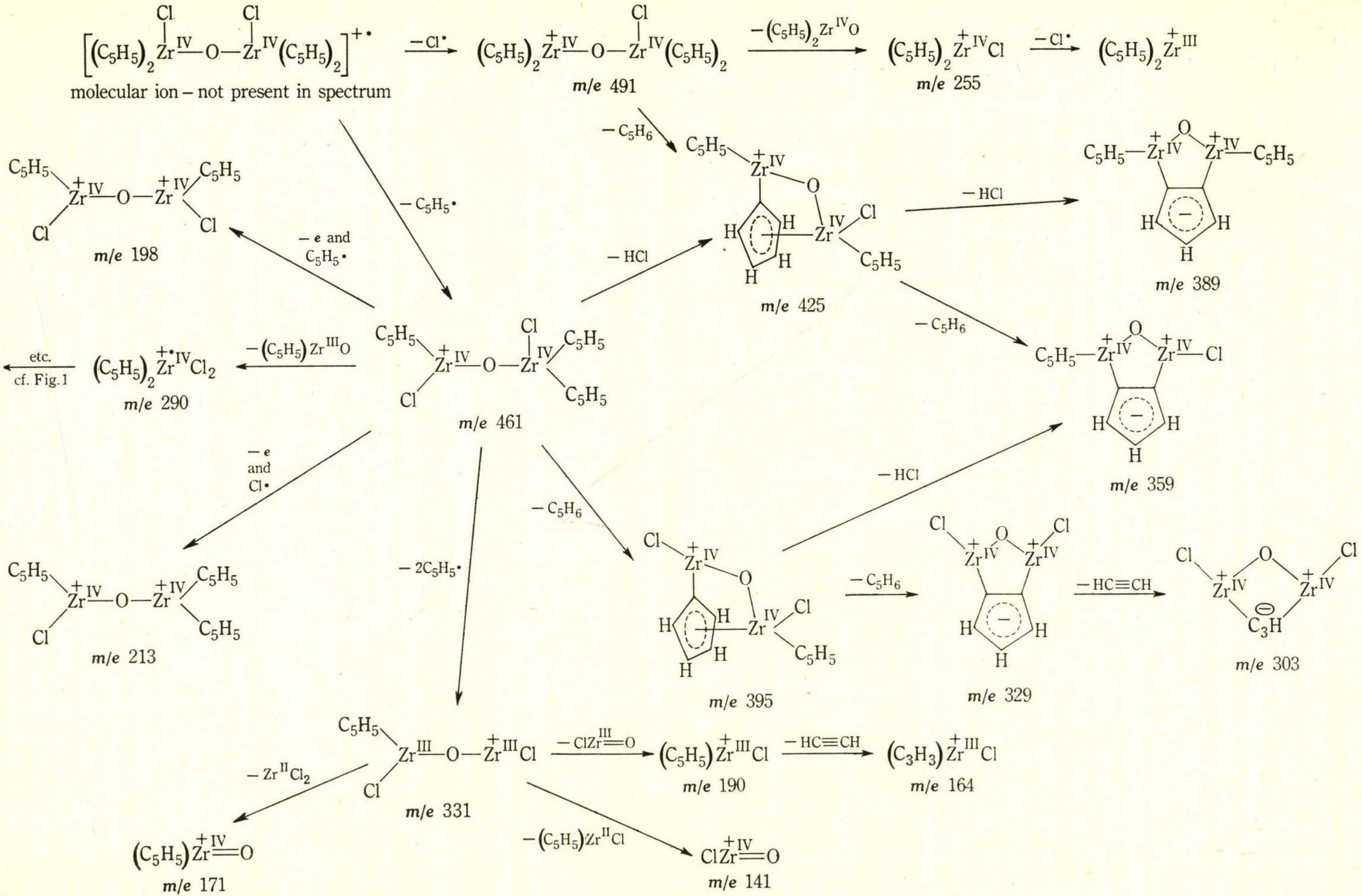


Fig. 5.—Suggested mechanisms for ionic fragmentation of bis[chloridodi(cyclopentadienyl)zirconium] oxide in the mass spectrometer.

(*b*) *Bis[chloridodi(cyclopentadienyl)zirconium] Oxide (II)*

This compound was prepared by the literature method,[1,2] namely addition of aniline or diethylamine to a solution of (I) in chloroform or other solvent. Aniline in excess of the stoicheiometric amount was not required when chloroform saturated with water was used as solvent and the mixture was shaken at room temperature for several minutes. The yield in the latter case was over 70%. The product was best purified by brief washing with water to remove aniline hydrochloride and any unchanged starting material, followed by sublimation, or recrystallization from methylene chloride or toluene. M.p. 306–309° (sealed tube, under nitrogen).

(*c*) *Infrared Spectra*

Samples were pressed in KCl disks and transmission spectra were recorded on a Perkin–Elmer 21 spectrometer for routine samples. Spectra in the 800–250 cm^{-1} region were recorded on a Perkin–Elmer 421 machine. In deuterium-labelling experiments, samples were separated from solution in the absence of air, ground with KCl and loaded into the pressing die in a dry-atmosphere glovebox to avoid exchange with atmospheric water. Such exchange was found to be very rapid with aniline deuteriochloride.

(*d*) *Near-Infrared Spectra*

The near-infrared combination spectra of solid compounds were obtained as reflection spectra using a Beckman DK2A recording spectrophotometer, as described elsewhere.[3]

(*e*) *X-ray Spectra*

X-ray powder photographs were obtained using a Philips 114 mm camera. Finely ground samples were sealed in 0·5 mm Lindeman glass capillaries. A sample of (II) showed identical X-ray powder patterns before and after sublimation.

(*f*) *Deuterium and Tritium Labelling Experiments*

For experiments using deuterium chloride, (II) was dissolved in toluene, the solutions were purged of air with dry nitrogen, and anhydrous deuterium chloride was bubbled through the solution. The solvent and excess DCl were removed under vacuum, and the infrared spectrum recorded. The product was again treated with aniline in toluene and the aniline hydrochloride produced was examined spectroscopically.

In tritium labelling experiments, toluene solutions of (I), prepared from (II) by the addition of tritiated HCl, were taken to dryness in vacuum, and the compound was then dissolved in fresh toluene for liquid scintillation counting.

Acknowledgments

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SYNTHESES OF DI(CYCLOPENTADIENYL) METAL DERIVATIVES BY USE OF DI(CYCLOPENTADIENYL)MAGNESIUM*

By A. F. Reid† and P. C. Wailes‡

Cyclopentadienylsodium in tetrahydrofuran or "diglyme" (2,5,8-trioxanonane) has been widely used[1–3] as an intermediate in the preparation of cyclopentadienyl compounds and is reported to be important on an industrial scale.[4] It has indeed been stated that this is the only route that need ever be used.[1] However, the direct synthesis by Barber[5] of di(cyclopentadienyl)magnesium from cyclopentadiene and magnesium has made this most convenient intermediate readily available, and in solution it has been used in the synthesis of cyclopentadienyl derivatives of titanium and zirconium.[6,7]

In the present work it has been demonstrated in a number of cases that solid crystalline di(cyclopentadienyl)magnesium can be mixed with or added to a stoicheiometric quantity of a metal halide, and reaction then induced by the addition of solvent. Little or no reaction occurs between the mixed solids, which may be stored for long periods. Manipulation of air- and moisture-sensitive solutions is avoided in the present procedure, and the amount of solvent required for reaction is in general much less than that required for solution preparations.

The route described gives readily and in high yield a number of known[1–3] cyclopentadienyl compounds. All of the compounds shown below in Table 2 were obtained as clean crystalline products. In addition to chemical analysis and melting point determination, all of the solid compounds were characterized as containing π-bonded cyclopentadienyl rings by an examination of their n.m.r. spectra or of their near-infrared spectra as described by Reid *et al.*[8] Values for the band positions for $(C_5H_5)_2Sn$, not previously reported, were found to agree closely with those of a large number of other cyclopentadienyl compounds.[8] Di(cyclopentadienyl)manganese was found to show the unusual magnetic susceptibility behaviour reported by Wilkinson *et al.*,[9] the values obtained lying within 2% of those reported over the range 80–300°K.

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[2] Fischer, E. O., *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, 61.
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[7] Reid, A. F., and Wailes, P. C., *J. Organomet. Chem.*, 1964, **2**, 329.
[8] Reid, A. F., Scaife, D. E., and Wailes, P. C., *Spectrochim. Acta*, 1964, **20**, 1257.
[9] Wilkinson, G., Cotton, F. A., and Birmingham, J. A., *J. Inorg. Nucl. Chem.*, 1956, **2**, 95.

Experimental

(*a*) *General*

Manipulations of air-sensitive solid compounds were performed in an evacuable argon-filled dry box containing a reagent balance. The solid reactants were weighed into flasks which were stoppered and removed from the dry box.* A ground joint T-piece with a condenser on a horizontal side-arm was fitted to the flask, and immediately flushed with nitrogen by means of a probe reaching into the flask. By the use of rubber "Suba-Seals" and hypodermic syringe techniques, dry solvent was added to the cooled reaction mixture, the mixture was heated under reflux with the condenser inclined upwards, and the solvent was then distilled off with the condenser inclined downwards, a dry nitrogen atmosphere being maintained throughout. Final traces of solvent were removed in vacuum.

Products were either sublimed in vacuum directly from the flask into a glass column, silicone high-vacuum grease being used in the joint, or the reaction mixture removed in a dry box to a vacuum sublimation vessel or a solvent extraction apparatus. In some cases, where the product was sufficiently stable (e.g. ferrocene), methylene dichloride was used to extract the product directly from the reaction flask. This solvent rapidly decomposes any residual di(cyclopentadienyl)magnesium. The latter can also be removed as an insoluble, involatile carboxylic magnesium salt by bubbling carbon dioxide through the reaction solution[2,9] or by adding solid carbon dioxide to reaction mixtures.

(*b*) *Di(cyclopentadienyl)magnesium*

Di(cyclopentadienyl)magnesium was prepared by the method of Barber.[5] A 3-cm internal diameter reaction column was used, packed for 20 cm of its length with magnesium turnings. The column terminated in a B34 ground glass joint, to which a 2-l. flask with side-arms was attached. The joint, greased with silicone grease, was placed just inside the furnace (35 cm long) used to heat the column. The centre section of the furnace was maintained at 520–550°c, and the joint at 180–200°. With this arrangement the di(cyclopentadienyl)magnesium formed by the reaction of cyclopentadiene with heated magnesium fell in a steady stream of fine crystals to the bottom of the flask and did not condense and block the joint. The exit of the flask was protected with a 30-cm column 2 cm in diameter containing a loose plug of glass wool and leading to a paraffin oil bubbler.

After collection of 30–40 g of the loose crystals, occupying approximately a third of the volume of the flask, the column was allowed to cool, and the flask removed, quickly stoppered, and transferred to a dry box.

(*c*) *Metal Halides*

Anhydrous ferrous chloride was prepared by the reduction of ferric chloride with chlorobenzene,[10] and anhydrous manganous chloride by the action of thionyl chloride on the hydrate.[11] Laboratory reagent lead chloride was oven-dried and used without further treatment. Fused anhydrous stannous chloride, prepared by the reaction of tin with chlorine above its melting point, was pumped free of slight surface hydrolysis products and crushed in a dry atmosphere. The crushed compound was of a clean white appearance.

(*d*) *Reaction of Ferrous Chloride with Di(cyclopentadienyl)magnesium*

Wilkinson *et al.*[9] have reported that a solution of di(cyclopentadienyl)magnesium in tetrahydrofuran reacts nearly quantitatively with ferrous chloride to give ferrocene. In the present work it has been found that addition of tetrahydrofuran to a dry mixture of ferrous chloride and

* In an alternative procedure which avoids the handling or transfer of di(cyclopentadienyl)-magnesium and the use of a dry box, the receiving flask and its stoppers are weighed before and after generation of the compound, and a stoicheiometric weight of a metal halide then added under an inert gas stream.

[10] Kovacic, P., and Brace, N. O., *Inorg. Synth.*, 1960, **6**, 172.

[11] Pray, A. R., *Inorg. Synth.*, 1959, **5**, 153.

di(cyclopentadienyl)magnesium give a very ready reaction, even when the amount of solvent is far from sufficient to dissolve the magnesium compound or the ferrocene. Better yields are obtained with relatively larger amounts of solvent, however, as the mixture forms a dry cake if too little is used. The results obtained are summarized in Table 1. Reactions were carried out with 4 g of di(cyclopentadienyl)magnesium and the stoicheiometric amount of ferrous chloride (3·3 g).

TABLE 1

EFFECT OF VARIOUS AMOUNTS OF TETRAHYDROFURAN (THF) ON THE REACTION BETWEEN FERROUS CHLORIDE AND DI(CYCLOPENTADIENYL)-MAGNESIUM

Ratio of THF to $Mg(C_5H_5)_2$ (ml/g)	Reaction Temp.	Reaction Time (min)	Reaction Mixture Produced	Yield (%)
0·5 : 1	100°	90	dry solid[a]	61
1 : 1	80	60	damp solid[a]	59
2 : 1	80	30	thick slurry[a]	81
5 : 1	80	30	solution + ppt.[b]	90

[a] Mixture extracted with methylene dichloride, to decompose di(cyclopentadienyl)magnesium and prevent further reaction during working-up procedures.

[b] Ferrocene sublimed directly from reaction mixture after removal of solvent.

TABLE 2

REACTION OF MIXTURES OF METAL CHLORIDES WITH STOICHEIOMETRIC AMOUNTS OF SOLID DI(CYCLOPENTADIENYL)MAGNESIUM AFTER ADDITION OF SOLVENT AND APPLICATION OF HEAT

Metal Halide	Reactant Wt. (g)		Solvent	Reaction Conditions	Product	Yield (%)
	Halide	$(C_5H_5)_2Mg$				
$FeCl_2$	3·30	4·0	THF, 20 ml	75°, 0·5 hr	$(C_5H_5)_2Fe$[a]	90
$MnCl_2$	3·60[b]	4·0	THF, 20 ml	75°, 1 hr	$(C_5H_5)_2Mn$[c]	68
$PbCl_2$	7·30	4·0	xylene, 20 ml	160°, 1 hr	$(C_5H_5)_2Pb$[d]	85
$SnCl_2$	5·30	4·0	xylene, 20 ml	160°, 1 hr	$(C_5H_5)_2Sn$[e]	90
$TiCl_3$	10·0	10·0	THF, 30 ml	75°, 1·5 hr	$(C_5H_5)_2TiCl$[f]	79
$ZrCl_4$	24·0	16·0	THF, 60 ml	75°, 2 hr	$(C_5H_5)_2ZrCl_2$[g]	63

[a] Sublimed at 120–150°. M.p. 173–174° (lit.[1] 173°).

[b] A 10% excess of $MnCl_2$ was used.

[c] Sublimed at 120–150° (Found: Mn, 29·1. Calc. for $C_{10}H_{10}Mn$: Mn, 29·7%).

[d] Sublimed at 150–180°. M.p. 138° (dec.) (lit.[1] 140° (dec.)) (Found: Pb, 60·4. Calc. for $C_{10}H_{10}Pb$: Pb, 61·4%).

[e] Sublimed at 150–180°. M.p. 102–105° (lit.[1] 104–105°) (Found: Sn, 47·1. Calc. for $C_{10}H_{10}Sn$: Sn, 47·7%).

[f] Sublimed at 160–200°. For discussion of properties see ref. 12.

[g] Sublimed at 150–180°. M.p. 247–249° (lit.[6] 248°) (Found: C, 41·2; H, 24·3; Cl, 24·3; Zr, 31·2. Calc. for $C_{10}H_{10}Cl_2Zr_2$: C, 41·1; H, 24·0; Cl, 24·0; Zr, 31·4%).

[12] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 9.

With diphenylamine, toluene, or light petroleum as solvent, little or no reaction occurred on heating the sealed mixtures to a temperature as high as 200°.

(*e*) *Reaction of Stannous Chloride, Lead Chloride, Manganous Chloride, and Zirconium Tetrachloride with Di(cyclopentadienyl)magnesium*

The results of these reactions are summarized in Table 2, that for ferrous chloride under comparable conditions being also included. The reaction of titanium trichloride, included for completeness, is discussed more fully in a separate paper.[12] The products were sublimed from the dry reaction mixtures onto a water-cooled cold finger in a vacuum sublimation vessel. No magnesium could be detected in any of the products. Ferrocene was characterized by mixed melting-point determination with an authentic sample. Ferrocene, $(C_5H_5)_2Pb$,[3] and $(C_5H_5)_2ZrCl_2$[7] each gave a single sharp n.m.r. peak in deuterochloroform or tetrahydrofuran.

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CONTRIBUTION FROM THE DIVISION OF MINERAL CHEMISTRY AND THE DIVISION OF ORGANIC CHEMISTRY,
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The Reaction of Molten Magnesium Cyclopentadienide with Fluorides and Other Metal Halides

BY A. F. REID AND P. C. WAILES

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Molten magnesium cyclopentadienide in the absence of solvent reacts with a large number of metal halides, and in particular fluorides, to give cyclopentadienyl metal compounds, frequently in good yield. The reaction is particularly suited to the preparation of the cyclopentadienyls of thorium, uranium, scandium, and the rare earths from their fluorides, which are readily accessible and relatively stable to moisture.

Introduction

Magnesium cyclopentadienide ($MgCp_2$) is a readily sublimable white solid which melts at 177° to a clear, mobile liquid boiling at 222°.[1] Although it is thermodynamically somewhat more stable than ferrocene, the high free energies of formation of the magnesium

(1) H. S. Hull, A. F. Reid, and A. G. Turnbull, *Australian J. Chem.*, **18**, 249 (1965).

halides will in principle allow the reaction of $MgCp_2$ with any halides other than those of the alkali metals and some of the alkaline earths.

The preparation of several metallocenes from anhydrous metal chlorides and $MgCp_2$ in solution has been reported.[2] This paper describes the reactions of molten $MgCp_2$ with a range of anhydrous halides, in particular, fluorides, in the absence of solvent.

Experimental Section

General.—All weighings of air-sensitive compounds were performed on a balance in an evacuable argon-filled drybox fitted with an evacuable lock. Air-sensitive compounds were generally transferred in the drybox, but were also manipulated under nitrogen or in a vacuum system using glass break-seals.

Metal Chlorides.—$AlCl_3$, $FeCl_3$, $PbCl_2$, and also PCl_3 were reagent grade chemicals, taken from freshly opened containers. $PbCl_2$ was air dried at 110°. The chlorides $CoCl_2$, $CrCl_3$, $FeCl_2$, $MnCl_2$, $MoCl_5$, $NbCl_5$, $NiCl_2$, $TiCl_3$, VCl_3, and WCl_6 were prepared by various methods published in *Inorganic Syntheses*, care being taken in all cases to avoid atmospheric contamination. Reagent grade $TiCl_4$ was redistilled over copper turnings, and $ZrCl_4$, prepared by the reaction of chlorine with zirconium turnings[3] at 700°, was purified by vacuum sublimation.

Metal Fluorides.—CeF_4 was prepared by fluorination of CeO at 500°;[4] ScF_3 and CeF_3 were prepared by hydrofluorination of Sc_2O_3 at 700° and CeO_2 at 500°.[5] ThF_4, UF_4, and ZrF_4 were prepared by dehydration of the hydrated salts in a stream of anhydrous HF at 400–500°.[5] NdF_3 and SmF_3 were precipitated from an alcoholic solution of the nitrates by addition of 40% hydrofluoric acid solution,[6] washed with alcohol and ether, and dried under vacuum. PbF_2 was reagent grade material, dried under vacuum at 250°.

Bromides and Iodides.—$ZrBr_4$ and ZrI_4 were prepared by the reactions under vacuum of bromine and iodine, respectively, with zirconium metal turnings. SmI_2 was made by vacuum disproportionation of ammonium samarium iodide hydrate first at 200°, then at 430°.[7]

Magnesium Cyclopentadienide.—Crystalline magnesium cyclopentadienide was prepared by an adaption[2] of the method of Barber.[8] In laboratory preparations the loose solid is conveniently weighed out in an inert atmosphere box, but it can be sublimed or melted into weighed or graduated vessels. Sublimation at 150° through ground joints lubricated with silicone high-vacuum grease can easily be carried out.

On a larger scale the molten material can be run through heated pipelines and is inert to glass, Teflon, steel, copper, aluminum, and brass.

Reaction Procedure.—Reactions were generally carried out in glass tubes 1.5 cm in diameter and 10–12 cm in length fitted with a spherical break-seal. $MgCp_2$ (2.0 g), anhydrous metal halide (sufficient for stoichiometric reaction), and 10–20 0.125-in. glass beads were placed in the tube in the glove box. After sealing under argon, the tube was placed inside a longer glass tube and held in place with asbestos packing. The larger tube was now rotated, *via* a flexible connection to a small motor, at 50–80 rpm inside a furnace heated to 180–280°. The tumbling action and the presence of glass beads served to mix the slurry of molten $MgCp_2$ and solid metal halide during reaction.

In attempts to increase the yield of ferrocene by this procedure, finely ground $FeCl_2$ (8 g) and $MgCp_2$ (10 g) were milled continuously in a larger version of this reaction tube 4 cm in diameter and one-third filled with glass beads. The reaction of crystalline ferrous chloride soon slowed, and even with finely divided $FeCl_2$, prepared by grinding in the absence of air or by dehydration of hydrated ferrous chloride with thionyl chloride, reaction was only 30–40% complete after 6–20 hr at 250–280°. Use of an excess of molten $MgCp_2$ had little effect. This is possibly due to the isomorphism of $MgCl_2$ with $FeCl_2$, their closely similar unit cell dimensions[9] allowing a coherent layer or solid solution of $MgCl_2$ on the surface of the $FeCl_2$ particles.

In the preparation of cyclopentadienylmanganese tricarbonyl, manganese dichloride (8 g) and magnesium cyclopentadienide (10 g) were weighed, either into a glass liner of a 450-ml Parr bomb or directly into the bomb. The latter procedure was preferable, as use of the liner allowed segregation of the reactants during heating of the bomb and thus lowered yields. The bomb was evacuated *via* its gas couplings, filled with CO to a pressure of 800 psi, and heated at 220° with rocking, for 12–15 hr. In one instance 20 ml of dry tetrahydrofuran (THF) was added before pressurizing, and in this case the reaction temperature was 150°.

The reactions of $NbCl_5$, $TaCl_5$, $MoCl_5$, and WCl_6 with $MgCp_2$ were violent, initiating at 100–120°. Reactions were eventually performed in a stainless steel tube sealed with a Teflon gasket and in each case produced dark brown or black, finely divided reaction products containing no unreacted $MgCp_2$.

Separation Procedures.—The bis(cyclopentadienyl) derivatives of Co, Cr, Mn, and V were not separated from the unreacted $MgCp_2$ but were cosublimed, and the amount of metal present was determined by standard titration methods after hydrolysis of the sublimate.

Ferrocene was separated by dissolution of the reaction mixture with methylene dichloride, which destroys excess $MgCp_2$,[2] filtration, evaporation of the solvent, and sublimation of the product. Cyclopentadienylmanganese tricarbonyl was similarly separated and purified.

Bis(cyclopentadienyl)lead was separated from the more volatile magnesium compound by vacuum sublimation along a heated tube, while the cyclopentadienyl derivatives of Ce, Nd, Sc, Sm, Th, Ti(III), and U, and also bis(cyclopentadienyl)-zirconium(IV) iodide, were freed of excess $MgCp_2$ by heating under vacuum at 100–120° and then sublimed from the reaction residue at 170–220°. Except for the thorium and uranium tetrakis(cyclopentadienyls), all of the latter group of compounds sublimed onto a cold finger or down a tube without decomposition.

Tetrakis(cyclopentadienyl)thorium sublimes with 1–2% of a hydrocarbon decomposition product[10] and must be finally purified by washing with petroleum ether (bp 40–60°). It is, however, air stable. Tetrakis(cyclopentadienyl)uranium was found to decompose partly on sublimation although an apparently pure sublimate was obtained on a cold finger in 12% yield based on UF_4. For this compound separation was also effected, after sublimation of excess $MgCp_2$, by extraction of the reaction residue with anhydrous benzene[11] under reduced pressure, a yield of 30% being thus obtained.

In the case of reactions with $NbCl_5$, $MoCl_5$, and WCl_6, no excess $MgCp_2$ nor unreacted metal halide was recovered even on strong heating. These reaction mixtures were extracted with chloroform or toluene and gave unidentified metal compounds containing considerable chlorine, which hydrolyzed to give dienes. The product of the reaction of PCl_3 with magnesium cyclopentadienide was extracted with chloroform, after sublimation of excess $MgCp_2$. Aluminum trichloride reacted completely with $MgCp_2$, no trace of $AlCl_3$ or any product being evolved from the reaction mixture on heating to 300°.

Characterization of Compounds.—Most of the π-cyclopentadienyl compounds listed in Table I have been prepared previously

(2) A. F. Reid and P. C. Wailes, *Australian J. Chem.*, **19**, 309 (1966).
(3) I. E. Newnham and J. A. Watts, *J. Am. Chem. Soc.*, **82**, 2113 (1960).
(4) W. J. Asker and A. W. Wylie, *Australian J. Chem.*, **18**, 959 (1965).
(5) G. Brauer, Ed., "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed, Academic Press, Inc., New York, N. Y., 1963.
(6) A. J. Popov and G. Glockler, *J. Am. Chem. Soc.*, **74**, 1357 (1952).
(7) (a) M. D. Taylor and C. P. Carter, *J. Inorg. Nucl. Chem.*, **24**, 387 (1962); (b) M. D. Taylor, *Chem. Rev.*, **62**, 503 (1962).
(8) W. A. Barber, *Inorg. Syn.*, **6**, 11 (1960).
(9) R. W. G. Wyckoff, "Crystal Structures," Vol. 1, 2nd ed, Interscience Publishers, Inc., New York, N. Y., 1963, p 272.
(10) E. O. Fischer and A. Treiber, *Z. Naturforsch.*, **17b**, 276 (1962).
(11) E. O. Fischer and Y. Hristidu, *ibid.*, **17b**, 275 (1962).

TABLE I

REACTIONS OF METAL HALIDES WITH MOLTEN MAGNESIUM CYCLOPENTADIENIDE (ON A 2-G SCALE)

Halide	Moles of $MgCp_2$/mole of halide	Reaction temp, °C	Reaction time, hr	Product	Yield,[a] %
CeF_3	1.5	220	4	$(C_5H_5)_3Ce$	48
CeF_4	2	220	5	$(C_5H_5)_3Ce$	15
$CoCl_2$	1	220	2	$(C_5H_5)_2Co$	10
$CrCl_3$	1.5	220	5	$(C_5H_5)_2Cr$	22
$FeCl_2$	1	250	2	$(C_5H_5)_2Fe$	8
$FeCl_2$	1.5 (10 g)	260	16	$(C_5H_5)_2Fe$	42
$FeCl_3$	1.5	260	1	$(C_5H_5)_2Fe$	10
$MnCl_2$	1	200	4	$(C_5H_5)_2Mn$	10
$MnCl_2$	1 (10 g) + CO	220	16	$C_5H_5 \cdot Mn(CO)_3$	25
$MnCl_2$	1 (10 g) + CO + THF	150	16	$C_5H_5 \cdot Mn(CO)_3$	37
MnF_2	1.25	230	4	$(C_5H_5)_2Mn$	28
NdF_3	1	260	0.5	$(C_5H_5)_3Nd$	37
NdF_3	1.5	260	4	$(C_5H_5)_3Nd$	39
$PbCl_2$	1	220	0.5	$(C_5H_5)_2Pb$	52
PbF_2	1	200	0.1	$(C_5H_5)_2Pb$	45
ScF_3	1.5	220	3	$(C_5H_5)_3Sc$	83
SmF_3	1.5	260	6	$(C_5H_5)_3Sm$	55
SmI_2	1.0	220	1	$(C_5H_5)_3Sm$	25
ThF_4	2	200	2	$(C_5H_5)_4Th$	61
$TiCl_3$	1.5	230	3	$(C_5H_5)_2TiCl$	nd
$TiCl_4$	2	80–200	0.5	$(C_5H_5)_2TiCl$	15
UF_4	2	230	0.7	$(C_5H_5)_4U$	30
VCl_3	1.5	220	3	$(C_5H_5)_2V$	32
ZrI_4	2	230	1.5	$(C_5H_5)_2ZrI_2$	72

[a] In most cases only one reaction was performed and yields can probably be improved. nd = not determined.

by methods given in the literature.[12-14] The compounds as produced by the present reaction process were each identified as containing C_5H_5 rings bonded with fivefold axial symmetry to the metal atom by examination of their near-infrared combination spectra as described elsewhere.[15] In a number of cases the presence of a single product was checked by examination of the nmr spectrum of the compound in solution in either deuteriochloroform or in tetrahydrofuran, using a Varian A-60 instrument. In each of these cases the characteristic single peak at 6–7 ppm,[16] due to a π-C_5H_5 ring or more than one equivalent ring, was obtained.

The known compounds were in addition variously identified by their colors, melting points or mixture melting points with other samples, elemental analyses, and correspondence of X-ray powder photographs with those of the same compound prepared by other published methods. This last procedure is particularly convenient for identifying members of a series of organometallic compounds such as these, since their powder patterns are quite distinctive and allow easy visual comparison of the patterns obtained from comparison samples. In addition, by this means the tetrakis(cyclopentadienyls) of thorium and uranium were found to be isomorphous.

X-Ray Powder Photographs.—Samples were finely ground in the drybox and loaded into 0.5-mm Lindemann glass capillaries, which were subsequently sealed off without exposure of the contents to air. Photographs were taken on a 114.6-mm powder camera using Cu Kα radiation filtered by nickel.

Melting Points.—Melting points were obtained using samples sealed in capillaries under nitrogen or argon.

Elemental Analyses.—These were performed by the Australian Microanalytical Laboratories, University of Melbourne, and by Mr. E. S. Pilkington of the Division of Mineral Chemistry, CSIRO.

Samples were compacted into pellets in the drybox and transferred under argon. The derivatives of lead, neodymium, thorium, titanium, and zirconium gave carbon analyses within 0.1 to 0.9%, hydrogen analyses within 0.1 to 0.2%, and metal analyses within 0.4 to 1.4% of those theoretically required.

After the separation procedures described above, each of the compounds was tested for magnesium content. In no case could magnesium be detected in the hydrolyzed solutions of the compounds.

Results and Discussion

For preparing the cyclopentadienyl compounds of scandium and the rare earths, the use of the fluorides, which do not react in solution preparations, is particularly convenient as they are often more readily prepared anhydrous than chlorides or other halides.[5,7b] For example, they can be precipitated from alcoholic solutions of the hydrated nitrates,[6] which are in turn made by the action of nitric acid on the oxides. The precipitated fluorides of uranium and thorium are readily dehydrated by heating in a stream of hydrogen fluoride and are relatively stable to atmospheric moisture. Their reaction with magnesium cyclopentadienide in sealed glass tubes is a considerably simpler operation than the solution procedures of Fischer, *et al.*,[10,11] and gives higher yields.

The cyclopentadienyl compounds of thorium, uranium, scandium, and the rare earths all sublime above 180–200°, and their separation from reaction mixtures is particularly simple. Excess $MgCp_2$ is sublimed off at 80–120°, and the product is sublimed from the reaction residue at the higher temperature. This procedure is also satisfactory for the separation of bis(cyclopentadienyl)titanium(III) chloride and bis(cyclopentadienyl)zirconium(IV) iodide. Bis(cyclopentadienyl)lead and bis(cyclopentadienyl)tin can be separated from the more volatile $MgCp_2$ by sublimation along a heated tube. However, separation by physical means of the bis(cyclopentadienyl) derivatives of the

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first-row transition metals from $MgCp_2$ is practically impossible because of their close similarities in melting points and vapor pressures, and, furthermore, in most cases only a moderate or low conversion of the transition metal dihalide was obtained. Chemical separation by removal of $MgCp_2$ with carbon dioxide[17] or chlorinated solvents[2] is useful only for ferrocene. The bis(cyclopentadienyl) compounds of the first transition metal series are better prepared by addition of solvent to the mixture of $MgCp_2$ and metal halide,[2] the latter reactant being in slight excess to ensure complete removal of the magnesium compound from the reaction mixture.

When a cyclopentadienyl metal carbonyl compound is required as the end product, the unseparated reaction mixture can be heated under a pressure of carbon monoxide, or, more conveniently, the metal halide and $MgCp_2$ can be placed together in the pressure vessel and heated together under carbon monoxide. This latter procedure allowed the preparation of cyclopentadienylmanganese tricarbonyl from manganese dichloride. This product was also obtained by heating manganese dichloride, $MgCp_2$, and tetrahydrofuran under carbon monoxide at 150° rather than 220° in the absence of solvent.

It was observed in the reactions of $CrCl_3$, VCl_3, $FeCl_3$, $TiCl_4$, and CeF_4 with excess $MgCp_2$ that reduction of the halides occurred, so that the reaction products were the bis(cyclopentadienyls) of chromium, vanadium, and iron, bis(cyclopentadienyl)titanium(III) chloride, and cerium tris(cyclopentadienide), respectively. Bis(cyclopentadienyl)titanium(III) chloride has previously been shown to be the product of the reaction of $TiCl_4$ with excess $MgCp_2$ in solution,[18] even at elevated temperatures, although sodium cyclopentadienide in solution at 125° gave tris(cyclopentadienyl)titanium.[19] Extraction in a Soxhlet apparatus of solid $MgCp_2$ with $TiCl_4$ was found to give moderate yields of bis(cyclopentadienyl)titanium(IV) chloride, but direct mixing of the reactants caused violent though not immediate reaction. With the use of inert solvent, yields of 75% are obtainable.[20]

Although ThF_4 and UF_4 reacted to give $ThCp_4$ and UCp_4, ZrI_4 gave only bis(cyclopentadienyl) diiodide even with excess $MgCp_2$. Similarly ThI_4 gave an iodine-containing product which appeared to be $(C_5H_5)_2ThI_2$.

Some halides did not react as readily as might be expected, in particular, ZrF_4, $ZrCl_4$, and $ZrBr_4$. Attempts to extend the reaction to metal derivatives other than halides were also unsuccessful, even though the estimated free energies of reaction favored reaction. Among potential reactants which were tried were $FeSO_4$, $MnSO_4$, $K_3Fe(CN)_6$, K_2ZrF_6, $Ni(CN)_2$, ThC_2, and the halides AgCl, CuCl, and $CuCl_2$. In each of these cases the magnesium compound was recovered unchanged after 1–2 hr at 200–250°.

The penta- and hexachlorides $NbCl_5$, $TaCl_5$, $MoCl_5$, and WCl_6 reacted violently when heated with magnesium cyclopentadienide, possibly undergoing reduction, to give black reaction mixtures containing colored metal compounds. These were extractable in chloroform, contained hydrolyzable organic groups and chlorine, and were very reactive toward air. π-Cyclopentadienyl groups were definitely absent, but the infrared spectra indicated the presence of diene-containing ligands. Identification of these products is currently in progress. Both $AlCl_3$ and PCl_3 reacted completely to give nonvolatile compounds. The phosphorus compound could be extracted with chloroform but was rapidly attacked by air, giving an odor of phosphines.

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290,355
44,926/64.

AUSTRALIA

COMMONWEALTH OF AUSTRALIA

PATENT SPECIFICATION

		Class	Int. Cl.
Application Number	44,926/64.	09.61-0.	C07f.
Lodged	26th May, 1964.		

Accompanied by a
Provisional Specification.

Complete Specification Entitled

IMPROVEMENTS IN OR RELATING TO THE SYNTHESIS OF CYCLOPENTADIENYL DERIVATIVES.

Lodged	26th May, 1965.
Accepted	21st April, 1969.
Published	1st December, 1966.

Convention Priority -

Applicant: COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANIZATION.

Actual Inventors: ALLEN FORREST REID and PETER CHARLES WAILES.

Related Art: 211,085(16,882/56) 09.6.

The following statement is a full description of this invention, including the best method of performing it known to US :

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290,355

This invention relates to improved methods of synthesizing the cyclopentadienyl derivatives of metals and non-metals. The invention is principally concerned with the formation of cyclopentadienyl derivatives by the use of bis-cyclopentadienyl magnesium or its substituted derivatives.

Previous synthetic methods employing bis-cyclopentadienyl magnesium have all been based on the use of solutions of this substance in tetrahydrofuran or other solvents.

We have now found that if bis-cyclopentadienyl magnesium or a substituted derivative thereof (hereinafter referred to as "magnesiumcompound") and a salt or other derivative of the metal or non-metal are contacted in the absence of solvent, compounds which could not be formed by the above method can be formed or greater yields are obtainable than with the above method.

According to the present invention there is provided a method for the formation of a cyclopentadienyl derivative of a metal or a non-metal selected from the class consisting of boron, silicon, phosphorus and nitrogen, wherein bis-cyclopentadienyl magnesium or a substituted derivative thereof, hereinafter called "magnesium compound", is contacted with a salt or other derivative of the metal or a halide or other derivative of the non-metal; said derivatives being a compeund containing attached to the metal or non-metal atom, one or more alkyl, aryl, acyl, alkenyl, acetylacetonyl, phosphine or amine groups, or halogenated derivatives of these groups, or one or more of the ligands ammonia, carbonyl, nitrosyl or hydride; in the absence of solvent and thereafter, if said cyclopentadienyl derivative of the metal or non-metal is not formed spontanecusly, initiating

reaction by the addition of a solvent and/or heating.

The magnesium compound may be in the solid, liquid or gaseous state. In the latter two cases, reaction between the bis-cyclopentadienyl magnesium and the metal or non-metal derivatives may occur on contact. When the solid magnesium compound is used, reaction does not usually occur spontaneously and, in such cases, the reaction is initiated either by heating the mixed or contacted reactants or by adding either a small quantity (such as, for example, 10% of the weight of the magnesium compound) of a suitable solvent or substance such as tetrahydrofuran and heating the whole to above the melting point of the magnesium compound, or an amount of solvent less than required to dissolve all of the magnesium compound and cyclopentadienyl products, but sufficient to form a slurry of the mixture, in which case reaction is either spontaneous or carried to completion by heating the mixture at temperatures such as 50° to 100°C. Reaction in general may be effected at reduced atmospheric or increased pressure.

In one preferred method according to the invention the appropriate quantity of dry solid magnesium compound is mixed with a suitable metal salt, usually an anhydrous halide, or with a solid non-metal halide, and the mixture is then heated under an inert gas or in vacuum. Alternatively, the magnesium compound, in the form of loose crystals or lumps formed by previous fusion, and the derivative of the metal or non-metal (hereinafter referred to as the intermediate) can be brought together in a suitable vessel, and the temperature raised to above the melting point of the magnesium compound. In an alternative procedure the magnesium compound is run as a liquid through heated pipelines into a reaction chamber containing

the intermediate. The mixture is agitated or stirred to produce a slurry of the intermediate in liquid magnesium compound. Agitation or mixing of the mixture during reaction is advantageous but not essential. Usually an isothermal enclosure is used, but the reaction container may also be arranged so that the magnesium compound refluxes aboveits melting point.

By the use of the above-and below- described general processes, a number of metal fluorides, not normally reactive in preparations employing solutions of the magnesium compound or cyclopentadienyl sodium in solvents such as tetrahydrofuran, can be employed. The use of fluorides is advantageous in that a number of anhydrous fluorides are more readily prepared than are the corresponding chlorides or other halides, and many are little affected by exposure to air.

Other halides, and especially the chlorides, are nevertheless equally satisfactory. In the case of some tetravalent iodides reaction ceases at the attachment of two cyclopentadienyl rings to the metal even when an excess of magnesium compound is used. In many cases e.g. $(C_5H_5)_4Th$ and $(C_5H_5)_4U$, four rings may be readily attached to the metal by the use of the metal chloride or fluoride as an intermediate. This is not possible when such intermediates are reacted with cyclopentadienyl sodium intetrahydrofuran solution, although use of cyclpoentadienyl potassium in a non-polar solvent (Fischer et al.) gives these compounds. The yields obtained by the present invention are considerably higher, however, and the method is also simpler to carry out.

In some instances the elemental halides may be too reactive for their safe utilization in the method of the invention or may give rise to undesirable side reactions. Such

didficulties as these can be overcome by using other metal compounds as intermediates.

The use of the magnesium compound in the absence of solvent allows the direct application of free energy considerations to determine with what intermediates the magnesium compound will react. The free energies and heats of formation of cyclopentadienyl compounds are relatively small compared with the free energies and heats of formation of the halides of magnesium. Not all elements are capable or have been shown to be capable of forming stable cyclopentadienyl derivatives; however, this invention is concerned with the use of bis-cyclopentadienyl magnesium or its substituted derivatives under the above-stated conditions to prepare those cyclopentadienyl derivatives of the elements which are stable or isolatable, and also the use of the described process to form derivatives of the elements in those cases where a reaction may occur but methods of isolating or characterizing the products have not yet been perfected.

As examples of those compounds of metals which can be isolated or characterized, we have prepared by the process in the above forms or by one of the alternatives given below, the following representative compounds using the appropriate halides or acetylacetonate, amine or ammine derivatives, or other intermediates of the required valency as intermediates -

Group IIA: $(C_5H_5)_2Be$.

Group IIIA: $(C_5H_5)_3Sc$, $(C_5H_5)_3Nd$, $(C_5H_5)_3Sm$.

Group IVA: $(C_5H_5)_2Ti$, $(C_5H_5TiCl_3$, $(C_5H_5)_2TiCl_2$, $(C_5H_5)_2TiCl$, $(C_5H_5)_2ZrCl_2$ $(C_5H_5)_2Zr^I{}_2$, $(C_5H_5)_2ThI_2$, $(C_5H_5)_4Th$.

Group IVB:	$(C_5H_5)_4Ge$,	$(C_5H_5)_2Ge$,	$(C_5H_5)_4Sn$,
	$(C_5H_5)_2Pb$,	$(C_5H_5)_4Si$.	
Group VA:	$(C_5H_5)_3B$.		
Group VIA:	$(C_5H_5)_2Cr$,	$(C_5H_5)_4U$,	$(C_5H_5)_3U$.
Group VIIB:	$(C_5H_5)_2Mn$,	$(C_5H_4.CH_3)_2Mn$.	
Group VIII:	$(C_5H_5)_2Fe$,	$(C_5H_5)_2Co$,	$(C_5H_5)_2Ni$.

When reaction has been carried out, any unreacted magnesium compound can be sublimed away at 60-120°C if the required product is sufficiently involatile, or removed by reaction with carbon dioxide, dilute acid, or a simple chlorinated solvent, if the required product is sufficiently stable. The required product is then sublimed or solvent-extracted from the reaction residue, or is already dissolved in the chlorinated solvent.

In many of the reactions of bis-cyclopentadienyl magnesium with elemental halides such as $AlCl_3$, PCl_3, BCl_3, NCl_3, $ZrCl_2$, $ZrBr_2$, $ZrCl_3$, ZrI_3, $ZrCl_4$, ZrF_4, CeF_4, $NbCl_5$, $TaCl_5$, $MoCl_5$ and WCl_6, spectrophotometric examination and analysis of reaction mixtures after removal of any unreacted bis-cyclopentadienyl magnesium by vacuum sublimation show that cyclopentadienyl derivatives of the elements have been formed, and while at this time suitable means of extracting the products have not been perfected, it is to be understood that the preparation of such compounds by the methods described is within the scope of this invention.

In the production of cyclopentadienyl metal compounds containing other ligands attached to the metal atom, e.g. cyclopentadienyl carbonyls and nitrosyls, the dry unreacted mixture of the magnesium compound and the appropriate metal intermediate may be treated directly with the ligand

(e.g. carbon monoxide or nitric oxide) without prior reaction and in the absence of solvent. In this way $C_5H_5Mn(CO)_3$, for example, was made in good yield by heating a mixture of manganese chloride and bis-cyclopentadienyl magnesium in an atmosphere of CO gas under pressure. Methylcyclopentadienyl manganese tricarbonyl can be prepared similarly.

In the preparation of $(C_5H_5)_2TiCL_2$ by the reaction of $TiCl_4$ with bis-cyclopentadienyl magnesium, a relatively low yield is obtained because the highly reactive $TiCl_4$ acts as a chlorinating agent as well as yielding the desired product. A similar loss of yield is observed in solution reactions. This loss of yield can in principle be avoided by converting the $TiCl_4$ to a suitable complex before carrying out the reaction. Suitable complexes include amine and chloro complexes, and complexes of acetylacetone. It has been found that solid complex $[(Ti(C_5H_7O_2)_3]_2TiCl_6$, bis tris (acetylacetonato) titanium (IV) hexachlorotitanate (IV) is particularly useful in this respect. This complex contains the correct proportion of chlorine to titanium to give $(C_5H_5)_2TiCl_2$ on reaction with $(C_5H_5)_2Mg$, and has the advantage of being easily synthesised from acetylacetone and titanium tetrachloride in a suitable solvent. It reacts smoothly as the solid with solvent-free bis-cyclopentadienyl magnesium to give $(C_5H_5)_2TiCl_2$ in high yield, plus bis-acetylacetonato magnesium, from which acetylacetone can be recovered by hydrolysis.

The preparation of $(C_2H_5)_2ZrCl_2$ is also greatly facilitated by the use of the corresponding zirconium acetyl-acetonate complex in a similar manner.

The complex salts Na_2TiCl_6 and Na_2ZrCl_6 or the corresponding potassium, calcium or other salt containing $TiCl_6^=$ or $ZrCl_6^=$ anions have also been found to be of considerable

value in the preparation of $(C_5H_5)_2TiCl_2$ and $(C_5H_5)_2ZrCl_2$ respectively.

Advantages of this invention include the absence of solvent either entirely or at least when handling mixtures of the magnesium compound and the intermediate, the ready melting of the magnesium compound to form slurries with the intermediate, its easy removal by sublimation or by reaction with carbon dioxide or dilute acid, and the use of metal fluorides which do not usually react in solution preparations. The magnesium compound may readily be mixed with the required amount of metal salt and the mixture stored until reaction is begun by heating. The magnesium compound may be synthesized and deposited directly into a vessel containing the appropriate amount of metal salt, and after closure the mixture heated without the need for handling or transfer of solutions.

A further modification of the method consists in premixing the reactants, with intermediate storage if desired, followed by the addition of a small amount of solvent such as tetrahydrofuran or diethyl ether to slurry the mixture. The slurry is then stirred and, if necessary, heated to a suitable temperature to complete the reaction. In this way $(C_5H_5)_2Fe$ has been prepared in 90% yield from an initially dry mixture of ferrous chloride and bis-cyclopentadienyl magnesium. $(C_5H_5)_2Mn$ has also been prepared under similar conditions with equally good results. Similarly C H $Mn(CO)_3$ was prepared by heating $MnCl_2$, $(C_5H_5)_2Mn$ has also been prepared under similar conditions with equally good results. Similarly $C_5H_5Mn(CO)_3$ was prepared by heating $MnCl_2$,$(C_5H_5)_2Mg$, tetrahydrofuran and CO under pressure. This variation of the process minimizes the use of solvent, avoids the need for formation or handling of separate bis-

cyclopentadienyl magnesium solutions, and avoids the addition of such solutions to solid salts or vice versa. The amount of solvent actually added in such cases will depend on the reaction conditions employed. For example if 10-20% by weight of solvent is added to the magnesium compound, high yields are obtained when the whole is heated above the melting point of the magnesium compound. If on the other hand, it is desired to carry out the reaction at moderate temperatures e.g. 50°-100°C, then it is usually

It will be seen that the method of the invention depends on the use of bis-cyclopentadienyl magnesium and its substituted derivatives in the manner described above. The preparation of these magnesium compounds can be carried out by any suitable known procedure.

While the above description relates more particularly to unsubstituted cyclopentadienyl compounds it is to be understood that the invention is not limited thereto but includes within its scope the production of substituted cyclopentadienyl compounds by the reaction of substituted bis-cyclopentadienyl magnesium compounds with metal or non-metal derivatives under the reaction conditions specified above. For example alkyl, aryl, or halogen substituted magnesium cyclopentadienides may be used in the method of the invention.

The claims defining the invention are as follows:-

1. A method for the formation of a cyclopentadienyl derivative of a metal or a non-metal selected from the class consisting of boron, silicon, phosphorus and nitrogen, wherein bis-cyclopentadienyl magnesium or a substituted derivative thereof, hereinafter called "magnesium compound" is contacted with a salt or other derivative of the metal or a halide or other derivative of the non-metal; said derivatives being a compound containing attached to the metal or non-metal atom, one or more alkyl, aryl, acyl, alkenyl, acetylacetonyl, phosph-ne or amine groups, or halogenated derivatives of these groups, or one or more of the ligands ammonia, carbonyl, nitrosyl or hydride; in the absence of solvent and thereafter, if said cyclopentadienyl derivative of the metal or non-metal is not formed spontaneously, initiating reaction by the addition- of a solvent and/or heating.
(26th May, 1964)

2. The method as claimed in claim 1,wherein the magnesium compound is first mixed with the metal salt or derivative or the non-metal derivative in the solid or liquid state. (26th May, 1964)

3. The method as claimed in claim 2, wherein the reaction is initiated by heating the mixture.
(26th May, 1964)

4. The method as claimed in claim 2, wherein the reaction is initiated by adding a small quantity of a solvent to the mixture and, if necessary, heating the resultant mixture. (26th May, 1964)

5. The method as claimed in claim 2, wherein the reaction is initiated by adding to the mixture a sufficient quantity of a solvent to form a slurry with the mixture and,

if necessary, heating the slurry. (26th May, 1964)

6. The method as claimed in claim 4 or claim 5, wherein the solvent is tetrahydrofuran or diethyl ether- (26th May, 1964)

7. The method as claimed in claim 1, wherein liquid or gaseous magnesium compound is contacted with the metal salt or derivative or the non-metal derivative in the solid liquid or gaseous state, whereupon reaction between the two substances proceeds spontaneously. (26th May, 1964)

8. The method as claimed in claim 1, for the formation of a cyclopentadienyl derivative of a metal which also contains another ligand attached to the metal atom, in which the salt or other derivative of the metal is contacted with magnesium compound in the presence of the other ligand, such ligand being capable of reacting with the metal under the reaction conditions. (26th May , 1964)

9. The method as claimed in claim 1 for the formation of a cyclopentadienyl derivative of a metal which also contains a carbonyl or nitrosyl ligand attached to the metal atom, in which the salt or other derivative of the metal is contacted with magnesium compound in the presence of carbon monoxide or nitric oxide. (26th May, 1964)

10. A method for the formation of a cyclopentadienyl derivative of a metal or non-metal, substantially as hereinbefore described. (26th May, 1964)

Dated this 4th day of June, 1969.

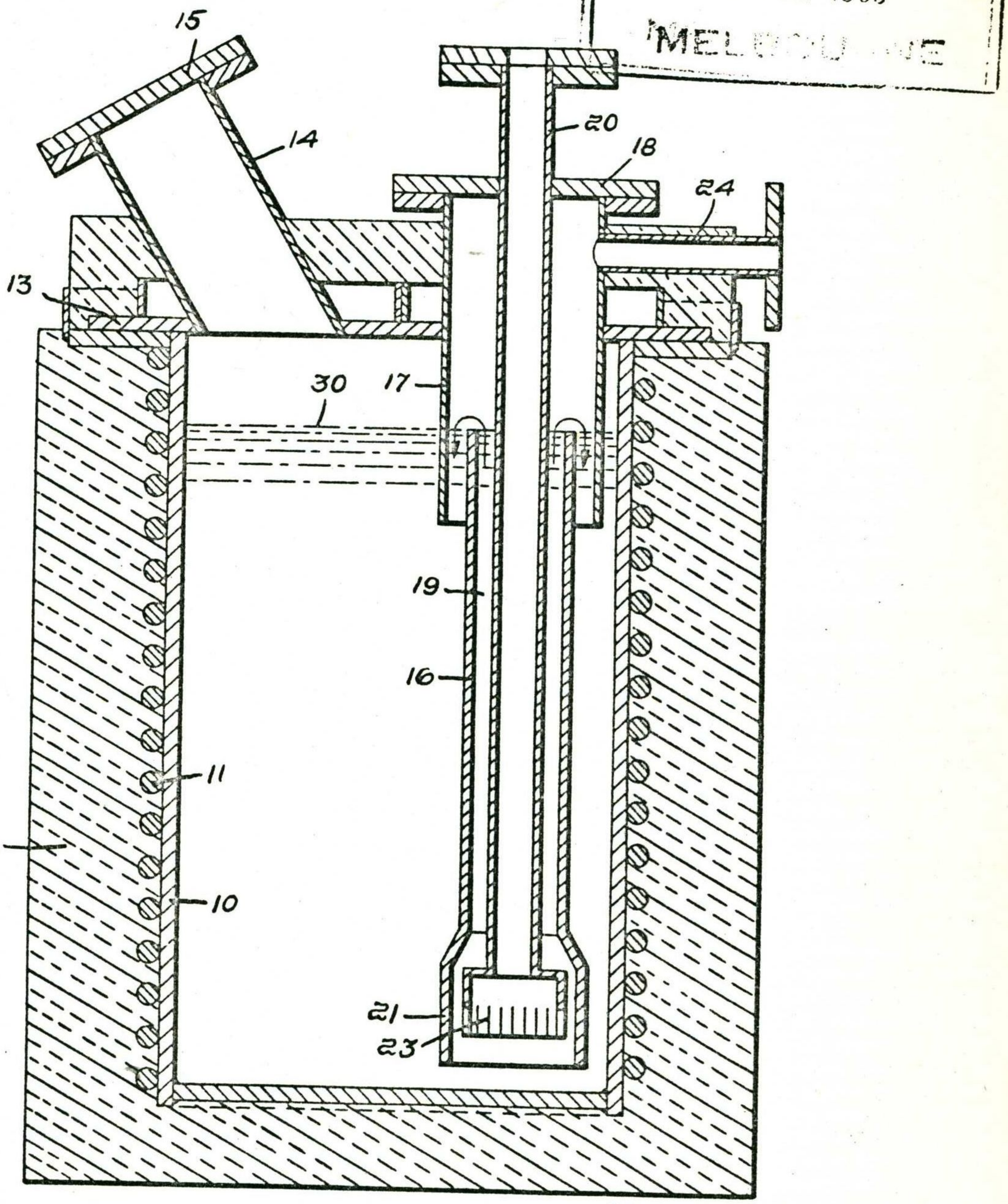
COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION
By its Patent Attorneys
DAVIES & COLLISON.

Oct. 8, 1968 R. L. DAVEY ET AL 3,405,186

METHOD FOR PREPARING DICYCLOPENTADIENYL MAGNESIUM

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Patented Oct. 8, 1968

3,405,186
METHOD FOR PREPARING DICYCLOPENTADIENYL MAGNESIUM

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Filed June 16, 1965, Ser. No. 464,487
1 Claim. (Cl. 260—665)

ABSTRACT OF THE DISCLOSURE

The invention is directed to an improvement in a method for preparing magnesium dicyclopentadienyl wherein cyclopentadiene is reacted at an elevated temperature with magnesium to form magnesium dicyclopentadienyl, the improvement comprising bringing cyclopentadiene in contact with a molten alloy containing about 35 weight percent of magnesium and about 65 weight percent of lead at said elevated temperature at a selected point within a confined reaction zone while causing the molten alloy to move along an endless path passing through said point, a portion of said path extending upwardly from said point.

This invention contemplates a novel method for the preparation of a metaldicyclopentadienyl, such as dicyclopentadienylmagnesium, and an apparatus for use in the preparation of such compounds.

The United States patent to William A. Barber, No. 2,788,377, describes a method for preparing dicyclopentadienyl by reacting cyclopentadiene with solid magnesium, such as magnesium turnings, at a temperature between about 450° C. and about 600° C. or higher. We found that in the practice of this method carbon or magnesium carbide or magnesium acetylide collects on the metal surface, and eventually reaction ceases.

In accordance with the present invention cyclopentadiene is introduced into a body of a molten magnesium alloy at a point a substantial distance below the surface of the molten alloy whereby the cyclopentadiene reacts with the magnesium in the molten alloy to form hydrogen and gaseous dicyclopentadienyl, which separate from the molten alloy at its surface and are caused to pass into a condenser, where the dicyclopentadienyl is condensed to a liquid or solid. Any solid by-products of the reaction are carried out of the zone of reaction to the surface of the molten alloy by upwardly flowing gas stream. The temperature of the molten alloy is maintained between about 450° C. and about 600° C. but a temperature as high as 1000° C. may be used. We have found a temperature between about 540° C. and about 555° C. particularly suitable. Solid magnesium metal may be added from time to time to replace the magnesium consumed by the reaction.

In the practice of the invention we prefer to employ an alloy of magnesium and lead. However, the lead may be replaced by other metals which form sufficiently low-melting binary alloys with magnesium, such as aluminum, silver, bismuth, calcium, cadmium, copper, gallium, mercury, nickel, tin, thallium or zinc. Ternary alloys containing these and other metals also may be used. The preferred alloy contains about 35 weight percent of magnesium and about 65 weight percent of lead.

A particularly suitable apparatus for use in the practice of the invention is illustrated in the single figure of the accompanying drawing. This apparatus comprises a

cylindrical vessel **10**, preferably of mild steel, wound with an electrical heating coil **11**, and provided with suitable insulation **12**. The vessel **10** is provided with a hermetically sealed top or cover **13**, pierced by a conduit **14**, through which the molten alloy, or replacement magnesium metal, may be introduced into the vessel **10**. The outer end of the conduit **14** is normally closed by a detachable cover **15**.

A mild steel tube **16** is suitably suspended within the vessel **10** by means (not shown) with its open bottom end spaced from the bottom of the vessel and its open top end spaced from the top of the vessel, the lower end, portion **21**, of the tube **16** being slightly enlarged. A mild steel tube **17**, supported by the cover **13** by means (not shown), extends through the cover **13** into the vessel **10** and surrounds the tube **16** with its lower open end below the upper end of the tube **16** to provide an annular passage therebetween. The upper end of the tube **17** is closed by a cover **18** secured thereto by means (not shown). A conduit **20** for introducing cyclopentadiene into the vessel **10** extends through the cover **18** of the tube **17** and into the tube **16** with its lower end slightly above the lower end of the tube **16**, the conduit **20** being suitably supported by means (not shown) to provide an annular passage **19** between its outer surface and the inner surface of the tube **16**. Preferably, the conduit **20** is provided with an enlarged slotted lower end, portion **23**. The upper end of the conduit **20** communicates with a source (not shown) of cyclopentadiene under pressure. A conduit **24** provides communication between the interior of the tube **17** and a suitable condenser (not shown) for condensing gaseous dicyclopentadienylmagnesium to liquid or solid.

In operation of the apparatus, molten magnesium alloy is introduced into the vessel **10** to a level indicated at **30**, namely, about 18 inches above the lower end of the tube **16**, and the apparatus is purged with an inert gas, such as argon. The molten alloy is maintained at a desired temperature by the heating coils **11**. Cyclopentadiene is introduced into the conduit **20** under a pressure sufficient to overcome the hydraulic head of the molten alloy and passes into the passage **19** in contact with the molten alloy. As the cyclopentadiene reacts with the molten magnesium alloy in the passage **19** the gaseous dicyclopentadienylmagnesium and hydrogen formed flow upwardly in the passage **19** and separate from the molten alloy at the surface of the latter and then pass through the conduit **24** to the condenser. The upward flow of the gaseous products causes molten metal to flow in an endless path upwardly in the passage **19**, downwardly between the tubes **16** and **17**, and thence upwardly in the passage **19**. If desired, flow of the molten metal may be augmented by a pump withdrawing molten metal from within the vessel **10** and discharging into the bottom open end of the tube **16**. In a given run of 40 hours, 50 liters of liquid cyclopentadiene (run at a flow rate corresponding to 1 to 2 liters liquid cyclopentadiene per hour) were converted in 32 percent yield to the desired dicyclopentadienylmagnesium.

We claim:

1. In a method for preparing magnesium dicyclopentadienyl wherein cyclopentadiene is reacted at an elevated temperature with magnesium to form magnesium dicyclopentadienyl, the improvement wherein the cyclopentadiene is contacted with a molten alloy of magnesium and lead at said elevated temperature at a selected point within a confined reaction zone while causing molten alloy to move along an endless path passing through said point, a portion of said path extending upwardly from said point, said alloy containing about 35

weight percent of magnesium and about 65 weight percent of lead.

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THE REACTION OF CHLORIDOBIS(CYCLOPENTADIENYL)TITANIUM(III) WITH DISULPHIDES

By R. S. P. Coutts,* J. R. Surtees,* J. M. Swan,*† and P. C. Wailes*

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Summary

Chloridobis(cyclopentadienyl)titanium(III) (cp_2TiCl) cleaves dialkyl and diaryl disulphides to give monothio compounds, $cp_2Ti(Cl)SR$, together with varying amounts of cp_2TiCl_2 and $cp_2Ti(SR)_2$. The latter bisthio compounds were prepared independently by the reaction of cp_2TiCl_2 with the sodium salts of the corresponding thiols.

Introduction

Chloridobis(cyclopentadienyl)titanium(III) (I) is a green to brown solid best prepared from titanium trichloride and magnesium cyclopentadienide.[1] It is oxidized readily by atmospheric oxygen[2] and reacts rapidly with organic azides.[3] This paper reports the reaction of (I) with organic disulphides, RSSR (II, R = Me, Et, Ph, CH_2Ph).

Results and Discussion

When a solution of a dialkyl or diaryl disulphide in benzene or tetrahydrofuran was added under nitrogen to cp_2TiCl (I) in the same solvent, the colour changed from green to blood-red. This colour change, together with the appearance of a sharp band in the proton magnetic resonance spectrum, indicated formation of titanium(IV) compounds. These were identified by analysis and p.m.r. spectroscopy as monothio derivatives, $cp_2Ti(Cl)SR$ (III). The yields could be estimated accurately from the p.m.r. spectra and ranged from 65% (R = CH_2Ph) to over 90% (R = Et), the other products being dichloridobis(cyclopentadienyl)titanium(IV) (IV) and the bis(alkyl- or phenyl-thio) compounds (V) in approximately equal quantities. These impurities could be separated from the major products by chromatography on neutral alumina.

In the case of (III; R = CH_2Ph), a slow disproportionation was observed in deuterochloroform. Over a period of 24 hr the cyclopentadienyl absorption band in the p.m.r. spectrum of $cp_2Ti(Cl)SCH_2Ph$ decreased by 50% with a corresponding increase in the intensity of the bands due to cp_2TiCl_2 and $cp_2Ti(SCH_2Ph)_2$. This spontaneous disproportionation did not occur in the case of the other alkyl- or phenyl-thio compounds.

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[1] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 9.
[2] Giddings, S. A., *Inorg. Chem.*, 1964, **3**, 684.
[3] Coutts, R. S. P., and Surtees, J. R., *Aust. J. Chem.*, 1966, **19**, 387.

Chloridobis(cyclopentadienyl)titanium(III) contains an unpaired electron and gives reactions typical of a free radical. Thus it reacts with carbon tetrachloride at room temperature to give dichloridobis(cyclopentadienyl)titanium(IV). We suggest that the formation of all of the observed products of the reaction of cp_2TiCl with disulphides can be explained by the processes shown in equations (1)–(5), the initial reaction being a homolytic scission of the sulphur–sulphur bond.*

$$\underset{(I)}{cp_2Ti^{III}Cl} + \underset{(II)}{RSSR} \rightarrow \underset{(III)}{cp_2Ti^{IV}(Cl)SR} + RS\cdot \quad (1)$$

$$RS\cdot + \underset{(I)}{cp_2Ti^{III}Cl} \rightarrow \underset{(III)}{cp_2Ti^{IV}(Cl)SR} \quad (2)$$

$$\underset{(I)}{cp_2Ti^{III}Cl} + \underset{(III)}{cp_2Ti^{IV}(Cl)SR} \rightarrow \underset{(IV)}{cp_2Ti^{IV}Cl_2} + cp_2Ti^{III}SR \quad (3)$$

$$cp_2Ti^{III}SR + RSSR \rightarrow \underset{(V)}{cp_2Ti^{IV}(SR)_2} + RS\cdot \quad (4)$$

$$RS\cdot + cp_2Ti^{III}SR \rightarrow \underset{(V)}{cp_2Ti^{IV}(SR)_2} \quad (5)$$

In moist air the sulphur–titanium bond of $cp_2Ti(Cl)SR$ is hydrolysed readily, with formation of the orange bridged oxide, $cp_2Ti(Cl)OTi(Cl)cp_2$, and the corresponding thiol. The bisthio derivatives, $cp_2Ti(SR)_2$ (V; R = Me, Et, Ph, CH_2Ph), were synthesized by reaction of cp_2TiCl_2 with the sodium salts of the corresponding thiols. These purple crystalline compounds were stable to air and to moisture. The preparation of (V; R = Me, Ph) was published in 1961[5] and Köpf and Schmidt[6] have just reported the synthesis of (V; R = Et, Ph, CH_2Ph), both by slightly different procedures.

Experimental

(*a*) *General*

Manipulations of cp_2TiCl and the monothio compounds were performed in a nitrogen-filled glove box or in vacuum, and all reactions were carried out under nitrogen.

(*b*) *Materials*

cp_2TiCl was prepared as described earlier.[1] Solvents were purified by refluxing over sodium hydride and distilling.

(*c*) *Reaction of cp_2TiCl with Disulphides*

General Method.—cp_2TiCl (2 mmoles) was suspended in benzene (5 ml) and a solution of the disulphide (1·1 mmoles) in benzene (3 ml) was added under nitrogen with magnetic stirring. The colour changed from green to red immediately. After 3 hr stirring solvent was removed under vacuum at *c.* 40° and the residue was triturated with benzene/light petroleum (1 : 3) to remove excess disulphide. With dimethyl and diethyl disulphides the use of tetrahydrofuran as

* The scission of disulphides by phenyl radicals has been discussed by Pryor and Guard.[4]

[4] Pryor, W. A., and Guard, H., *J. Am. chem. Soc.*, 1964, **86**, 1150.

[5] Giddings, S. A., U.S. Pat., 3,030,395.

[6] Köpf, H., and Schmidt, M., *Z. anorg. allg. Chem.*, 1965, **340**, 139.

solvent gave satisfactory results but with the diphenyl and dibenzyl disulphides more of the unwanted by-products were produced. The yields of monothio derivatives are given below and analyses, melting points, and p.m.r. data are shown in Table 1.

Compound	Yield
Chloridobis(cyclopentadienyl)methylthiotitanium, $cp_2Ti(Cl)SCH_3$	90%
Chloridobis(cyclopentadienyl)ethylthiotitanium, $cp_2Ti(Cl)SC_2H_5$	>90%
Chloridobis(cyclopentadienyl)phenylthiotitanium, $cp_2Ti(Cl)SC_6H_5$	75%
Benzylthiochloridobis(cyclopentadienyl)titanium, $cp_2Ti(Cl)SCH_2C_6H_5$	65%

TABLE 1

MONO AND BISTHIOTITANIUM COMPOUNDS

Satisfactory analyses of the monothio compounds were difficult to obtain, but in all cases integration of the p.m.r. spectra afforded excellent confirmation of the proposed structures

Compound	M.P.	P.M.R. (δ, $CDCl_3$)	C (%)		H (%)		Cl (%)		Ti (%)	
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$cp_2Ti(Cl)SMe$	179° *	6·34 3·12	50·7	50·7	5·0	5·0	10·8	12·3	18·6	18·4
$cp_2Ti(Cl)SEt$	108–110*	6·34 3·62 1·31	52·9	52·5	5·4	5·5	13·1	12·9	17·5	17·4
$cp_2Ti(Cl)SPh$	140*	7·32 6·21	59·2	59·55	4·9	4·7	11·0	11·0	15·2	14·8
$cp_2Ti(Cl)SCH_2Ph$	134–135·5*	7·16 6·29 4·63	60·5	60·6	5·5	5·1	11·3	10·5	15·6	14·2
$cp_2Ti(SMe)_2$	184	6·12 2·62	53·0	52·9	5·9	5·9	—	—	17·4	17·6
$cp_2Ti(SEt)_2$	117*	6·10 3·07 1·18	56·5	56·0	6·9	6·7	—	—	16·0	16·0
$cp_2Ti(SPh)_2$	200–202*	7·40 6·03	67·0	66·7	5·1	5·1	—	—	11·8	12·1
$cp_2Ti(SCH_2Ph)_2$	178*	7·15 6·12 4·19	67·7	67·9	5·5	5·7	—	—	11·2	11·3

* Decomposition.

(*d*) *Chromatographic Purification*

For chromatography, the pH of the alumina was critical. The adsorbent was best prepared by soaking alumina in ethyl acetate for 1 hr, followed by drying at 100–110° overnight. The crude products were applied in a 1 : 1 mixture of benzene/light petroleum (b.p. 60–80°). Elution with the same solvent gave the purple dithio compound together with any disulphide present, followed by the red monothio derivative. The dichloride remained on the column.

(*e*) *Preparation of* $cp_2Ti(SR)_2$

General Method.—Sodium (2×10^{-3} g-atom) was added to liquid ammonia (10 ml), followed after several minutes by the thiol (2 mmoles). Ammonia was allowed to evaporate through a

KOH drying tube and the residue was pumped free of traces of ammonia. The salt was suspended in benzene (15 ml) by vigorous stirring and cp_2TiCl_2 (1 mmole) was added. The mixture was stirred overnight or heated under reflux for 1 hr; then the reaction mixture was poured onto a short column of untreated alumina and the purple bisthio derivative was eluted with benzene and recrystallized from benzene/petrol mixtures. Yields were almost quantitative.

Sublimation was used for the purification of some samples but partial decomposition always occurred at the temperatures required (150°/10^{-4} mm). Analyses, melting points, and p.m.r. data are shown in Table 1.

(*f*) *P.m.r. Spectra*

These were obtained in $CDCl_3$ with a Varian A60 instrument. In the spectra of the monothio compounds the band due to the protons of the cp ligands is 0·2–0·3 p.p.m. upfield from the corresponding band of cp_2TiCl_2. In the case of the bisthio derivatives the shift is 0·4–0·5 p.p.m. upfield.

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THE CYANATO AND THIOCYANATO DERIVATIVES OF BIS(CYCLOPENTADIENYL)TITANIUM(IV) AND BIS(CYCLOPENTADIENYL)ZIRCONIUM(IV)

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Summary

The cyclopentadienyl metal compounds, $cp_2Ti(NCO)_2$,† $cp_2Ti(NCS)_2$, $cp_2Zr(NCO)_2$, and $cp_2Zr(NCS)_2$, have been prepared and the modes of attachment of the cyanato and thiocyanato ligands determined by infrared spectroscopy. All are bonded to the metals through nitrogen and are therefore isocyanato and isothiocyanato derivatives. $cp_2Zr(NCO)_2$ is sensitive to moisture which converts it into the bridged oxide $cp_2Zr(NCO)–O–Zr(NCO)cp_2$. This reaction can be reversed with anhydrous cyanic acid.

Introduction

As part of a broad investigation of cyclopentadienyl compounds of three- and four-valent titanium and zirconium, the cyanato and thiocyanato derivatives have been prepared. This paper deals with the synthesis and properties of the four-valent derivatives formulated in the Summary. Both the cyanato and more particularly the thiocyanato groups have attracted attention because of the three possible modes of attachment to other elements, i.e. through nitrogen, through sulphur (or oxygen), or through both when the ligand is bridging, e.g.:

M–NCS	M–SCN	M–NCS–M
(Ia)	(Ib)	(Ic)

In addition to these possibilities, there arises the question of whether the ligand is linear, giving a true tetrahedral molecule, or bent with corresponding loss of symmetry. Assignment of symmetry requires accurate infrared assignments and even crystal structure analysis, so is outside the scope of this paper.

The only compound of the four mentioned in the literature is $cp_2Ti(NCS)_2$. It was reported by Jensen[1] who studied the kinetics of its reaction with LiCl and LiSCN, but apparently did not isolate it. In another kinetics study, Langford and Aplington[2] prepared and analysed the same derivative but they reported no physical properties.

* Division of Organic Chemistry, CSIRO, Chemical Research Laboratories, Melbourne.

† cp, π-cyclopentadienyl.

[1] Jensen, A., Proc. 7th Int. Congr. Coord. Chem., p. 254 (1962).

[2] Langford, C. H., and Aplington, J. P., *J. organomet. Chem.* 1965, **4**, 271.

Results and Discussion

(a) *Syntheses*

The thiocyanato derivatives were conveniently prepared from potassium thiocyanate and bis(chlorido)bis(cyclopentadienyl)titanium(IV) (or zirconium(IV)) in acetone. Unfortunately, the alkali metal cyanates are not sufficiently soluble in acetone to be employed in a similar manner. Treatment of cp_2TiCl_2 with excess silver cyanate in boiling benzene afforded a satisfactory synthesis of the bis(cyanato)-titanium derivative. In the case of the zirconium analogue the bis(cyanato) compound (II) was always mixed with the bridged oxide (III), apparently formed from adventitious water:

$$\underset{\text{(II)}}{2cp_2Zr(NCO)_2} + H_2O \rightleftharpoons \underset{\text{(III)}}{cp_2Zr(NCO)\text{–}O\text{–}Zr(NCO)cp_2} + 2HNCO$$

The presence of (III) could be shown by its characteristic infrared band at 750 cm^{-1} (Zr–O–Zr)[3] and a peak in the p.m.r. spectrum at δ 6·46. Fortunately the hydrolysis can be reversed with anhydrous cyanic acid giving a quantitative yield of (II). As a consequence of this ready conversion of (II) into (III), molecular weight determinations (carried out in acetone because of insolubility of $cp_2Zr(NCO)_2$ in non-polar solvents) always gave high values. Similarly infrared spectra of (II) free of the Zr–O–Zr band at 750 cm^{-1} were difficult to obtain in potassium bromide disks unless the bromide was first baked to 600° and the die loaded in a dry-box.

The p.m.r. spectrum of (II) showed a single peak immediately after preparation from cyanic acid in tetrahydrofuran or acetone. On standing, the excess cyanic acid polymerized to cyanuric acid with simultaneous appearance of the peak due to the bridged oxide (III).

(b) *Properties*

Some of the physical properties of these compounds are shown in Table 1. All except $cp_2Zr(NCO)_2$ are reasonably stable in air and sublime in high vacuum with some decomposition.

Although Jensen states[1] that $cp_2Ti(NCS)_2$ is dimeric in acetone, our measurements in this solvent at 37° (Mechrolab osmometer) indicate that all of the compounds are monomeric. If the NCS or NCO ligands are bridging as in (Ic) then the CN band frequency around 2100 cm^{-1} should show a shift to lower frequency in acetone compared with Nujol or potassium bromide disk. No such shift was observed in any of the compounds so we must conclude that it is unlikely that the ligands are bridging.

(c) *Site of Attachment of Metal to Ligand*

Metal thiocyanates (M–SCN) show a CS stretching vibration at 690–720 cm^{-1} and metal isothiocyanates (M–NCS) show a similar band at higher frequency[4] (780–860 cm^{-1}). In the cyclopentadienyl compounds under discussion this latter band would be masked by the strong absorption around 840 cm^{-1} due to the CH out-of-plane bending vibration of the rings. However, the absence of any bands

[3] Reid, A. F., Shannon, J. S., Swan, J. M., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 173.
[4] Turco, A., and Pecile, C., *Nature*, 1961, **191**, 66.

in the region 800–650 cm^{-1}, together with the higher intensity of the 840 cm^{-1} band relative to that at 1020 cm^{-1} (CH in-plane bending), is strong indication of the M–NCS structure in our compounds.

For metal cyanates (M–OC≡N), no fundamental frequencies are expected between 1200 and 2000 cm^{-1}, while metal isocyanates (M–N=C=O) have a pseudo-

TABLE 1

PHYSICAL PROPERTIES

Compound	M.P.	Colour	Sublim. Temp. (10^{-4} mm)	Mol. Wt.		P.M.R. (δ)	I.R. Ligand Bands (cm^{-1})
				Found	Calc.		
$cp_2Ti(NCO)_2$	275–277° *	orange	160°	268	262	6·62	2250
$cp_2Zr(NCO)_2$	218*†	colourless	175	388	306	6·66	2240
$[cp_2Zr(NCO)]_2O$	275–277*	colourless	—	520	544	6·46	2240
$cp_2Ti(NCS)_2$	305–307*	purple	200	266‡	294	6·77	2090
$cp_2Zr(NCS)_2$	279–281	yellow	200	331	338	6·54	2040

* Decomposition.

† Probably low due to traces of oxide.

‡ Low concentration (2 mg/ml) due to insolubility.

symmetric stretch near 1400 cm^{-1}.[5] $cp_2Ti(NCO)_2$ shows two medium intensity bands in this region (1300 and 1370 cm^{-1}) as does $cp_2Zr(NCO)_2$ (1350 and 1370 cm^{-1}). (One of these bands is probably the first harmonic of the bending frequency of NCO).[6] We conclude that the compounds are true isocyanates bonded through nitrogen.

TABLE 2

ANALYTICAL DATA

Compound	C (%)		H (%)		N (%)		Metal (%)	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$cp_2Ti(NCO)_2$	54·9	55·0	4·3	3·85	10·5	10·7	18·2	18·3
$cp_2Zi(NCO)_2$	47·2	47·1	3·4	3·3	9·2	9·2	30·0	30·05
$[cp_2Zr(NCO)]_2O$	48·7	48·5	4·4	3·7	5·0	5·15	33·3	33·8
$cp_2Ti(NCS)_2$	49·3	49·0	3·4	3·4	9·6	9·5	16·3	16·3
$cp_2Zr(NCS)_2$	42·3	42·6	3·4	3·0	8·4	8·3	27·3	27·2

Both titanium and zirconium have *d*-orbitals available for $p\pi$–$d\pi$ bonding with the "spare" electrons on nitrogen leading to structures such as $M^{-}\leftarrow{}^{+}N{=}C{=}O$, similar to that predicted for $Si(NCO)_4$.[5] Such structures require the –N=C=O group to be essentially linear leading to a true tetrahedral molecule, but with the evidence available the shape of the ligand cannot be determined.

[5] Miller, F. A., and Carlson, G. L., *Spectrochim. Acta*, 1961, **17**, 977.

[6] Waddington, T. C., *J. chem. Soc.*, 1959, 2499.

Experimental

General

Melting points were determined in evacuated capillaries and are uncorrected. Infrared spectra were measured as potassium bromide disks on a Perkin–Elmer 137 Infracord spectrophotometer. Proton magnetic resonance spectra were determined in acetone on a Varian A60 instrument. Molecular weight measurements were made in acetone on a Mechrolab osmometer.

Preparation of Thiocyanato Compounds

cp_2TiCl_2 or cp_2ZrCl_2 was dissolved in the minimum of acetone and added to a saturated solution of anhydrous KSCN (50% excess) in acetone. Precipitation of KCl began almost immediately. After 0·5 hr at room temperature, the suspension was filtered and the filtrate evaporated to dryness. Sublimation of the residue at 200°/10^{-4} mm (with some decomposition) gave the bis(thiocyanato) compounds. Physical constants are shown in Table 1 and analytical data in Table 2.

Preparation of Cyanato Compounds

cp_2TiCl_2 or cp_2ZrCl_2 was boiled under reflux in benzene for 2 hr or shaken in nitrobenzene at room temperature with a fourfold excess of dry AgNCO. The suspension was filtered and the filter cake was extracted three times with chloroform. Extracts and filtrate were combined and evaporated to dryness leaving a residue free of chloride. Sublimation at 160–175°/10^{-4} mm gave the bis(cyanato) compound in the case of titanium and a mixture with the bridged oxide in the case of zirconium.

When cp_2ZrCl_2 was shaken under nitrogen in nitromethane with a fourfold excess of AgNCO for 0·5 hr, a quantitative yield of $cp_2Zr(NCO)–O–Zr(NCO)cp_2$ was obtained.

Cyanic Acid Experiments

Anhydrous HNCO was prepared by pyrolysis of cyanuric acid $(HNCO)_3$,[7] the gaseous product being collected as a liquid in a trap cooled in acetone/solid CO_2. In a stream of CO_2 the cyanic acid was then swept into a solution of $cp_2Zr(NCO)–O–Zr(NCO)cp_2$ or its mixture with $cp_2Zr(NCO)_2$ in tetrahydrofuran until the p.m.r. spectrum of the solution showed a single peak in the δ 6–7 range.

Solvent was pumped away immediately and the residue was recrystallized from dry methylene dichloride or toluene under nitrogen, then sublimed under high vacuum, giving pure $cp_2Zr(NCO)_2$. Physical constants are shown in Table 1 and analytical data in Table 2.

[7] Gattermann, L., and Rossolymo, A., *Ber. dt. chem. Ges.*, 1890, **23**, 1192.

INORG. NUCL. CHEM. LETTERS Vol. 3, pp. 1-5, 1967. Pergamon Press Ltd. Printed in Great Britain. 10

PSEUDOHALOGEN DERIVATIVES OF BIS(CYCLOPENTADIENYL)TITANIUM^{III}

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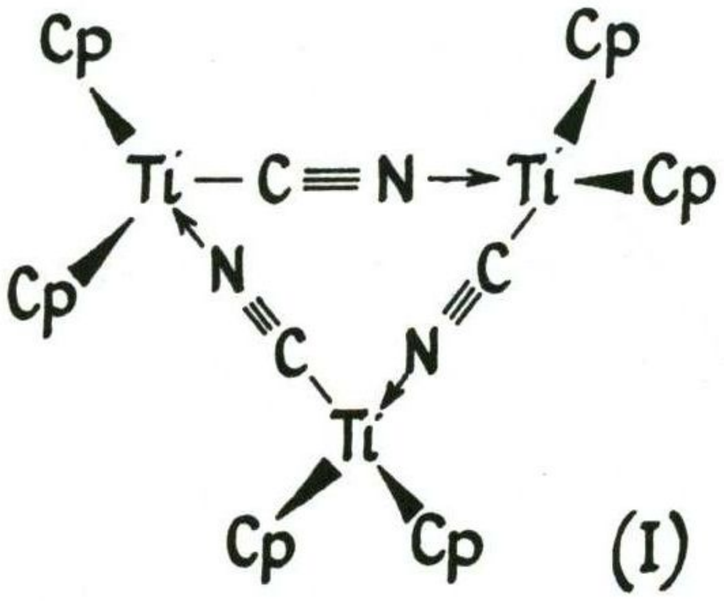
THE REDUCTION of bis(cyclopentadienyl)titanium^{IV} chloride by electrolytic or chemical means has been shown (1,2) to give solutions containing the Cp_2Ti^+ cation ($Cp=C_5H_5$). The aqueous chemistry of this ion has received little attention, but we now find that in air-free water it is possible to prepare many derivatives of Cp_2Ti^+ which cannot conveniently be made in organic solvents. This paper reports the isolation of a trimeric cyanide, $(Cp_2TiCN)_3$, a trimeric isothiocyanate, $(Cp_2TiNCS)_3$, and a monomeric isocyanate, Cp_2TiNCO, by this method. An azide was also precipitated but decomposition with gas evolution began immediately and the compound exploded on warming.

Bis(cyclopentadienyl)titanium^{III} chloride, from which all of these derivatives were prepared, was obtained as a greenish-brown crystalline sublimate from the reaction between titanium trichloride and magnesium cyclopentadienide in tetrahydrofuran (3). When quite pure it dissolves in air-free water giving a bright blue solution which is extremely sensitive to oxygen and which has the molar conductance of a 1:1 electrolyte. Using a Schlenk tube system (4), the pseudohalogen derivatives were precipitated by the addition of air-free solutions of sodium cyanide, thiocyanate, cyanate or azide. The precipitates were collected by filtration under nitrogen, washed with water, and pumped dry.

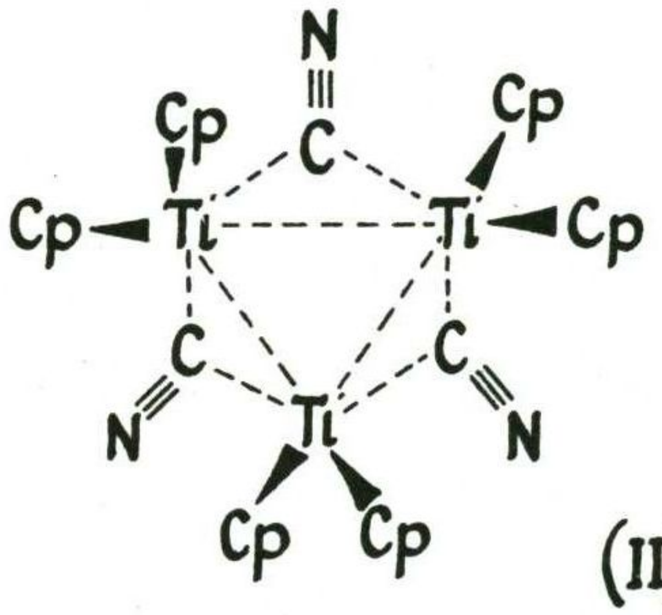
All of the compounds are extremely sensitive to oxygen which converts them into yellow bridged oxides $Cp_2Ti(X)\text{-}O\text{-}Ti(X)Cp_2$, although the pseudohalogen ligand is lost to some extent during this process. The oxides are readily recognized by a strong band in the infra-red (5) around 720 cm^{-1}.

Magnetic susceptibilities of the cyanide were determined over the temperature range 120-320°K. After correcting the experimental susceptibilities for the temperature-independent paramagnetism (T.I.P.) of 318 x 10^{-6} cgs, the Curie-Weiss law is obeyed at temperatures below 290°K with $\theta = -25°$. The resultant μ eff = 1.00 $\pm$ 0.05 B.M. per Ti atom. This magnetic behaviour is strong indication of a cyclic trinuclear unit (cf. Re_3Cl_{12} (6), Mo_3Cl_9 (7), and the titanium^{III} cation (8), $[Ti_3(OMe)_3(CH_3OH)_6]^{6+}$).

The cyanide ligands must be bridging but whether they are linear as in (I) or of the three-centre type as in (II) has not yet been determined.



(I)



(II)

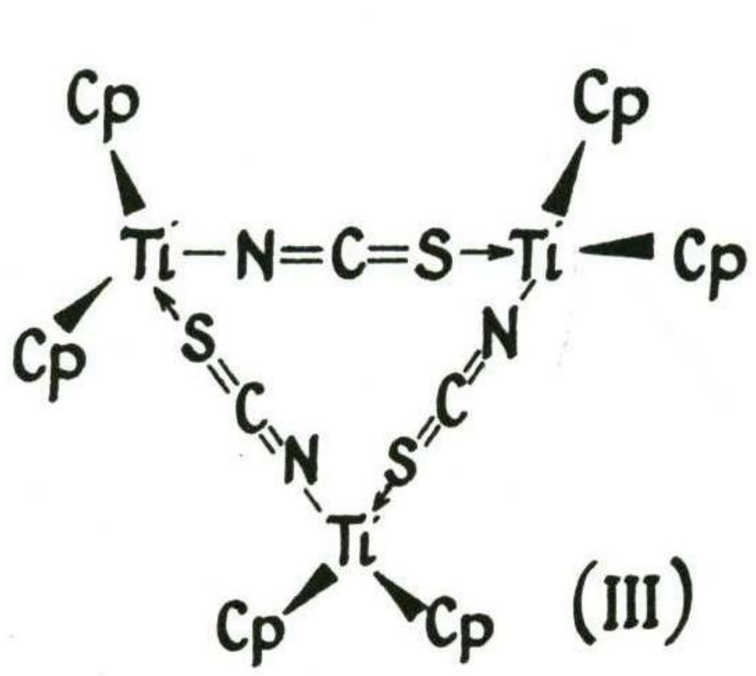
The latter type of bridging has been predicted for the $[Ni_2(CN)_6]^{4-}$ complex (9). It is hoped to establish the structure unequivocally by crystal structure determination.

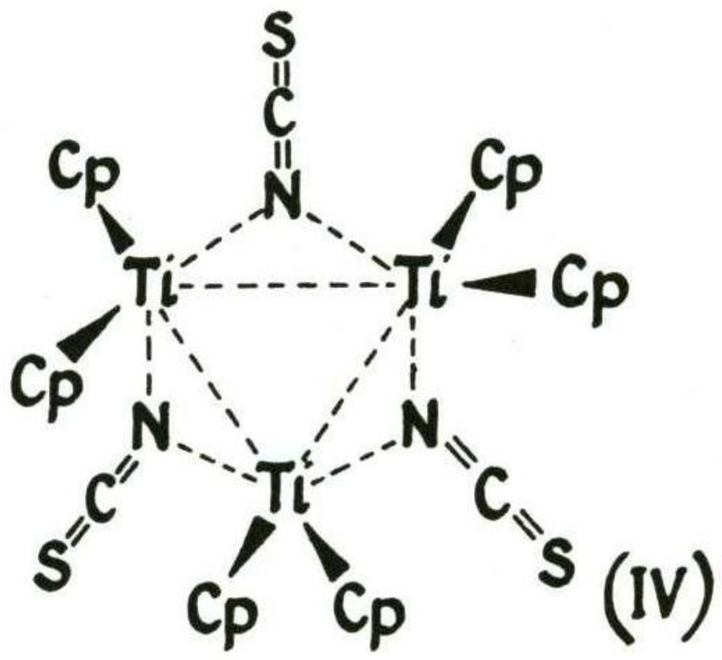
Mass spectral evidence supports the trimeric nature of the cyanide with a mass peak at m/e 612 (parent ion) and lower mass numbers corresponding to loss of Cp, CN or Cp_2TiCN from the parent.

$(Cp_2TiCN)_3$ is virtually insoluble in all of the common organic solvents so that its molecular weight could not be confirmed by solution methods.

The magnetic properties of the isothiocyanate proved to be very similar to those of the cyanide. Susceptibilities were determined over the range 150-320°K, and after applying a correction for T.I.P. of 237 x 10^{-6} cgs the Curie-Weiss law is obeyed at temperatures below 280°K with $\theta = 24°$.

μ eff = 1.04 ± 0.05 B.M. per Ti atom. We consider that the isothiocyanate is a cyclic trimer with weakly bonded NCS bridging between Ti atoms as in (III) or (IV).





That the trinuclear unit is readily broken up is shown by the lower sublimation temperature of the thiocyanate relative to that of the cyanide (see Table), its increased solubility in polar organic solvents and the absence of any mass peak above m/e 236 (Cp_2TiNCS) in the mass spectrum. Lower mass numbers correspond to the loss of Cp or NCS.

The infra-red spectrum shows no band around 700 cm^{-1} so that the thiocyanate is not S-bonded(10).The compound is therefore an isothiocyanate as would be expected for a first row transition metal.

The pale green isocyanate differs in behaviour in some respects from the previous two compounds. Thus the magnetic properties indicate that the isocyanate is monomeric. Susceptibilities were determined over the range 120-320°K. After a T.I.P. correction of 100×10^{-6} cgs the Curie-Weiss law is obeyed at temperatures below 290°K, with $\theta = -28°$, and μ eff = 1.68 ± 0.05 B.M. per Ti atom, i.e. 1 unpaired electron. The mass spectrum shows a high intensity parent peak at m/e 220 and above this two low intensity peaks at 257 ($Cp_2Ti(NCO)C_3H^+$) and 259 ($Cp_2Ti(NCO)C_3H_3^+$). This type of ion,formed by recombination of the parent with fragments of the cyclopentadiene ring, has been observed in ferrocene and nickelocene(11).Prominent peaks at lower masses correspond to loss of Cp and NCO and even loss of oxygen from the

ligand, e.g. m/e 74 ($TiNC^+$). Fragments of the latter type help to confirm the isocyanate formulation, first predicted from the infra-red spectrum, but the possibility of rapid rearrangement in the mass spectrometer should not be overlooked.

In addition to the pseudohalogen derivatives mentioned above Cp_2TiCl forms water-insoluble compounds with $[BPh_4]^-$, $[AuBr_4]^=$, $[Mn(CO)_5]^-$ and a range of organic acids $[RCOO]^-$. Its reactions with $[PtCl_4]^=$, $[PtCl_6]^=$, $[BF_4]^-$, $[TiF_6]^=$ and $[HgI_4]^=$ have also been investigated. Results of this work will be published in the Australian Journal of Chemistry.

TABLE

Compound	Colour	m.p. (°C)	I.R. ligand (KBr) (cm^{-1})	Sublim. Temp. (°C/ 10^{-4}mm)	Analyses %	N	Ti
Cp_2TiCl	green-brown	282	-	150		-	-
$(Cp_2TiCN)_3$	purple	dec.	2100	280	Found	6.4	23.7
					Calc.	6.86	23.47
$(Cp_2TiNCS)_3$	red-brown	210	2070 2040	170	Found Calc.	5.8 5.73	20.0 20.29
Cp_2TiNCO	green	dec.	2175	160	Found	6.5	21.0
					Calc.	6.36	21.76
Cp_2TiN_3	yellow	-	2050	-		-	-

Acknowledgements

The authors thank Professor R. L. Martin, Dr. D. Scaife and Dr. A. F. Reid for helpful discussion.

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CARBOXYLATO DERIVATIVES OF BIS(CYCLOPENTADIENYL)TITANIUM(III)

By R. S. P. Coutts* and P. C. Wailes*

[*Manuscript received February* 24, 1967]

Summary

Several carboxylato derivatives of bis(cyclopentadienyl)titanium(III), of general formula $cp_2TiOOCR$, have been prepared by precipitation from air-free aqueous solutions of cp_2TiCl ($cp = C_5H_5$). The compounds are blue or green and paramagnetic, having one unpaired electron per titanium atom. All of the available evidence indicates that the carboxylato ligands are bidentate, symmetrical, and covalently bound to the metal.

Introduction

The reactions of cp_2TiCl have been under study in this laboratory for some time, and the isolation of several pseudohalogen derivatives by precipitation from air-free water has already been described.[1] Two of these, the cyano and isothiocyanato derivatives, were found to be novel cyclic trinuclear units in which spin–spin interaction between titanium atoms lowers the magnetic susceptibility. In view of this work and the known tendency of titanium(III) methoxides to form trinuclear clusters,[2] other derivatives of cp_2Ti^{III} are being prepared and their magnetic and spectral properties investigated.

This paper describes the preparation of, and assignment of structures to, eight carboxylato derivatives of bis(cyclopentadienyl)titanium(III). They are potentially useful intermediates and their reactions with trialkyl and triaryl aluminiums are being studied.

Results and Discussion

Preparation of Carboxylato Derivatives

All of the compounds were prepared by mixing filtered air-free aqueous solutions of cp_2TiCl and of the sodium salt of the appropriate acid, using a Schlenk tube system[3] to protect the reactants and the product from oxygen.

$$cp_2TiCl + NaOOCR \rightarrow cp_2TiOOCR + NaCl$$

The carboxylato derivative precipitated immediately as a blue or green solid.

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[1] Coutts, R., and Wailes, P. C., *Inorg. nucl. chem. Lett.*, 1967, **3**, 1.
[2] Winter, G., *Inorg. nucl. chem. Lett.*, 1966, **2**, 161.
[3] Herzog, S., and Dehnert, J., *Z. Chemie, Lpz.*, 1964, **4**, 1.

Properties of Carboxylato Derivatives

The formate, $cp_2TiOOCH$, was moderately soluble in water and the acetate was slightly soluble, but with increase in chain-length of the carboxylic acid solubility in water became negligible. All were extremely sensitive to air; the dicarboxylato compounds in particular inflamed spontaneously when exposed in a densely-packed form. Slow oxidation of all compounds gave bright yellow or orange coloured titanium(IV) compounds of unknown composition. All derivatives, and particularly those from monocarboxylic acids, were exceptionally volatile (see Table 1) and could be purified readily by sublimation under vacuum.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA

Compound	Colour	M.P.	Sublim. Temp. (10^{-5} mm)	Ti* (%)		Mol. Wt.†		Λ_M‡
				Found	Calc.	Found	Calc.	
Monocarboxylato Derivatives $cp_2TiOOCR$								
R = H, formato	green	92°	90°	21·6	21·5	200	223	18·6
R = CH_3, acetato	royal blue	110	50	20·4	20·2	226	237	3·6
R = $CH_3(CH_2)_8$, caprato	royal blue	*c.* 5	110	13·9	13·7	—	—	0
R = $CH_3(CH_2)_{16}$, stearato	royal blue	35	120	10·1	10·4	456	461	0
R = Ph, benzoato	dark green	83–85	100	16·1	16·0	299	299	0
Dicarboxylato Derivatives $(cp_2TiOOC)_2R'$								
R′ = $-CH_2CH_2-$, succinato	grey blue	245–250 (dec.)	200	20·0	20·3	—	—	0
R′ = –CH=CH– (*cis*), maleato	pale green	290–300 (dec.)	190	20·2	20·4	—	—	18·3
R′ = –CH=CH– (*trans*), fumarato	mauve	260–262 (dec.)	190	20·7	20·4	—	—	6·0

* Sample weighed in a nitrogen-filled glove-box using a R.I.I.C. Electrobalance with remote control. Analyses for carbon and hydrogen, carried out by conventional methods by the Australian Microanalytical Service, Melbourne, gave, with one exception, values which were 1–1·6% low for carbon. This is no doubt due to the extreme instability of these compounds in air. The exception was the formate which remains apparently unchanged in air for several minutes and which consequently gave correct analytical values (Found: C, 59·1; H, 5·0. $C_{11}H_{11}O_2Ti$ requires C, 59·2; H, 5·0%).

† Ebulliometric in benzene.

‡ Molar conductance in mho cm^2 $mole^{-1}$, 10^{-3}M in methanol. The molar conductance of cp_2TiCl in 10^{-3}M methanolic solution is 86·4 mho cm^2 $mole^{-1}$.

The melting points varied greatly with chain-length, being lowest for the caprate (*c.* 5°) but rising again for the stearate (35°). Molecular weights of the monocarboxylato derivatives (with the exception of caprate, which was an oil) were determined ebulliometrically in benzene and indicated monomeric structures (see Table 1). The dicarboxylato compounds were not sufficiently soluble for molecular weight determinations to be made.

The electrical conductivities of the complexes in methanol are shown in Table 1. The formato, maleato, and to a lesser extent fumarato and acetato derivatives show some degree of dissociation, although their molar conductances are considerably less than that of cp_2TiCl (86·4 mho cm^2 $mole^{-1}$). The remaining four carboxylates show no measurable conductivity. This partial dissociation of some complexes is reflected in slightly lower molecular weight values.

Magnetic Susceptibility

In a one-electron system such as exists in titanium(III) compounds the temperature-independent paramagnetism assumes some importance. For this reason the variation of susceptibility with temperature over the range 120–320°K was examined and a correction for temperature-independent paramagnetism was applied for each compound.

A Curie–Weiss law was then obeyed, the Weiss constants, θ, being quite small (see Table 2). The resultant values for μ_{eff} are shown in Table 2 and are consistent with monomeric structures with one unpaired electron per titanium atom. This behaviour is rather surprising in view of the known tendency of titanium(III) methoxides[2] and the cyano- and isothiocyanato-bis(cyclopentadienyl)titanium(III) compounds[1] to form trinuclear units with spin–spin interactions.

TABLE 2

MAGNETIC DATA

Compound	$10^6 \times$T.I.P. Correction (CGS)	Weiss Constant* (θ)	μ_{eff}† (B.M.)
Monocarboxylato derivatives			
Formato	210	−12°	1·69
Acetato	100	−2	1·71
Caprato	0	−4	1·72
Stearato	200	−2	1·55‡
Benzoato	200	+6	1·62
Dicarboxylato derivatives			
Succinato	330	+4	1·66
Maleato	133	−4	1·61
Fumarato	300	−4	1·68

* The Curie–Weiss equation $\chi = C/(T-\theta)$ was used.

† All values $\pm 0{\cdot}05$.

‡ The low melting point and waxy nature of the stearato compound led to poor uniformity of packing in the tube which probably accounts for the low value.

Mass Spectra

The mass spectra of all of the carboxylato compounds showed molecular ion peaks (M), intense in the case of monocarboxylato but weak and difficult to obtain with dicarboxylato derivatives. Prominent peaks at mass numbers corresponding to loss of cp, cpTi, cp_2Ti, and cp_2TiO were also present.

A regular fragmentation pattern of the carbon chain was observed with stearato and caprato compounds when peaks, initially strong but diminishing in intensity, were recorded at m/e $(M-CH_2)^+$, $(M-2CH_2)^+$, $(M-3CH_2)^+$, etc. After $(M-4CH_2)^+$ those peaks two mass numbers less, presumably from $(M-nCH_2-O)^+$, assumed more prominence. All except stearato showed strong acyl peaks, $(RCO)^+$.

Recombination bands above the molecular ion were always present but of very low intensity. With formato and acetato complexes recombination with fragments of the cyclopentadiene ring occurred, e.g. $(M+C_3H_3)^+$, whereas stearato and caprato

derivatives showed $(M+CH_2)^+$, $(M+2CH_2)^+$, $(M+3CH_2)^+$. In the case of the benzoato compound mass peaks above the parent ion were due to recombination with oxygen.

The maleato and fumarato compounds showed their strongest peaks around $\frac{1}{2}M$, the most intense in each case being *m/e* 251, i.e. $(\frac{1}{2}M+O)^+$.

Spectra

All compounds were examined over the range 500–30000 cm^{-1} using KBr disks and tetrahydrofuran solutions over the normal infrared range and diffuse reflectance over the remainder. This latter technique for examining air-sensitive compounds has already been described.[4]

TABLE 3

INFRARED BANDS DUE TO CYCLOPENTADIENYL RINGS IN $cp_2TiOOCR$ AND $(cp_2TiOOC)_2R'$

Formato	Acetato	Caprato	Stearato	Benzoato	Succinato	Maleato	Fumarato	Frequency Assignment
595w	590w	590w	585w	600w,sh	590sh	595vw	590sh	ring deform.*
790s	785s	790s	800s	790s	790s	790s	795s	CH deform.*
830sh	835sh	840sh	840sh	860s	845sh	860s	840sh	CH deform.*
1010s	1005s	1010s	1010s	1020s	1010s	1010s	1010s	CH deform.†
1120w	1120m	1120sh	—	1120m	1120m	1120m	1120m	CH deform.*
1440s	1460s	1460m	1460s	1445sh	1450s	1460s	1450m	CC stretch
3080bd	3080bd	3100m	3095m	3085bd	3085sh, 3100bd	3105m	3100m	CH stretch
3140vw	3140vw	3140w	3140w	3140w	3140w	3140w	3140w	CH stretch

* Vibrations perpendicular to *z*-axis.

† Vibrations parallel to *z*-axis.

(i) *Infrared spectra.*—In some areas of the spectrum there is considerable overlap between bands due to cyclopentadienyl and bands due to carboxylato ligands, and care must be taken in making some assignments. Those which follow in Table 3 are based on those of Stammreich[5] from Raman spectra and polarization measurements.*

The four strongest bands in the fundamental spectra which are indicative of cyclopentadienyl groups appear at 840, 1010, 1450, and 3100 cm^{-1} and are due to CH out-of-plane bending, CH in-plane bending, CC stretching, and CH stretching respectively. Binary combinations of these four bands appear as the strongest peaks in the near infrared spectra (see below).

* Evidence presented later in this paper indicates that carboxylato ligands are bidentate. Since the arrangement of cyclopentadienyl rings about the titanium atom is not expected to change during formation of the carboxylato derivatives, the symmetry will be C_{2v} or C_s. Stammreich's assignments, based on D_{5d} symmetry, are therefore still relevant.

[4] Reid, A. F., Scaife, D. E., and Wailes, P. C., *Spectrochim. Acta*, 1964, **20**, 1257.

[5] Stammreich, H., personal communication to Fritz, H. P., *Adv. organomet. Chem.*, 1964, **1**, 239.

The aliphatic carboxylato groups showed the usual alkane vibrations,[6] with CH stretching frequencies in the range 2850–2950 cm^{-1} and CH deformation at 1340–1410 cm^{-1}. The benzoato derivative showed the bands expected from a monosubstituted benzene and the fumarato compound absorbed strongly at 975 cm^{-1} (CH out-of-plane deformation of H–C=C (*trans*)). The corresponding vibration of the *cis* isomer was masked.

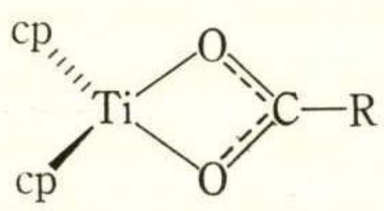
TABLE 4

COO STRETCHING FREQUENCIES (cm^{-1})

Compound	Asym., ν_2	Sym., ν_1	$(\nu_2-\nu_1)$
Monocarboxylato derivatives			
Formato	1550*	1435*	115
Acetato	1525	1460	65
Caprato	1520	1460	60
Stearato	1520	1460	60
Benzoato	1505	1425	80
Dicarboxylato derivatives			
Succinato	1515	1435	80
Maleato	1515	1440	75
Fumarato	1520	1420	100

* These values in tetrahydrofuran solution. In KBr disk a band at 1608 cm^{-1} was present, which disappeared and was replaced by the band at 1435 cm^{-1} in tetrahydrofuran solution. All other derivatives showed no significant difference between spectra in KBr disks and in tetrahydrofuran solution.

In all carboxylato complexes of metals the symmetrical (ν_2) and unsymmetrical (ν_1) carboxyl stretching vibrations are of interest since their positions and the separation between them can help in determining the type of bonding between acid and metal. These frequencies and separations are shown in Table 4. In the monocarboxylato complexes (ν_1) overlaps the CC stretching vibration of the cyclopentadienyl ligand but the consistency in frequency of the latter allows both to be assigned without much doubt. The separations ($\nu_2-\nu_1$) are small (Table 4), suggesting symmetrically bonded carboxyl groups.[7,8]



The low melting points of the monocarboxylato derivatives, their solubility in non-polar solvents, together with the magnetic and spectral data and molecular weight measurements, all point to the monomeric bidentate structure shown at left in which the metal is covalently bound to both oxygen atoms. Conductivity measurements indicate that the degree

[6] Bellamy, L. J., "The Infra-red Spectra of Complex Molecules." 2nd Edn. (Methuen: London 1958.)

[7] Nakamoto, K., "Infra-red Spectra of Inorganic and Coordination Compounds." (John Wiley: New York 1963.)

[8] Stephenson, T. A., and Wilkinson, G., *J. inorg. nucl. Chem.*, 1966, **28**, 2285; Poller, R. C., *J. inorg. nucl. Chem.*, 1962, **24**, 593; Cummins, R. A., and Dunn, P., *Aust. J. Chem.*, 1964, **17**, 185.

of covalency of the Ti–O bonds varies somewhat, but it is undoubtedly very high for most of these complexes. There is no reason to believe that the bonding in the dicarboxylato derivatives is any different.

All compounds showed weak or very weak bands at 1620–1635 and 1710–1725 cm^{-1}. Since both of these bands become strong on exposure of the compounds to oxygen, they are obviously associated with traces of titanium(IV) oxidation products. The first is thought to be due to an ester-type titanium salt,[9] TiOC(=O)–R, and the second to free carboxylic acid which is known to be formed on oxidation.

TABLE 5

ELECTRONIC TRANSITION BANDS (cm^{-1})

Compound	Charge Transfer	*d–d* Transitions*		
Monocarboxylato derivatives				
Formato	26300	—	14500	11800
Acetato	27000	16700	13900	10600
Caprato	27800	16900	13900	10500
Stearato	31250	16700	13900	10900
Benzoato	25000	17200	13300	10400
Dicarboxylato derivatives				
Succinato	25600	16700	14100	10800
Maleato	27800	16700	13900	10200
Fumarato	25600	17500	13500	10500

* With the exception of the formato derivative, the two lowest bands are shoulders, the lowest being very weak.

(ii) *Reflection spectra.*—All of the spectra were markedly similar in the near infrared region (3600–10000 cm^{-1}) since the main features are the four strong combination bands mentioned above. These are combinations of the CH stretching frequency at 3140 cm^{-1} with each of the four strong fundamentals and occur at 3940, 4170, 4480, and 6135 cm^{-1}. With the exception of the last band all above 4600 cm^{-1} are ternary combinations and are therefore weak.

The solid state spectra also show electronic transition bands above 10000 cm^{-1} (see Table 5). The highest of these is probably a charge-transfer band but the others are believed to be due to *d–d* transitions within the titanium atom. The frequencies of the main *d–d* transition band are somewhat higher than that observed[10] for cp_2TiCl (13300 cm^{-1}), which is consistent with the carboxylato groups having higher ligand field strengths than a chlorido ligand.

EXPERIMENTAL

Manipulations of air-sensitive compounds were carried out in a nitrogen-filled glove-box or in vacuum. Melting points were determined in evacuated capillaries and are uncorrected.

[9] Janssen, M. J., Luijten, J. G. A., and van der Kerk, G. J. M., *Recl Trav. chim. Pays-Bas Belg.*, 1963, **82**, 90.

[10] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 9.

Infrared spectra were run in KBr disks protected by pure KBr pressed on either side of the sample, on a Perkin–Elmer 521 spectrophotometer. Reflection spectra were determined on a Beckman DK2A spectrophotometer fitted with a reflectance attachment. Samples in powder form were pressed against a quartz window in the cell previously described.[4] Samples for mass spectra determination were introduced under argon into the Hitachi Perkin–Elmer RMU6D mass spectrometer. Magnetic susceptibilities were determined by the Gouy method.

Materials

cp_2TiCl was prepared from titanium trichloride and magnesium cyclopentadienide in tetrahydrofuran as previously described.[10] Sodium salts of carboxylic acids were reagent grade and were degassed under vacuum. Water was freshly boiled for 10–15 min and cooled under nitrogen. All nitrogen for use in Schlenk tube experiments was further purified by passage through molecular sieves and precipitated copper (B.A.S.F. BTS Catalyst) at 150°.

Preparation of Carboxylato Compounds

cp_2TiCl (2·1 g, 10 mmole) was weighed into a 100-ml Schlenk flask in the glove-box, then dissolved in air-free water (40 ml). A tube with a sintered-glass filter was attached and in a stream of nitrogen the blue solution was filtered into a solution of the sodium salt of the acid. The carboxylato derivative which precipitated immediately was filtered by reversing the flow of nitrogen and pushing the supernatant liquid back into the first flask. The precipitate was washed by introducing air-free water from a hypodermic syringe, then pumped dry under high vacuum and sublimed if necessary.

Physical properties and analytical data for all compounds are given in the Tables.

Acknowledgments

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Metal–metal Bonds between Elements of Groups IVA and IVB

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A RECENT report[1] of the isolation of an organosilyl derivative of zirconium has prompted us to report the preparation of several compounds containing bonds between Ti^{III}, Ti^{IV}, or Zr^{IV} and Sn^{IV} or Ge^{IV}.

The transition-metal derivative, cp_2TiCl, cp_2TiCl_2, or cp_2ZrCl_2 ($cp = \pi$-C_5H_5) in tetrahydrofuran (THF) solution was mixed with a stoicheiometric amount of $NaSnPh_3$ or $LiGePh_3$ in the same solvent under argon at acetone–dry ice temperature, and the mixture was then allowed to warm to room temperature. After removal of inorganic salts the products shown in the Table were isolated. All were handled in an inert atmosphere although the derivatives of Ti^{IV} and Zr^{IV} are probably sensitive only to moisture. Compounds were characterized by determination of total ash, and the ratio of integrated ^1H n.m.r. peaks.

The Ti^{III} derivatives were isolated as solvates, the fourth co-ordination position on the titanium being occupied by THF, the presence of which was shown by a band in the i.r. spectrum (KBr disc) at 1040 $cm.^{-1}$. The variation with temperature of the magnetic susceptibilities of the Ti^{III} compounds shows no evidence of spin–spin interaction; a Curie–Weiss law is followed, there being one unpaired electron per Ti atom.

Surprisingly the Ti^{IV} derivatives are green in colour, but their diamagnetism, satisfactory chlorine analyses, and the positions of their CH bending ($\perp$) bands in the i.r. spectrum (*ca.* 825 $cm.^{-1}$) are good confirmation of the presence of Ti^{IV}. Several attempted preparations of $cp_2Ti{\cdot}(GePh_3)_2$ gave only a burgundy-coloured product, the nature of which has yet to be established. The lead derivative $cp_2ClTi{\cdot}PbPh_3$ could be formed as a bright green solution in tetrahydrofuran at low temperatures, but deposition of lead occurred rapidly at room temperature.

Two Zr^{IV} compounds have been prepared similarly and have been isolated as pale yellow solids, but they have not yet been obtained completely pure. Their ^1H n.m.r. spectra in $CDCl_3$ are consistent with their formulation as $cp_2ClZr{\cdot}SnPh_3$ (δ 7·32, 6·32) and $cp_2ClZr{\cdot}GePh_3$ (δ 7·40, 6·15).

(*Received, January 8th*, 1968; *Com.* 028.)

TABLE

Characterization of metal–metal bonded compounds

(M = Ti or Zr, M′ = Sn or Ge)

Compound	Colour	M.p.	^1H n.m.r. (δ values in $CDCl_3$)
		M^{III}–M′ *Derivatives*	
$cp_2Ti{\cdot}SnPh_3$, THF	Emerald-green	80°[a]	b
$cp_2Ti{\cdot}GePh_3$, THF	Emerald-green	110°[a]	b
		M^{IV}–M′ *Derivatives*	
$cp_2ClTi{\cdot}SnPh_3$	Dark green	177—180°[a]	7·32,[c] 6·25
$cp_2ClTi{\cdot}GePh_3$	Dark green	193—196°[a]	7·30,[c] 6·15
		M′–M^{IV}–M′ *Derivatives*	
$cp_2Ti(SnPh_3)_2$	Green	80°[a]	7·10,[c] 6·77

[a] Decomposition.

[b] Paramagnetic, with one unpaired electron per Ti atom. In $CDCl_3$ solution these compounds abstract Cl· and show the spectrum of $cp_2ClTi{\cdot}M'Ph_3$.

[c] Ph protons; this peak is a singlet in pure compounds.

[1] D. J. Cardin, S. A. Keppie, B. M. Kingston, and M. F. Lappert, *Chem. Comm.*, 1967, 1035.

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THIOCARBOXYLATO DERIVATIVES OF BIS(CYCLOPENTADIENYL)TITANIUM(III)

By R. S. P. Coutts* and P. C. Wailes*

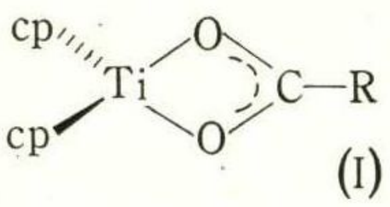
[*Manuscript received August* 31, 1967]

Summary

Thioformato, thioacetato, thiopropionato, thiostearato, and thiobenzoato derivatives of bis(cyclopentadienyl)titanium(III) have been prepared by precipitation from air-free aqueous solutions of cp_2TiCl ($cp = \pi\text{-}C_5H_5$). The compounds are deep green in colour, readily oxidized by air, and are paramagnetic monomers having one unpaired electron per titanium atom.

Infrared and visible spectral data are reported, together with conductivities in methanol, magnetic properties, and molecular weight values.

Introduction



(I)

The preparation and properties of several carboxylato derivatives of bis(cyclopentadienyl)titanium(III) have been reported in a previous paper.[1] These derivatives were assigned the symmetrical, bidentate, covalent structure (I).

Interest in the properties of the titanium–sulphur bond prompted us to examine the effect of replacing one of the oxygens of the carboxyl group by sulphur. Five thiocarboxylato derivatives were prepared and their structures examined, mainly by infrared analysis.

Results and Discussion

Preparation and Properties of Thiocarboxylato Derivatives

The compounds were precipitated under argon by mixing degassed aqueous solutions of cp_2TiCl and of the sodium salt of the thioacid:

$$cp_2TiCl + NaSOCR \rightarrow cp_2TiSOCR + NaCl$$

In the case of the thioformate the considerable solubility of $cp_2TiSOCH$ in water necessitated chilling the mixture before filtering in order to obtain a reasonable yield. The same procedure was necessary with the thiostearate, not because of solubility, but because its low melting point caused precipitation as an oil. Eight preparations of the thiostearato derivative were carried out, and in no case could a product

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[1] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1967, **20**, 1579.

with satisfactory analysis and magnetic properties be obtained. All of the thiocarboxylato titanium compounds showed much lower thermal stability than the carboxylato derivatives, and in the case of the thiostearate this instability apparently prevented the isolation of a pure product under the conditions used. Nevertheless under high vacuum all but the thiostearate could be sublimed safely at the temperatures shown in Table 1.

A point of interest with all derivatives is their change of colour on drying. When precipitated all were bluish green, apparently due to hydration, but on pumping dry the colour changed to deep green.

In air the thiocarboxylates were instantly oxidized to yellow titanium(IV) compounds showing the band at 720 cm^{-1} in the infrared indicative of Ti–O–Ti, free thiocarboxylic acid being formed at the same time.

TABLE 1

PHYSICAL PROPERTIES AND ANALYTICAL DATA OF THIOCARBOXYLATO DERIVATIVES

Compound $cp_2TiSOCR$	Colour	M.P.	Sublim. Temp. (10^{-5} mm)	Mol. Wt.[a]		Λ_M[b]	Ti (%)[c]	
				Found	Calc.		Found	Calc.
R=H	dark green	56°[d]	90°	263	239	23	20·2	20·0
$R=CH_3$	dark green	96–99	60	259	253	5	18·9	18·9
$R=CH_3CH_2$	dark green	44–46[d]	70	308	267	4·7	17·6	17·9
$R=CH_3(CH_2)_{16}$	dark green	40	160	—	478	—	10·6	10·0
R=Ph	teal blue	88–89[d]	110	310	315	2·8	15·0	15·2

[a] Ebulliometric in benzene. [b] Molar conductance in mho cm^2 $mole^{-1}$, 10^{-3}M in methanol. [c] Sample was pelleted in a glove box, weighed under nitrogen, and ashed. [d] Decomposition.

Molecular weight determinations of the $cp_2TiSOCR$ complexes in boiling benzene, in which all were very soluble, indicated monomeric structures, and conductivity measurements in oxygen-free methanol indicated only weak dissociation in most cases. The exception was the thioformate which, in common with the formate of the carboxylato series, showed a molar conductance several times those of its higher homologues (Table 1).

Magnetic Susceptibilities

The variation of susceptibility with temperature for each compound was examined over the range 120–320°K. After applying a correction for temperature-independent paramagnetism* (T.I.P.) a Curie–Weiss law was obeyed, the Weiss constant (θ)† being highest for the thioformato but very low for all other derivatives as in the carboxylato series.

The μ_{eff} values are shown in Table 2 and clearly indicate one unpaired electron per titanium atom with no spin–spin interaction.

* From plot of $1/T$ against χ'_M (χ_M + diamagnetic corrections for all atoms).
† From plot of T against $1/\chi'_M$ (corrected for T.I.P.).

Spectra

All compounds were examined over the range 500–30000 cm^{-1} using KBr disks and diffuse reflectance as described earlier.[2]

(i) *Infrared spectra*.—The main infrared bands are shown in Table 3, together with their assignments. As usual the four strongest bands due to the cyclopentadienyl

TABLE 2

MAGNETIC DATA

Compound $cp_2TiSOCR$	$10^6 \times$T.I.P. Correction (CGS)	Weiss Constant* (θ)	μ_{eff}† (B.M.)
R=H	0	−17°	1·64
R=CH_3	75	−4°	1·74
R=CH_3CH_2	41	−6°	1·64
R=$CH_3(CH_2)_{16}$	10	−4°	1·55‡
R=Ph	88	−2°	1·71

* The Curie–Weiss equation $\chi = C/(T-\theta)$ was used.

† All values $\pm 0 \cdot 5$.

‡ The waxy nature of the thiostearate necessitated melting the sample into the tube. This low susceptibility is probably caused by the resultant partial decomposition.

TABLE 3

INFRARED DATA FOR $cp_2TiSOCR$ COMPOUNDS

R= H	R= CH_3	R= CH_3CH_2	R= $CH_3(CH_2)_{16}$	R= Ph	Assignment*
590m	590w	590m	595w	590w	ring deform. ⊥
785s	790s	790s	790s	790s	CH deform. ⊥ of ring
1005s	1005s	1005s	1010s	1010s	CH deform. ∥ of ring
1125vw	1120wsh	1105w	—	—	CH deform. ⊥ of ring
—	1160s	1155m	1155m	1165m	=C–C– stretch of thio acid group
1435m, 1605s	1470s	1460s	1460s	1455s	CC stretch of ring
—	3080m	3080m	3075m	—	CH stretch of ring
—	—	3140vw	3140vw	—	CH stretch of ring
1390s	1430m	1435m, 1395m	1395s	1425s	SCO stretch

* ⊥ and ∥ denote vibration perpendicular and parallel to the z-axis; "ring" refers to cp.

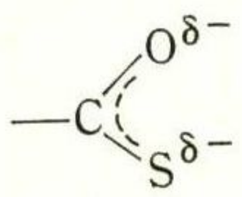
ligands are at 790, 1010, 1460, and 3100 cm^{-1} and combinations of these bands occur in the near-infrared spectra (see below). The very weak absorption sometimes observed at 3140 cm^{-1} and attributed to CH stretching[3] is absent in three of the samples and the 1120 cm^{-1} absorption (CH deformation) is sometimes masked by a medium

[2] Reid, A. F., Scaife, D. E., and Wailes, P. C., *Spectrochim. Acta*, 1964, **20**, 1257.

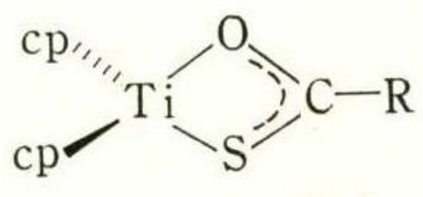
[3] Fritz, H. P., *Adv. organomet. Chem.*, 1964, **1**, 239.

to strong band at 1160 cm^{-1}. This was assigned by Nyquist and Potts[4] to $-\overset{\|}{C}-C-$ stretching in thiocarboxyl derivatives, and the absence of this absorption in the spectrum of the formate would appear to confirm this assignment.

Little data are available on metal derivatives of thioacids, but Nyquist and Potts[4] assign a band around 1520 cm^{-1} as analogous to the asymmetric stretching frequency of carboxyl groups of acids and indicating a structure such as (II) for the alkali metal salts. The symmetric stretching band normally found at lower frequency with carboxylic acids and derivatives is, of course, absent in the spectra of thiocarboxylates. The sodium thiocarboxylates used in this work all absorbed at 1520–1530 cm^{-1}, and sodium thioformate showed an additional band at 1600 cm^{-1}.



(II)



(III)

The conductivities of the $cp_2TiSOCR$ compounds indicate covalent bonding rather than ionic, and the infrared spectra of all of these compounds show bands at 1460 and 1410 cm^{-1}. The first has been assigned to the CC stretch of the cyclopentadiene ring, so that the 1410 cm^{-1} absorption must be due to the S–C–O group, and its low frequency indicates bonding of both oxygen and sulphur to titanium. In view of their monomeric natures the compounds are given the structure (III), analogous to that of the carboxylato complexes.[1]

The thioformate, $cp_2TiSOCH$, again shows anomalous behaviour with a band in the infrared at 1610 cm^{-1} in addition to the one around 1400 cm^{-1}. Presumably the 1610 cm^{-1} band is similar to that found in the spectrum of sodium thioformate and also to the 1608 cm^{-1} band of $cp_2TiOOCH$.[1] In contrast, the 1610 cm^{-1} of $cp_2TiSOCH$ remains unchanged in dry tetrahydrofuran solution, whereas the 1608 cm^{-1} band of $cp_2TiOOCH$ disappeared under these conditions. These bands have yet to be assigned.

(ii) *Reflection spectra.*—In common with the carboxylato derivatives and most other cyclopentadienyl metal compounds,[2] the near-infrared spectra (3600–10000 cm^{-1}) of the thiocarboxylates show four strong combination bands at 3950, 4100, 4500, and 6130 cm^{-1} which are combinations of the CH stretching frequency at 3100 cm^{-1} with each of the four fundamentals at 790, 1010, 1460, and 3100 cm^{-1}. This characteristic pattern of four bands is recognizable in all of the cyclopentadienyl metal compounds so far examined.

As shoulders on these bands are various weak ternary combinations of varying intensity, the most persistent of which is that at 5600–5700 cm^{-1}, ascribable to several possible ternary combinations.[2]

Above 10000 cm^{-1} electronic transition bands occur, the frequencies of which are listed in Table 4. The most intense is around 16000 cm^{-1} with a second at 13000 cm^{-1} overlapping, and on the latter a shoulder sometimes appears around 10000 cm^{-1}.

[4] Nyquist, R. A., and Potts, W. J., *Spectrochim. Acta*, 1959, **15**, 514.

At higher frequencies a band of much greater intensity is evident. This is probably charge transfer in origin, and occurs at 23500–26000 cm^{-1} although the frequency is difficult to determine with any accuracy.

All of these frequencies are somewhat lower than those of the carboxylato derivatives.

TABLE 4

ELECTRONIC TRANSITION BANDS (cm^{-1}) IN $cp_2TiSOCR$ COMPOUNDS

Compound	*d–d* Transitions		
R=H	16400	13800	10000
$R=CH_3$	15800	13700	10600
$R=CH_3CH_2$	15900	13200	10400
$R=CH_3(CH_2)_{16}$	15900	13300	10500
R=Ph	16950	13100	—

EXPERIMENTAL

All manipulations of air-sensitive materials were carried out in a nitrogen-filled glove-box or under an atmosphere of pure argon or in vacuum. Melting points were determined in evacuated capillaries and are uncorrected. Infrared spectra were run in KBr disks protected by pure KBr pressed on either side of the sample, on a Perkin–Elmer 521 spectrophotometer. Reflection spectra were determined on a Beckmann DK2A spectrophotometer fitted with a reflectance attachment, as described previously.[2] Magnetic susceptibilities were determined by the Gouy method.

Materials

cp_2TiCl was prepared from titanium trichloride and magnesium cyclopentadienide;[5] sodium thioformate was obtained from phenylformate and NaHS;[6] thiostearic acid from stearoyl chloride and NaHS,[7] and thiopropionic acid from propionic acid and excess thiobenzoic acid.[8] The latter acid and thioacetic acid are commercially available.

Methods

The thioacid and enough NaOH to neutralize it were degassed by evacuation, dissolved in air-free water, and combined with an equimolar amount of cp_2TiCl in the same solvent in a stream of argon, using a Schlenk tube system as described in the previous paper. The highly coloured products were collected by filtration, washed with water, pumped dry, and sublimed when necessary.

Physical properties and analytical data are given in Table 1.

ACKNOWLEDGMENTS

The authors are grateful to Dr D. E. Scaife for the use of a magnetic balance, to Mr B. Kaucner for experimental assistance, and to the Stauffer Chemical Co. for a gift of titanium trichloride.

[5] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 9.
[6] Auger, V., *C. r. hebd. Séanc. Acad. Sci., Paris*, 1904, **139**, 800.
[7] Hirabayashi, Y., Mizuta, M., and Mazume, T., *Bull. chem. Soc. Japan*, 1964. **37**, 1002.
[8] Ford, I. A. M., and Thompson, S. A. M., *Nature*, 1959, **185**, 96.

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THE MAGNETIC PROPERTIES OF THE CYCLOPENTADIENYL-TITANIUM(III) DERIVATIVES, $cpTiCl_2$, cp_2TiCl, AND cp_3Ti*

By A. J. Canty,† R. S. P. Coutts,‡ and P. C. Wailes‡

In previous papers, we have reported the magnetic properties of trivalent cyclopentadienyltitanium derivatives ($3d'$ configuration) of both spin-paired[1] and magnetically dilute[2] type. In this communication the effect on the magnetic properties of titanium trichloride of introducing successively one, two, and three cyclopentadienyl ligands is examined.

In the case of α-titanium trichloride (violet form), exchange through bridging chlorine is demonstrated by measuring the variation with temperature of the paramagnetic susceptibility. The susceptibility does not follow any sort of Curie–Weiss law but rises rapidly above 200°K, with a point of inflexion at 215°K, and reaches a maximum at 258°K (Fig. 1). Ogawa reported similar results[3] and attributes this behaviour to a magnetic transition at 217°K caused by a lattice distortion.

Table 1

MAGNETIC PROPERTIES OF $cpTiCl_2$

Temp. (°K)	$10^6\chi_M$[a]	μ_{eff} (B.M.)[b]	Temp. (°K)	$10^6\chi_M$[a]	μ_{eff} (B.M.)[b]
322	1149	1·68	220	1730	1·68
298	1260	1·69	190	2028	1·68
273	1383	1·69	158	2502	1·69
247	1533	1·69	121	3403	1·69

[a] Not corrected for T.I.P.; ligand correction 106×10^{-6} CGS.
[b] $\theta = +17$°K; T.I.P. = 0 CGS.

The effect of introducing one cyclopentadienyl group is quite dramatic; $cpTiCl_2$ behaves as a magnetically dilute compound whose susceptibility follows a Curie–Weiss law, i.e. is independent of temperature after correcting for temperature-independent paramagnetism (T.I.P.)§ and applying a Weiss constant (θ)‖ of +17° (Table 1). Although the susceptibility ($\mu_{eff} = 1{\cdot}69 \pm 0{\cdot}05$ B.M.) indicates little if any spin–spin interaction, from its insolubility in non-coordinating solvents $cpTiCl_2$

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§ From plot of $1/T$ against χ'_M (χ_M + diamagnetic corrections for all atoms).
‖ From plot of T against $1/\chi'_M$ (corrected for T.I.P.).

[1] Coutts, R. S. P., and Wailes, P. C., *Inorg. nucl. chem. Lett.*, 1967, **3**, 1.
[2] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1967, **20**, 1579.
[3] Ogawa, S., *J. phys. Soc. Japan*, 1960, **15**, 1901.

is apparently not monomeric. A chlorine-bridged dimer or oligomer suggested by Bartlett and Seidel[4] would probably lead to spin pairing and lowered susceptibility, so that the degree and mechanism of association is still not known.

With two cyclopentadienyl groups present (cp_2TiCl), spin–spin interaction through chlorine bridges becomes evident. This compound is a dimer[5] and its susceptibility is reported[6] to reach a maximum at 170°K. Our doubly-sublimed sample behaved similarly but the Néel temperature is 195°K (Fig. 1).

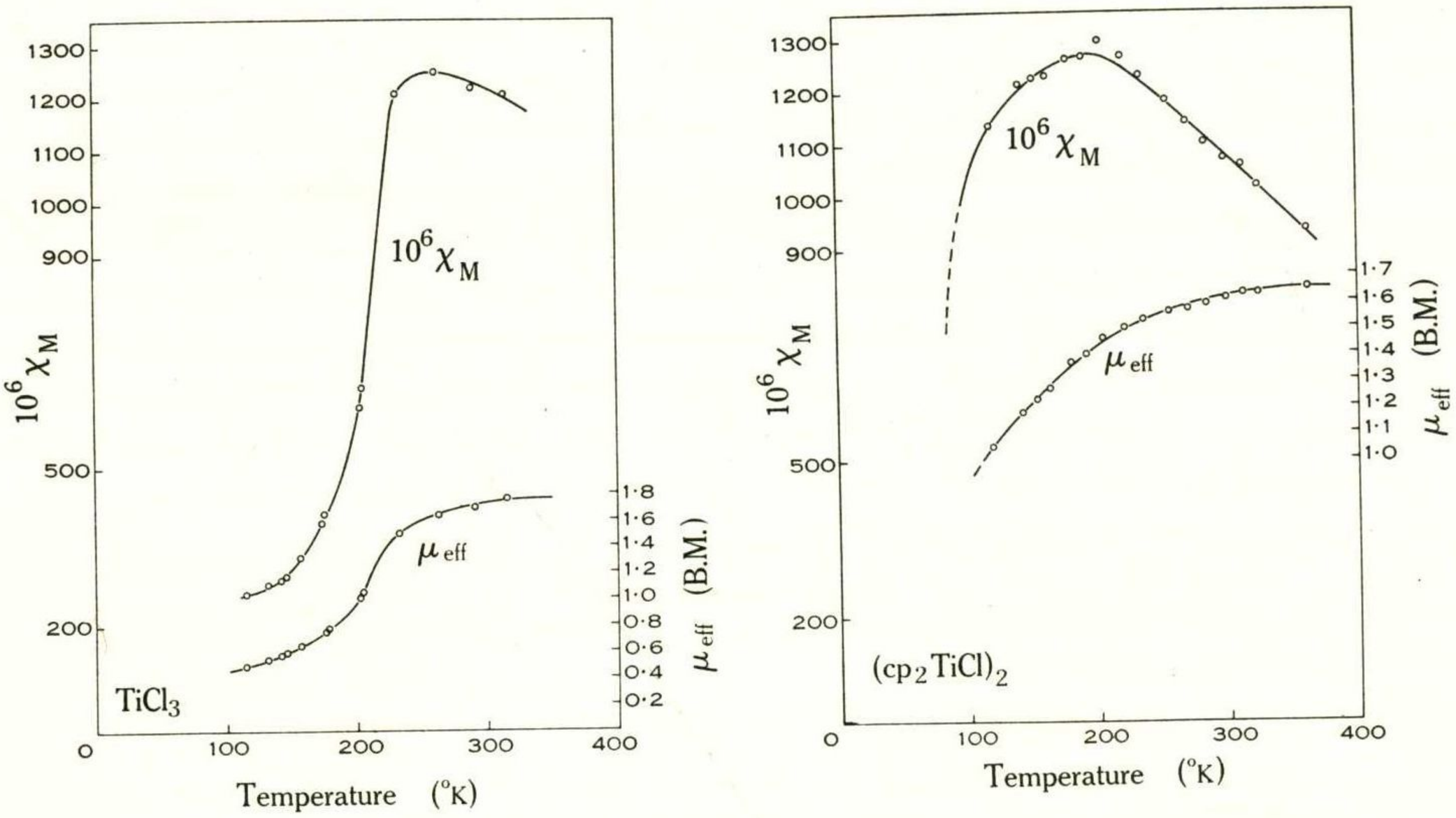


Fig. 1.—Variation of magnetic susceptibility and magnetic moment with temperature for $TiCl_3$ and $(cp_2TiCl)_2$.

A preparation of tris(cyclopentadienyl)titanium(III) in "low-yield" from cp_2TiCl_2 was reported in 1960 by Fischer and Löchner.[7] Its magnetic susceptibility at three temperatures was also given and indicated that the compound shows little or no spin–spin interaction, with μ_{eff} 1·69 at 293°K and θ −4°.[8]

In connection with other work in these laboratories, a new synthesis of cp_3Ti from cp_2TiCl and sodium cyclopentadienide was investigated. This produced cp_3Ti in 70% yield. Its susceptibility was determined between 100° and 320°K and was found to be independent of temperature over this range. After correcting for T.I.P. and applying a Weiss constant, μ_{eff} was found to be 1·71 B.M. (Table 2). The volatility and solubility of cp_3Ti are strong indication of its monomeric nature.

The spectra of the four compounds were measured over the range 250–30000 cm^{-1} using KBr disks over the normal infrared range and diffuse reflectance over the

[4] Bartlett, P. D., and Seidel, B., *J. Am. chem. Soc.*, 1961, **83**, 581.
[5] Nöth, H., and Hartwimmer, R., *Chem. Ber.*, 1963, **93**, 2246; Natta, G., *Angew. Chem.*, 1959, **71**, 205.
[6] Martin, R. L., and Winter, G., *J. chem. Soc.*, 1965, 4709.
[7] Fischer, E. O., and Löchner, A., *Z. Naturf.*, 1960, **15b**, 266.
[8] Figgis, B. N., and Lewis, J., *Prog. inorg. Chem.*, 1964, **6**, 104.

remainder. As with all cyclopentadienyl metal compounds, the four strongest fundamental bands in the infrared combine to produce binary combinations in the near infrared (Table 3). The 6100 cm^{-1} band is not as pronounced as observed previously in other compounds,[9] since this band is partly absorbed into the strong, broad electronic transition bands at higher frequency.

TABLE 2

MAGNETIC PROPERTIES OF cp_3Ti

Temp. (°K)	$10^6\chi_M$[a]	μ_{eff} (B.M.)[b]	Temp. (°K)	$10^6\chi_M$[a]	μ_{eff} (B.M.)[b]
322	1146	1·70	220	1681	1·72
298	1253	1·71	190	1928	1·72
273	1371	1·72	158	2312	1·72
247	1509	1·71	121	2932	1·71

[a] Not corrected for T.I.P.: ligand correction 143×10^{-6} CGS.
[b] $\theta = -4$°K; T.I.P. = 50 CGS.

TABLE 3

SPECTRAL DATA (cm^{-1})

cp_3Ti	cp_2TiCl	$cpTiCl_2$	$TiCl_3$*	Assignment
785s	795s	815s		CH deform (1)
1010s	1015s	1012s		CH deform (2)
1435m	1435m	1430m		CC stretch (3)
3080w	3085w	3090w		CH stretch (4)
3900w	3950w	3950w		(1)+(4)
4170w(sh)	4130m	4180w(sh)		(2)+(4)
4500br	4490br	4550br		(3)+(4)
6100w	6150w	6150w		(4)+(4)
14300sh	8850s	9600s	12600w(sh)	*d–d* transition
16800s	13900vs	14100vs	14200s	*d–d* transition
24700vs	20600vs	19600vvs	19200vs	charge transfer
		26000vvs	27400vs	charge transfer

* These values are in substantial agreement with those reported (Dijkgraaf, C., and Rousseau, J. P. G., *Spectrochim. Acta*, 1967, **23A**, 1267).

In the absence of single crystal spectra, it is difficult to assign with any certainty the electronic absorption bands, but from a consideration of relative intensity and position, the first two are assigned to *d–d* transitions and the remainder to charge transfer. In those derivatives containing chlorine, the first main band (around 14000 cm^{-1}) occurs at somewhat lower frequency than that of cp_3Ti, but the symmetry is so low that little information on the relative positions of cp and Cl in the spectrochemical series can be deduced from this.

[9] Reid, A. F., Scaife, D. E., and Wailes, P. C., *Spectrochim. Acta*, 1964, **20**, 1257.

Experimental

All handling of air-sensitive materials was carried out in a nitrogen-filled glove box or in vacuum. Magnetic susceptibilities were determined by the Gouy method.

Materials

cp_3Ti was prepared by the method described below; cp_2TiCl was obtained from $TiCl_3$ and magnesium cyclopentadienide as described earlier;[10] $cpTiCl_2$ was prepared by the method of Bartlett and Seidel[4] from cp_2TiCl_2 and diisobutylaluminium chloride; $TiCl_3$ was a commercial product from the Stauffer Chemical Company. All of these compounds analysed satisfactorily.

Synthesis of Tris(cyclopentadienyl)titanium(III)

cp_2TiCl (3·75 g) and sodium cyclopentadienide (2·2 g, 25% excess) were heated together under reflux in dry tetrahydrofuran (40 ml) in a nitrogen atmosphere for 2 hr. The solvent was removed under vacuum and the residue sublimed onto a cold finger condenser under high vacuum. cp_3Ti was obtained as a deep green crystalline sublimate (3·0 g, 70% yield) (Found: Ti, 19·6; Cl, none. Calc. for $C_{15}H_{15}Ti$: Ti, 19·7%).

[10] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 9.

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OXYANIONIC COMPLEXES OF BIS(CYCLOPENTADIENYL)TITANIUM(III)

By R. S. P. Coutts* and P. C. Wailes*

[*Manuscript received January* 4, 1968]

Summary

Several oxyanionic derivatives of bis(cyclopentadienyl)titanium(III) have been prepared by precipitation from air-free aqueous solutions. Two of these, $(cp_2Ti)_2SO_4$ and $(cp_2Ti)_2CO_3$, where cp = π-cyclopentadienyl, are described in detail. Infrared and molecular weight evidence shows that the sulphato and carbonato ligands are bridging, but whereas the magnetic susceptibility variation with temperature indicates that the sulphato derivative is magnetically dilute, the carbonato compound shows spin–spin interaction.

Introduction

The bis(cyclopentadienyl)titanium(III) cation (cp_2Ti^+) can be precipitated from air-free water by a great number of anions, including the pseudohalides,[1] carboxylates,[2] and thiocarboxylates.[3] Oxyanions in particular readily form complexes with cp_2Ti^+, and in all of these so far examined, the ligand has acted as a bidentate to give an essentially tetrahedral structure.

Several oxyanionic complexes have now been prepared and two of these, the sulphato and carbonato derivatives, are described in some detail. They are particularly suited to structural interpretation from infrared data.

Results and Discussion

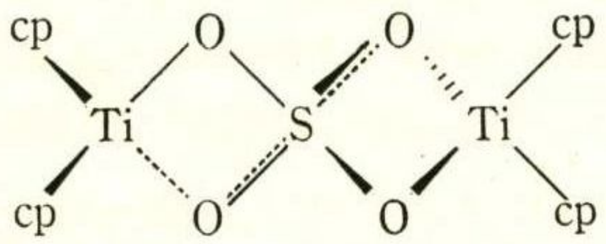
The sulphato derivative precipitated as a pale green crystalline solid when air-free aqueous solutions of cp_2TiCl and sodium sulphate were mixed. The carbonato derivative, prepared similarly using sodium carbonate, was pale blue in colour. Both readily oxidized in air to yellow titanium(IV) compounds.

$(cp_2Ti)_2SO_4$

Free sulphate ion has high symmetry (T_d) and only two of its four fundamental vibrations are infrared active, viz. 1104 and 613 cm^{-1}. Coordination to a metal lowers the symmetry, resulting in splitting of these two bands and possible appearance of the other fundamentals at 970–990 and 440–460 cm^{-1}.[4]

* Division of Applied Chemistry, CSIRO Chemical Research Laboratories, P.O. Box 4331, Melbourne, Vic. 3001.

[1] Coutts, R. S. P., and Wailes, P. C., *Inorg. nucl. Chem. Lett.*, 1967, **3**, 1.
[2] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1967, **20**, 1579.
[3] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 373.
[4] Nakamoto, K., Fujita, J., Tanaka, S., and Kobayashi, M., *J. Am. chem. Soc.*, 1957, **79**, 4904.



(I)

In $(cp_2Ti)_2SO_4$, both of the infrared active bands are moved to higher frequency and split, the 1100 cm^{-1} band into three (1200, 1155, and 1090 cm^{-1}) and the 613 cm^{-1} band into three (665, 645, and 590 cm^{-1}). A third fundamental appears as a weak band at 1050 cm^{-1}. This pattern of bands is similar, but of somewhat higher frequency, to that found for bridging bidentate sulphato.[4,5] Structure (I) is assigned to $(cp_2Ti)_2SO_4$.

Conductivity measurements indicate some dissociation (see Table 1), which is also reflected in the slightly low molecular weight value.

TABLE 1

PHYSICAL PROPERTIES AND ANALYSES

Compound	Colour	Sublim. Temp. (10^{-4} mm)	M.P.	Mol. Wt.[a] Found	Mol. Wt.[a] Calc.	Λ_M[b]	Ti (%) Found	Ti (%) Calc.
$(cp_2Ti)_2SO_4$	pale green	200°	248° (dec.)	387	452	62	21·0	21·2
$(cp_2Ti)_2CO_2$	pale blue	—	280° (dec.)	440	416	4	22·9	23·0

[a] Ebulliometric in tetrahydrofuran.

[b] Molar conductance in mho cm^2 $mole^{-1}$, 10^{-3}M in methanol.

TABLE 2

MAGNETIC DATA FOR $(cp_2Ti)_2SO_4$

The Curie–Weiss equation $\chi = C/(T-\theta)$ was used. T.I.P. $= 190 \times 10^{-6}$ CGS units, obtained from plot of $1/T$ against χ'_M, i.e. χ_M + diamagnetic corrections for all atoms (228×10^{-6} CGS units). $\theta = -1°$, obtained from plot of T against $1/\chi'_M$ (corrected for T.I.P.)

Temp. (°K)	$10^6\chi_M$	$10^6\chi'_M$ per Ti Atom	μ_{eff} (B.M.)	Temp. (°K)	$10^6\chi_M$	$10^6\chi'_M$ per Ti Atom	μ_{eff} (B.M.)
322	2183	1206	1·63	190	3678	1953	1·65
298	2393	1311	1·64	175	3974	2101	1·65
273	2592	1410	1·64	158	4349	2289	1·64
247	2854	1541	1·64	140	4895	2562	1·64
220	3184	1706	1·64				

The magnetic behaviour of $(cp_2Ti)_2SO_4$ shows no spin–spin interaction; the susceptibility follows a Curie–Weiss law after correcting for temperature-independent paramagnetism (T.I.P.), with μ_{eff} $1·64 \pm 0·05$ B.M., the Weiss constant, θ, being $-1°$ (see Table 2).

$(cp_2Ti)_2CO_3$

On chelation, the D_{3h} symmetry of the planar carbonato ion is lowered to C_{2v} or C_s. A distinction cannot always be made between bidentate and monodentate

[5] Beadle, P. J., and Grzeskowiak, R., *Inorg. nucl. Chem. Lett.*, 1967, **3**, 245.

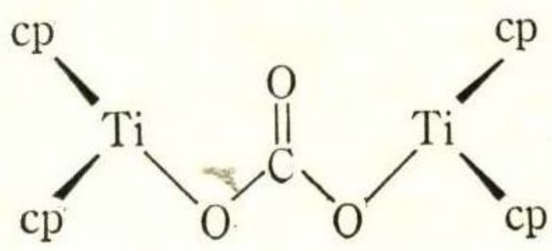
on the basis of their infrared spectra although the splitting of the degenerate vibrations is generally larger in the bidentate than in the unidentate complex.[6,7] In the case of $(cp_2Ti)_2CO_3$ this splitting is large (Table 3) and, in conjunction with the appearance of a weak band at 1065 cm^{-1}, would seem to indicate that the carbonato ligand is bidentate. (A strong band expected around 800 cm^{-1} is masked

TABLE 3

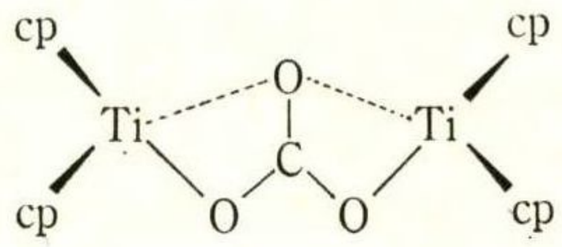
INFRARED DATA

Wave Numbers (cm^{-1})				Assignment
		$(cp_2Ti)_2SO_4$		
1050w	—	1090m 1155s 1200m	590m 645s 665s	SO_4
795vs	1010s	1360w 1395m 1435s	3100w	cp
		$(cp_2Ti)_2CO_3$		
1065w	1570sh 1530s 1355s	—	680w 665s	CO_3
790s	1010s 1120w	1435m	3095w	cp

by the cyclopentadienyl absorption in this area.) The molecular weight value of 440 suggests that the carbonato group is bridging, and it is possible for the third oxygen atom to become involved in chelation but the extent, if any, to which this occurs is not known [see structures (IIa) and (IIb)].



(IIa)



(IIb)

The magnetic properties of $(cp_2Ti)_2CO_3$ are interesting in that no form of Curie–Weiss law is followed, and there is definite spin–spin interaction of the $3d^1$ electrons of the titanium atoms. The susceptibility rises with temperature, but at about 100°C decomposition begins and the gradient increases sharply (Fig. 1). Spin–spin interaction probably occurs by super-exchange through the delocalized

[6] Nakamoto, K., "Infra-red Spectra of Inorganic and Coordination Compounds." (John Wiley: New York 1963.)

[7] Gatehouse, B. M., Livingstone, S. E., and Nyholm, R. S., *J. chem. Soc.*, 1958, 3137.

π-electrons of the symmetric O–C–O group, by a mechanism similar to that proposed for copper formate,[8] but the possibility of direct Ti–Ti interaction should not be overlooked.

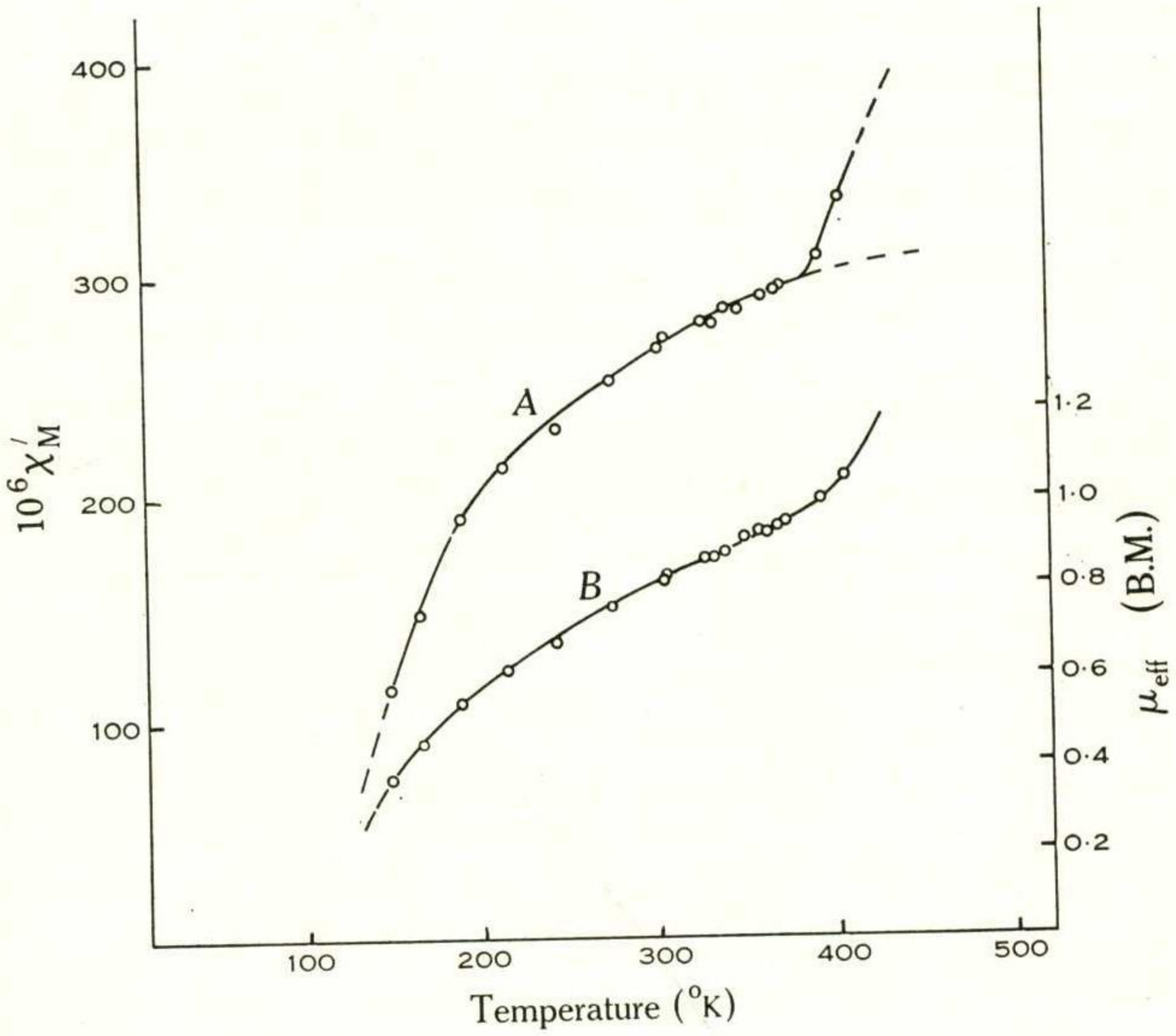


Fig. 1.—Variation of
(*A*) magnetic susceptibility
(*B*) magnetic moment
with temperature for $(cp_2Ti)_2CO_3$.

Above its decomposition temperature (100°c), the colour of $(cp_2Ti)_2CO_3$ changes to deep blue with evolution of a gas believed to be CO_2. This residue is involatile below 200° at 10^{-4} mm pressure and is insoluble in all but the most polar

TABLE 4

REFLECTION SPECTRA BANDS (cm^{-1})

$(cp_2Ti)_2SO_4$	$(cp_2Ti)_2CO_3$	Assignment
3940	3940	3100+ 790 } cp
4150	4130	3100+1010 } cp
4500	4500	3100+1435 } cp
6170	6150	3100+3100 } cp
9350w	10800sh	*d–d* transition
13900s	12200sh	*d–d* transition
	13700s	*d–d* transition
21740vs	—	charge transfer

solvents. In the mass spectrum at high temperatures (320°), all of the high mass peaks are based on cp(R)TiOTi(R′)cp^+ where R and R′ are fragments of cyclopentadienyl rings (C_3H_3 or C_2H_3). The compound is believed to be a polymer of $cp_2TiOTicp_2$.

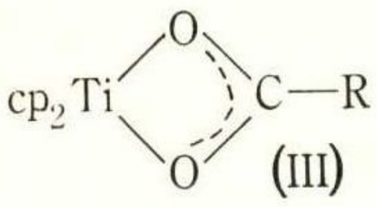
[8] Pellizer, G., and De Alti, G., *J. inorg. nucl. Chem.*, 1967, **29**, 1565.

Several of the prominent peaks, particularly *m/e* 281, i.e. $cpTiOTi(C_3H_3)cp^+$, are found also in the mass spectrum of a similar residue from pyrolysis of $cp_2Ti(H_2O)_3BPh_4$.[9]

Reflection Spectra

In the near infrared, the solid samples of $(cp_2Ti)_2SO_4$ and $(cp_2Ti)_2CO_3$ show the four strong combination bands typical of cyclopentadienyl compounds[10] (Table 4).

The electronic transition bands occur above 9000 cm^{-1}, the most intense being at 13900 (sulphato) and 13700 cm^{-1} (carbonato). Between 9000 and 13000 cm^{-1} both show weak bands or shoulders at the frequencies shown in Table 4. $(cp_2Ti)_2SO_4$ shows an additional more intense absorption at high frequency which is attributed to charge transfer. These spectra are very similar to that of cp_2TiCl[11] but the frequencies are lower than those found for the carboxylates (III),[2] and the corresponding thiocarboxylates.[3]



(III)

Other Anions

On addition of $NaHCO_3$ and $NaHSO_4$ to solutions of cp_2TiCl, only the carbonato and sulphato derivatives described above were precipitated, even when the concentrations were kept high to suppress ionization of HCO_3^- and HSO_4^-.

Other anions which formed blue or green precipitates are PO_4^{3-}, SO_3^{2-}, $S_2O_3^{2-}$, and $S_2O_6^{2-}$. Extensive decomposition occurred in the case of SeO_4^{2-} and TeO_4^{2-} with liberation of Se and Te respectively. The ions, NO_3^-, NO_2^-, and CrO_4^{2-} caused precipitation of yellow polymeric oxidized compounds probably bridged through the oxyanions.

Experimental

General

All manipulations of air-sensitive materials were carried out in a nitrogen-filled glove-box or under an atmosphere of pure argon or in vacuum. Melting points were determined in evacuated capillaries and are uncorrected. Infrared spectra were run in KBr disks protected by pure KBr pressed on either side of the sample, on a Perkin–Elmer 521 spectrophotometer. Reflection spectra were determined on a Beckmann DK2A spectrophotometer fitted with a reflectance attachment, as described previously.[10] Magnetic susceptibilities were measured by the Gouy method. Samples for mass spectra determination were introduced under argon into the Hitachi Perkin–Elmer RMU 6D mass spectrometer. Molecular weights were measured under argon in a Gallenkamp ebulliometer using a 3-ml cell.

Method

The sodium salt of the appropriate anion was degassed by evacuation, dissolved in air-free water, and combined with an equivalent amount of cp_2TiCl (from $TiCl_3$ and $Mgcp_2$[11]) in the same solvent in a stream of argon, using a Schlenk tube system as described earlier.[2] The products were collected by filtration under argon, washed with water, and pumped dry under high vacuum.

[9] Coutts, R. S. P., and Wailes, P. C., unpublished data.
[10] Reid, A. F., Scaife, D. E., and Wailes, P. C., *Spectrochim. Acta*, 1964, **20**, 1257.
[11] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 9.

The sulphato derivative could be sublimed satisfactorily as an emerald green crystalline solid, but, as mentioned above, the carbonato compound decomposed above 100°C. Physical properties and analytical data are shown in Table 1.

Acknowledgments

The authors are grateful to Dr D. E. Scaife for the use of a magnetic balance and, together with Dr A. F. Reid, for helpful discussion, to Mr B. Kaucner for experimental assistance, and to the Stauffer Chemical Company for a gift of $TiCl_3$.

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AUSTRALIAN JOURNAL OF CHEMISTRY

COMPLEXES OF BIS(CYCLOPENTADIENYL)TITANIUM(III) CHLORIDE WITH SOME BIDENTATE LIGANDS

By R. S. P. Coutts* and P. C. Wailes*

[*Manuscript received March* 4, 1967]

Summary

Bis(cyclopentadienyl)titanium(III) chloride (cp_2TiCl) complexes with 1,10-phenanthroline (phen), 2,2′-dipyridyl (dipy), *o*-phenylenediamine (phm), and α-picolylamine (picam) in anhydrous tetrahydrofuran to give $cp_2TiCl,1\cdot5L$ where L is the bidentate ligand. In air-free water all showed the conductivity of 1 : 1 electrolytes, but were insoluble in the common organic solvents.

Introduction

Complexes of titanium(IV) halides and zirconium(IV) halides with dipyridyl and phenanthroline have been known since 1963[1] and complexes of titanium trichloride with dipyridyl[2] and phenanthroline[3] were reported soon after. The four-valent metal halides generally form 1 : 1 complexes giving a six-coordinate metal and $TiCl_3$ forms either a 1 : 1 or 1 : 1·5 complex with dipyridyl. It was suggested that $TiCl_3$,dipy is a chlorine-bridged dimer, so that again the titanium is six-coordinate.

By contrast $cp_2Ti(CO)_2$ has been shown to react with 2,2′-dipyridyl with displacement of carbon monoxide giving a 1 : 1 complex cp_2Ti,dipy in which the titanium(II) is four-coordinate.[4]

During work in these laboratories on bis(cyclopentadienyl)titanium(III) chloride[5] (cp_2TiCl), it was found that complexes with *N*,*N*-bidentate chelating agents were readily formed and isolated. Adducts with 1,10-phenanthroline, 2,2′-dipyridyl, *o*-phenylenediamine, and α-picolylamine are described below.

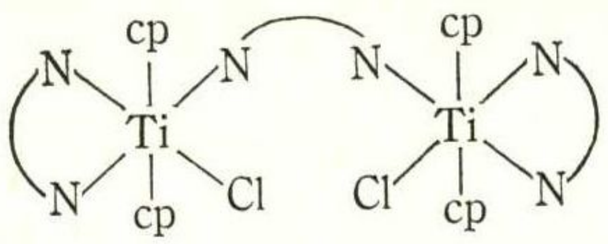
Results and Discussion

Complexes were prepared by mixing air-free tetrahydrofuran solutions of cp_2TiCl and of the chelate compound under argon. Analyses showed that a 1 : 1·5 complex was precipitated even when the proportions were varied between 1 : 1 and 1 : 2. Presumably two titanium atoms are bridged by one molecule of the chelating

* Division of Applied Chemistry, CSIRO Chemical Research Laboratories, P.O. Box 4331, Melbourne, Vic. 3001.

[1] Fowles, G. W. A., and Walton, R. A., *J. Less-common Metals*, 1963, **5**, 510.
[2] Fowles, G. W. A., Hoodless, R. A., and Walton, R. A., *J. inorg. nucl. Chem.*, 1965, **27**, 391.
[3] Khan, M. M., and Ahmad, N., *Bull. chem. Soc. Japan*, 1967, **40**, 1254.
[4] Fischer, E. O., and Amtmann, R., *J. organomet. Chem.*, 1967, **9**, 15.
[5] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 1181, and references quoted therein.

ligand (cf. $TiCl_3$,1·5dipy [2]) giving dimeric complexes (I) insoluble in the common organic solvents. For this reason, it was not possible to determine molecular weights.



(I)

All are soluble in air-free water and show the equivalent conductances of 1 : 1 electrolytes (Table 1). The phenanthroline complex, cp_2TiCl,1·5phen, in particular is somewhat deliquescent and stable for some hours in air; it dissolves in water to give a purple solution which probably contains the ion $\{[cp_2Ti(OH_2)phen]_2phen\}^{2+}$ and forms water-insoluble compounds with various anions. Its reactions are being studied further.

TABLE 1

CHARACTERIZATION OF COMPLEXES

Compound	Colour	Λ[a]	Cl[b] (%)		Ti[c] (%)	
			Found	Calc.	Found	Calc.
cp_2TiCl,1·5phen	mauve	120	7·1	7·3	9·6	9·9
cp_2TiCl,1·5dipy	blue	115	7·9	7·9	11·0	10·7
cp_2TiCl,1·5phm	pale green	120	[d]	—	12·8	12·7
cp_2TiCl,1·5picam	fawn	117	9·4	9·4	13·2	12·7

[a] Equivalent conductance in mho cm^2 equiv.$^{-1}$, 10^{-3} equiv. in water.

[b] Boiled with alkali, acidified with HNO_3, and titrated by the Volhard method.

[c] Sulphated ash.

[d] Too deeply coloured to give an end point.

The other three complexes are unstable in air, oxidizing exothermally to orange-coloured titanium(IV) compounds. All decompose without melting and cannot be sublimed under high vacuum before decomposition is complete. Their magnetics (Table 2) show no evidence of spin–spin interaction; a Curie–Weiss law is followed with one unpaired electron per titanium atom.

The main bands in the infrared spectra of the complexes are shown in Table 3. The effect of coordination can be seen in the phenanthroline complex in the shift to higher frequencies of the bands at 1500 and 1600 cm^{-1} due to ring vibrations in the chelating ligand. The cyclopentadienyl groups show four main bands around 800, 1000, 1430 (overlapping with a chelate band), and 3060 cm^{-1}. In all spectra, two weak to medium bands at 405–410 and 450–460 cm^{-1} can be assigned to TiCl.

The reflection spectra of the complexes show four bands in the near infrared which are binary combinations of the 3060 cm^{-1} band with the 800, 1000, and 1430 cm^{-1} bands and with itself. These always occur at 3900, 4100, 4500, and 6100 cm^{-1}

TABLE 2

MAGNETIC PROPERTIES OF COMPLEXES

T (°K)	$10^6\chi'_M$	μ_{eff} (B.M.)	T (°K)	$10^6\chi'_M$	μ_{eff} (B.M.)
$cp_2TiCl,1\cdot5phen$[a]			$cp_2TiCl,1\cdot5dipy$[b]		
			348·1	1120	1·77
315·1	1281	1·81	319·5	1319	1·84
286·7	1474	1·85	291·8	1405	1·82
259	1628	1·84	263·9	1547	1·81
229·6	1756	1·80	234·6	1718	1·80
204·7	1936	1·79	205·5	1960	1·80
176·2	2256	1·79	179·3	2246	1·80
147·9	2641	1·78	143·0	2731	1·78
131·6	3000	1·78	131·3	2974	1·77
			122·3	3144	1·76
$cp_2TiCl,1\cdot5phm$[c]					
348·2	1303	1·91	$cp_2TiCl,1\cdot5picam$[d]		
320·8	1411	1·91	319·8	1266	1·81
292·4	1590	1·94	291·8	1231	1·66
264·9	1721	1·92	264·2	1441	1·75
235·7	1924	1·91	234·8	1598	1·74
205·1	2187	1·90	205·2	1843	1·75
181·0	2402	1·87	177·1	2069	1·72
154·1	2736	1·84	160·3	2262	1·67
125·7	3309	1·83	135·9	2401	1·62

[a] Ligand correction for $10^6\chi'_M$, $308\cdot2\times10^{-6}$ CGS units. Magnetic moment uncorrected; θ $-10°$, T.I.P. 160×10^{-6} CGS units. Corrected μ_{eff}, 1·77 B.M.

[b] Ligand correction, 264×10^{-6} CGS units. Magnetic moment uncorrected; θ $-6°$, T.I.P. 140×10^{-6} CGS units. Corrected μ_{eff}, 1·76 B.M.

[c] Ligand correction, 229×10^{-6} CGS units. Magnetic moment uncorrected; θ $-10°$, T.I.P. 200×10^{-6} CGS units. Corrected μ_{eff}, 1·83 B.M.

[d] Ligand correction, $217\cdot8\times10^{-6}$ CGS units. Magnetic moment uncorrected; θ $-2°$, T.I.P. 200×10^{-6} CGS units. Corrected μ_{eff}, 1·64 B.M.

TABLE 3

MAIN INFRARED ABSORPTION BANDS OF COMPLEXES

} signifies overlapping peaks

Compound	Frequency (cm^{-1}, KBr disk)					Assignment
$cp_2TiCl,1\cdot5phen$	725	850	1065, 1140	1515, 1620, 3040		phen
			}1425			
	810	1005			3060	cp
$cp_2TiCl,1\cdot5dipy$	680, 780		1320	1475, 1600, 3030		dipy
		}1020	}1440			
	810				3060	cp
$cp_2TiCl,1\cdot5phm$	745, 750	1005	1110, 1280	1500, 1600	3100	phm
	}805					
		1010	1440		3050	cp
$cp_2TiCl,1\cdot5picam$	770	1170, 1290	1490, 1610			picam
			}1440	}3090		
	815, 1020					cp

and are diagnostic for cyclopentadienyl groups.[6] In the visible region the electronic transition bands are evident and the positions of these in the solid state are not significantly different from those in solution in water (Table 4).

TABLE 4

VISIBLE SPECTRA OF COMPLEXES IN AQUEOUS SOLUTION

Compound	ν (cm^{-1})	ϵ	Compound	ν (cm^{-1})	ϵ
$cp_2TiCl,1\cdot5phen$	11600	54	$cp_2TiCl,1\cdot5phm$	9090sh	26
	13000sh	47		13500sh	54
	17850	134		14300	57
$cp_2TiCl,1\cdot5dipy$	11300	72	$cp_2TiCl,1\cdot5picam$	13400	85
	13300	65		17200	120
	17600	180			

EXPERIMENTAL

General

All air-sensitive materials were handled under inert atmosphere or in vacuum. Infrared spectra were measured in KBr disks on a Perkin–Elmer 521 spectrophotometer. Reflection spectra were determined in a sealed cell[6] on a Beckman DK2A spectrophotometer fitted with a reflectance attachment, and absorption spectra in the visible region were recorded on a Beckman DK2 instrument. Magnetic susceptibilities were measured by the Gouy method.

Method

Degassed tetrahydrofuran solutions of cp_2TiCl[7] (5 mmole) and of the *N*,*N*-bidentate chelate compound (7·5 mmole) were mixed under argon and the resulting precipitate was collected and washed with tetrahydrofuran using the Schlenk tube system described earlier.[8] The products were pumped dry under high vacuum. Physical properties and analytical data are shown in Table 1.

ACKNOWLEDGMENTS

The authors are grateful to Mr B. Kaucner for experimental assistance and to the Stauffer Chemical Company for a gift of titanium trichloride.

[6] Reid, A. F., Scaife, D. E., and Wailes, P. C., *Spectrochim. Acta*, 1964, **20**, 1257.
[7] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 9.
[8] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1967, **20**, 1579.

Dithiocarbamates of Titanium(III)

By R. S. P. Coutts and P. C. Wailes*
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and J. V. Kingston
(*School of Physical Sciences, La Trobe University, Bundoora, Victoria*)

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Dithiocarbamates of Titanium(III)

By R. S. P. COUTTS and P. C. WAILES*

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and J. V. KINGSTON

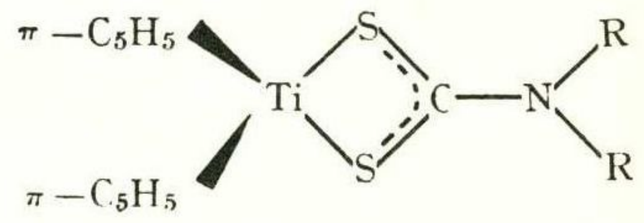
(*School of Physical Sciences, La Trobe University, Bundoora, Victoria*)

DITHIOCARBAMATES of titanium(III), previously unknown, have now been prepared from bis-(cyclopentadienyl)titanium chloride $(\pi\text{-}C_5H_5)_2TiCl$ and the sodium salt of the dithiocarbamate in air-free aqueous solution under an atmosphere of argon. The products, which precipitated as green air-sensitive solids, are substantially pure as isolated, but can be sublimed or distilled with some decomposition. Molecular-weight measurements of the compounds, R = Et, Pr^n, and Bu^n, in boiling tetrahydrofuran, indicated that these are essentially monomeric in this solvent. The first two of the series, R = H and Me, were too insoluble for ebulliometric measurements.

The magnetic susceptibilities of the first three compounds, R = H, Me, and Et, measured at room temperature by the Gouy method, clearly indicate one unpaired electron per titanium atom. Because of interference from the cyclopentadienyl absorption in the i.r. spectrum no definite conclusions can be drawn regarding the co-ordination number of the metal, but all other properties support a bidentate dithiocarbamato-ligand and a four-co-ordinate metal. The frequencies of the "thioureide" band (C–N stretch), common to most dithiocarbamates, are shown in the Table and indicate partial double-bond character for C–N. A shift to lower wave-number with increase in alkyl-chain lengths is also evident.

Characterisation of $(\pi\text{-}C_5H_5)_2TiS_2CNR_2$

R	Colour	M.p.	C–N stretch ($cm.^{-1}$)
NH_2	Pale green	160° (decomp.)	1390
NMe_2	Blue green	174 (decomp.)	1495
NEt_2	Deep green	100—102	1488
NPr^n_2	Deep green	56—59	1480 1490
NBu^n_2	Deep green	43—44	1480
$N(n\text{-}C_5H_{11})_2$	Deep green	oil	1475
NBz_2	Grey green	138 (decomp.)	1470
$N[CH_2]_5$	Deep green	162—164 (decomp.)	1480



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TETRAPHENYLBORATE DERIVATIVES OF TITANIUM(III)

By R. S. P. Coutts,* B. Kautzner,* and P. C. Wailes*

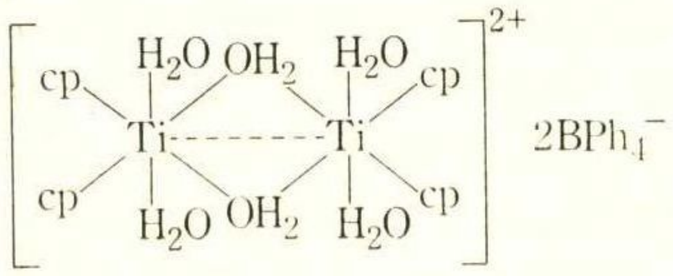
[Manuscript received January 30, 1969]

Summary

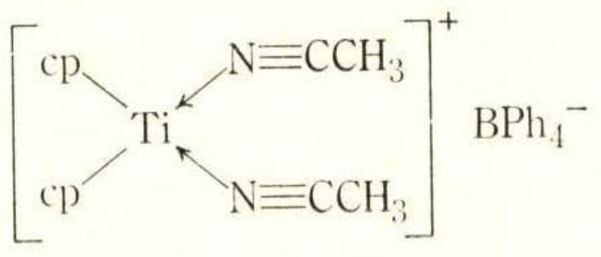
Three new titanium(III) compounds which incorporate solvent molecules have been prepared by replacing the chlorido ligand of cp_2TiCl by the non-coordinating group BPh_4^-. The new compounds are formulated as $[cp_2Ti(H_2O)_3]_2[BPh_4]_2$, $[cp_2Ti(N{\equiv}CCH_3)_2]BPh_4$, and $[cp_2Ti(py)_2]BPh_4$. The methyl cyanide and pyridine complexes are monomeric and show the normal paramagnetic behaviour of isolated titanium(III) compounds, but the aquo derivative is dimeric with magnetic interaction between titanium atoms.

Introduction and Discussion

A variety of anions have been used to precipitate the cp_2Ti^+ cation from air-free aqueous solutions.[1–5] All of the compounds previously formed in this way have been anhydrous species, but from cp_2TiCl and $NaBPh_4$, the hydrated complex $[cp_2Ti(H_2O)_3]BPh_4$ has now been isolated. All of the water is retained by the complex when it is warmed under high vacuum. The infrared spectrum (KBr disk) shows bands at 3520m, 3460s, 1610s, and 1595m, which indicates that water molecules are probably bound in the complex in two different ways. Magnetic data are consistent with formulation of the compound as a dimer. Thus, the variation of magnetic susceptibility with temperature does not follow the Curie–Weiss law, but shows titanium–titanium interaction (Fig. 1) with a maximum susceptibility at 365°K. At this temperature decomposition begins and the gradient increases sharply. These physical data, together with the observation that a bridged oxide is formed on pyrolysis of the compound (see below), are consistent with a solid state structure (I).



(I)



(II)

An hydroxy-bridged structure is rejected since this would require a higher oxidation state for the metal. The ionic nature of (I) is further supported by conductivity measurements in methanol.

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[1] Coutts, R. S. P., and Wailes, P. C., *Inorg. nucl. Chem. Lett.*, 1967, **3**, 1.
[2] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1967, **20**, 1579.
[3] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 373.
[4] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 1181.
[5] Coutts, R. S. P., Wailes, P. C., and Kingston, J., *Chem. Commun.*, 1968, 1170.

When cp_2TiCl and $NaBPh_4$ were combined in air-free methanol, a blue solution was obtained from which bright blue crystals of $[cp_2Ti(N{\equiv}CCH_3)_2]BPh_4$ were deposited on addition of methyl cyanide. This complex is soluble in polar solvents, and ebulliometric measurements in tetrahydrofuran under argon show that the

TABLE 1

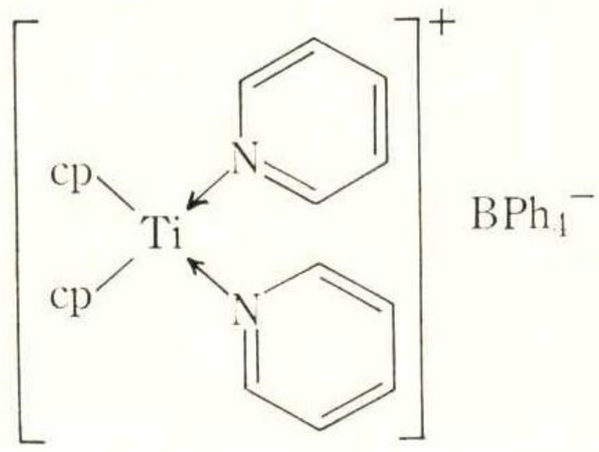
MAGNETIC PROPERTIES OF COMPLEXES (II), (III), AND (IV)

Temp. in °K; χ'_M and ligand correction in CGS units; μ_{eff} in B.M. All magnetic moments uncorrected

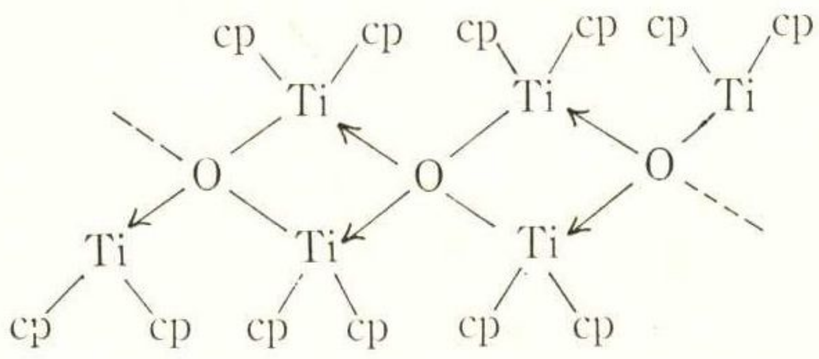
Temp.	$10^6\chi'_M$	μ_{eff}	Temp.	$10^6\chi'_M$	μ_{eff}	Temp.	$10^6\chi'_M$	μ_{eff}
$[cp_2Ti(N{\equiv}CCH_3)_2]BPh_4$			$[cp_2Ti(py)_2]BPh_4$			$[cp_2TiOTicp_2]_n$		
287	1310	1·74	311·5	1222	1·75	346	319	0·99
257·5	1495	1·76	288·7	1263	1·72	322	326	0·97
231	1672	1·77	276·5	1324	1·72	298	353	0·97
197	1940	1·76	260·5	1466	1·75	273	388	0·98
168	2204	1·73	224·5	1672	1·74	247	422	0·98
139	2637	1·72	193·5	1876	1·71	220	459	0·97
ligand corr. 354×10^{-6}			174	2210	1·75	190	500	0·95
θ −18°			135·5	2634	1·70	ligand corr. 206×10^{6}		
			108	3328	1·71	θ −34°		
			85	4604	1·77			
			ligand corr. 414×10^{-6}					
			θ 0°					

compound is essentially monomeric. Magnetic susceptibility measurements show no evidence of metal–metal interaction; a Curie–Weiss law, $\chi = C/(T-\theta)$, is followed with μ_{eff} 1·75 B.M. per titanium atom (Table 1). The high conductivity in methanol is in accord with the ionic structure (II).

On recrystallization from pyridine the methyl cyanide derivative (II) is converted into an analogous monomeric pyridino complex (III).



(III)



(IV)

The variation with temperature of the magnetic susceptibility of (III) shows no evidence of spin-coupling. The moment is independent of temperature with μ_{eff} 1·76 B.M. per titanium atom (Table 1).

Pyrolysis of the aquo complex (I) occurs above 100°, giving equimolar amounts of triphenylboron and benzene, and leaving a deep blue air-sensitive residue which is involatile below 200° at 10^{-2} mm, and is only slightly soluble in the most polar solvents. Infrared and mass spectral evidence (Experimental section) indicate a

titanocene oxide structure, $cp_2TiOTicp_2$ (IV), probably associated through the oxygen atoms. The formation of this compound is represented in equation (1):

$$(I) \rightarrow [cp_2TiOTicp_2]+2BPh_3+2PhH+5H_2O \quad (1)$$

Compound (IV) is paramagnetic and from the variation of its susceptibility with temperature it would appear to have a Néel temperature just below 100°C. Over a limited range (210–350°K), however, the Curie–Weiss law is followed with μ_{eff} 0·97 B.M. per titanium atom (Table 1). A compound similar to (IV) was obtained by the authors from pyrolysis of $(cp_2Ti)_2CO_3$.[4]

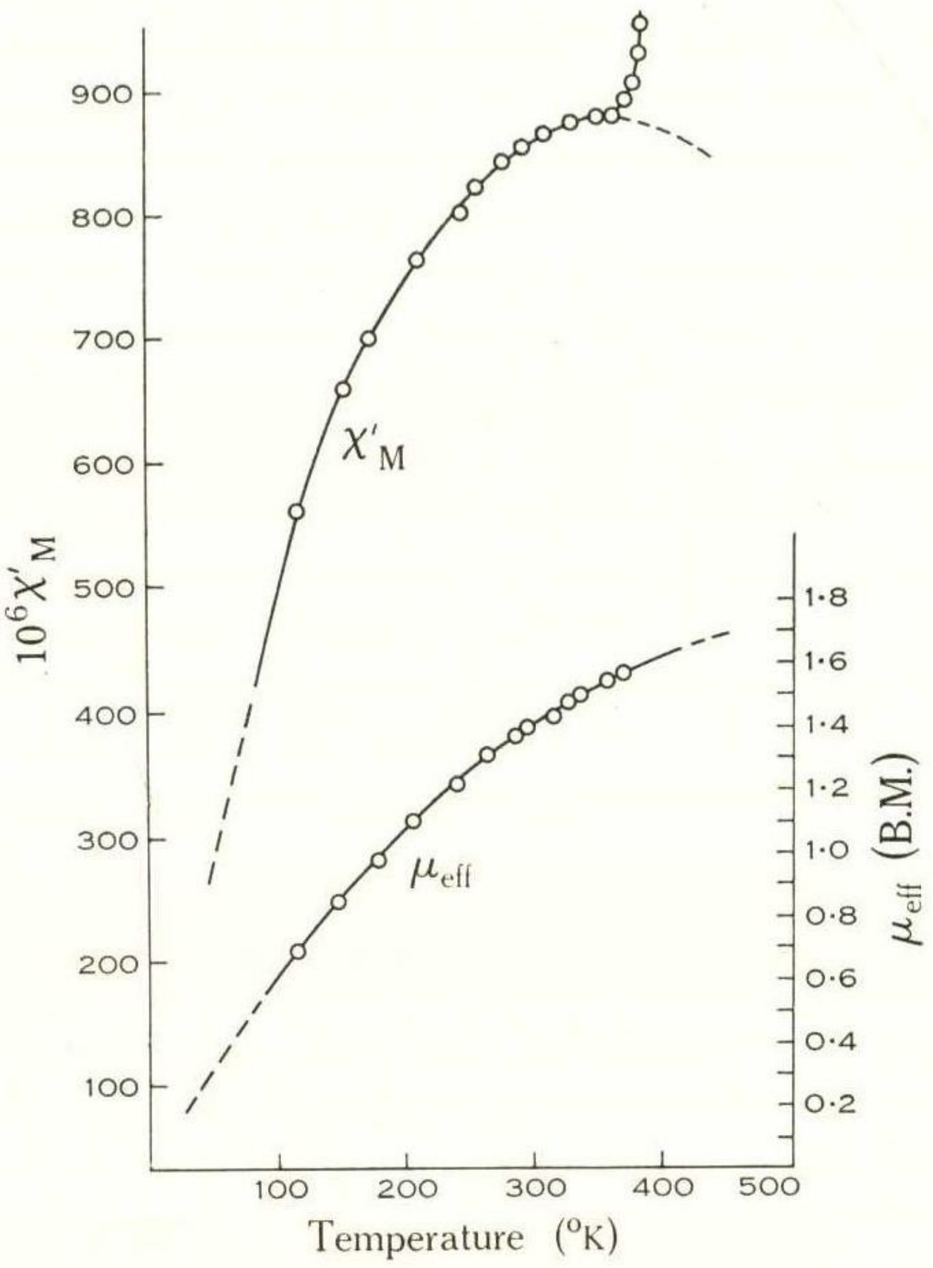


Fig. 1.—Variation of magnetic susceptibility and magnetic moment with temperature, for $[cp_2Ti(H_2O)_3]_2[BPh_4]_2$.

The thermal instability of (I) is clearly evident from Figure 1. At 365°K decomposition begins and the susceptibility increases sharply. The pyridine complex (III) is also thermally unstable since at about 335°K μ_{eff} ceases to be constant and drops below 1·6 B.M., although complete decomposition does not occur until 242–246°C. The methyl cyanide compound (II) is much more stable to heat and no evidence of thermal instability was found over the range used for magnetic susceptibility measurements. The instability of (I) and (III) is reflected in the molecular weight values, determined ebulliometrically in tetrahydrofuran under argon. The methyl cyanide complex (II) behaves as an undissociated monomer, whereas the pyridine complex (III) gives molecular weight values one-third that of the monomer, which must be due to the replacement of pyridine by tetrahydrofuran during the molecular weight determination. The aquo complex decomposes slowly in boiling tetrahydrofuran and no consistent molecular weight value could be obtained. In air-free methanol, all three tetraphenylborate compounds are extensively ionized and show conductivities approaching those of 1 : 1 electrolytes (55–80 $ohm^{-1}\,cm^2\,mole^{-1}$ in 10^{-3}M solution).

Experimental

General

All air-sensitive compounds were handled in a nitrogen-filled glove-box or in a stream of purified argon. Conductivity values were determined in a sealed cell under argon.

Analyses

In the presence of boron, metal analyses are difficult but a mixed ash of $TiO_2+B_2O_3$ could be obtained by burning in a stream of air.

Carbon, hydrogen, and nitrogen analyses were determined by the Australian Microanalytical Service, on samples sealed in indium tubing.

Aquo Complex (I)

A solution of $NaBPh_4$ (1·0 g) in air-free water (30 ml) was filtered under argon into a blue solution of cp_2TiCl (0·4 g) in the same solvent. A pale blue precipitate appeared immediately and was collected by filtration under argon, washed several times with air-free water, then dried by warming to 40–50° under high vacuum. The yield was quantitative; m.p. 92° (dec.) (Found: C, 74·9; H, 6·9; ash ($TiO_2+\frac{1}{2}B_2O_3$), 20·6; H_2O, 10·0.* Calc. for $C_{34}H_{36}BO_3Ti$; C, 74·0; H, 6·6; ash, 20·4; H_2O, 9·8%).

CH_3CN Complex (II)

When cp_2TiCl and $NaBPh_4$ were mixed as above in air-free methanol a blue solution resulted. This was evaporated to small bulk and excess anhydrous CH_3CN was added. An immediate precipitate of a bright blue crystalline complex formed, which was collected by filtration and washed with methyl cyanide. The yield was > 90%; m.p. 234° (dec.) (Found: C, 77·9; H, 6·4; N, 5·0; ash, 19·0%; mol. wt., 540 (ebulliometric in tetrahydrofuran). Calc. for $C_{38}H_{36}BN_2Ti$: C, 78·7; H, 6·3; N, 4·8; ash, 19·8%; mol. wt., 579).

Pyridine Complex (III)

The methyl cyanide complex (II) was dissolved in dry air-free pyridine and set aside for 24 hr. The dark green bis-pyridino compound (III) crystallized and was recovered by decantation, washed with pyridine, and pumped dry; m.p. 242–246° (dec.) (Found: C, 80·0; H, 6·2; N, 4·3; ash, 16·7; mol. wt., 220 (ebulliometric in tetrahydrofuran). Calc. for $C_{44}H_{40}BN_2Ti$: C, 80·5; H, 6·2; N, 4·3; ash, 17·5%; mol. wt., 656).

Pyrolysis Product (IV)

The aquo complex (I) (2·0 g) was heated under reduced pressure to 150° and the volatile products were collected on a water-cooled condenser (BPh_3, 0·66 g, identified by m.p. and mixed m.p. with an authentic sample) and in a trap cooled with acetone–solid CO_2 (benzene, 0·24 g, estimated by u.v. spectrometry, and water, 0·1 g, identified by i.r. spectrometry and estimated by weight difference). The deep blue air-sensitive residue showed a broad strong absorption around 720 cm^{-1} in the infrared, indicating Ti–O–Ti. All of the intense peaks in the mass spectrum at high temperature (280°) are based on cp(R)TiOTi(R′)cp where R and R′ are fragments of cyclopentadienyl rings (C_3H_3 or C_2H_3).

Magnetic Properties of Complexes

Magnetic susceptibilities of all four compounds at various temperatures were determined in sealed tubes by the Gouy method. The variation of magnetic susceptibility and magnetic moment with temperature of the aquo complex (I) is shown in Figure 1, and values for (II), (III), and (IV) are tabulated in Table 1.

* Estimated by three different methods: (1) measurement of methane evolved on reaction with $AlMe_3$ in xylene, and (2) with MeMgBr in tetrahydrofuran, (3) the Karl Fischer method.

Spectra of Complexes

(1) *Infrared.*—The infrared spectra were measured in KBr disks on a Perkin–Elmer 521 spectrophotometer. The frequencies of the bands due to BPh_4 are not shifted significantly from those shown by $NaBPh_4$, although the C–H out-of-plane deformation at 740 cm^{-1} is split in all cases. The BPh_4 bands occur at 600–605 (C–H in-plane deformation); 695–705, 725, and 740 (C–H out-of-plane deformation); 1425, 1475–1480, and 1580 (C=C stretch); 2980, 2990, and 3050 cm^{-1} (masked, C–H stretch).

In the spectrum of (II), the C≡N stretching band is split into a doublet (2265m and 2275m). A weak band at 2245 cm^{-1} is assigned to uncomplexed methyl cyanide formed by hydrolysis on the surface of the disk, and at 2295 cm^{-1} another weak band occurs. This is probably the combination band from the symmetric CH_3 deformation plus C–C stretch.[6]

(2) *Near infrared and visible.*—Reflection spectra were determined in a sealed cell on a Beckman DK2A spectrophotometer fitted with a reflectance attachment, and absorption spectra in the visible region were recorded on a Beckman DK2 instrument. In the near infrared reflectance spectra binary combinations of the 3050 cm^{-1} band with the three other bands and with itself are evident. In addition, the methyl cyanide complex shows additional combination bands at 4420 ($2 \times C{\equiv}N$ stretch) and 5290 cm^{-1} ($3050 + C{\equiv}N$ stretch).

Electronic absorption bands of the solid complexes occurring at the frequencies (cm^{-1}) shown below are undoubtedly due to *d–d* transitions:

(I)	9100, 14800
(II)	— 13000, 17800
(III)	11000, 13900
(IV)	11000, 13700, 17700

Acknowledgment

The authors would like to thank the Stauffer Chemical Co. for a gift of $TiCl_3$.

[6] Walton, R. A., *Q. Rev. chem. Soc.*, 1965, **19**, 126.

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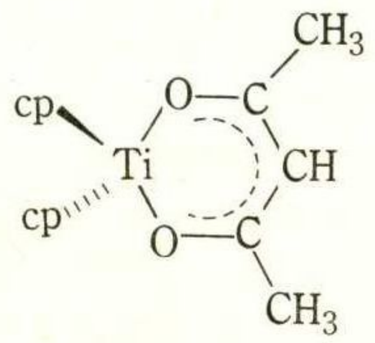
ACETYLACETONATOBIS(CYCLOPENTADIENYL)TITANIUM(III)

By R. S. P. Coutts* and P. C. Wailes*

[Manuscript received March 21, 1969]

Previous work in these laboratories has shown that bis(cyclopentadienyl)-titanium(III) complexes with bidentate chelate compounds can be formed readily with both four-[1] and five[2]-membered chelate rings. An obvious extension to this work is the synthesis of β-diketonate derivatives of titanium(III) in which the chelated rings will be six-membered.

When a fourfold excess of acetylacetone was added to a vigorously stirred solution of cp_2TiCl (cp = π-cyclopentadienyl) in air-free water, a deep blue air-sensitive precipitate was obtained, identified from the data given below as (I), i.e. $cp_2Ti(acac)$, formed as in equation (1).



(I)

$$cp_2TiCl + acacH \rightarrow cp_2Ti(acac) + HCl \qquad (1)$$

Pentane-2,4-dionatobis(cyclopentadienyl)titanium(III) (I) is monomeric and the magnetic moment is independent of temperature with one unpaired electron per titanium atom (Table 1).

TABLE 1

MAGNETIC PROPERTIES OF $cp_2Ti(acac)$

Ligand correction 152×10^{-6} CGS units

T (°K)	$10^6\chi'_M$	μ_{eff} (B.M.)	T (°K)	$10^6\chi'_M$	μ_{eff} (B.M.)
287	1316	1·74	196	1960	1·76
263	1415	1·73	166	2288	1·75
234·5	1632	1·76	136	2671	1·71
202·5	1862	1·74			

The yield of (I) is about 50%. The rest of the titanium is found in the red aqueous filtrate from which the titanium(IV) compounds $[cp_2Ti(acac)]ClO_4$ and $[cp_2Ti(acac)]BF_4$ can be precipitated by addition of ClO_4^- or BF_4^- under air-free conditions. These complexes are identical in every respect with those obtained from acetylacetone and $cp_2Ti(ClO_4)_2$ (or cp_2TiCl_2) in water, and which were recently characterized by Doyle and Tobias.[3]

* Division of Applied Chemistry, CSIRO Chemical Research Laboratories, P.O. Box 4331, Melbourne, Vic. 3001.

[1] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1967, **20**, 1579; 1968, **21**, 373; 1968, **21**, 1181; Coutts, R. S. P., Wailes, P. C., and Kingston, J., *Chem. Commun.*, 1968, 1170.

[2] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 2199.

[3] Doyle, G., and Tobias, R. S., *Inorg. Chem.*, 1967, **6**, 1111.

This oxidation to titanium(IV) could be brought about by protonation of titanium(III) species by the hydrochloric acid produced in the initial reaction. Alternatively, oxidation by an electron-transfer process involving chloride (similar to the oxidation of ferrocene to ferricenium ion; for a discussion see[4]) could occur.

Experimental

General

All manipulations were carried out in a nitrogen-filled glove-box or in a stream of purified argon.

Reaction of Acetylacetone with cp_2TiCl

The cp_2TiCl_2 (10 g) was stirred overnight in air-free water (150 ml) with excess granulated zinc (10 g). The solution was filtered in a stream of argon to remove unchanged zinc and a small amount of blue insoluble $Ti(OH)_3$ which is always formed. The deep blue filtrate* was vigorously stirred with acetylacetone (18 ml, added in small portions) for 2 hr, giving a deep blue precipitate (5·9 g) of $cp_2Ti(acac)$ which was removed by filtration and washed several times with air-free water. The product had m.p. 71° (dec.) (evacuated capillary) and sublimed readily at 100°/10^{-3} mm (Found:† C, 64·5; H, 6·2; Ti (sulphate ash), 17·4; mol. wt. 278.‡ Calc. for $C_{15}H_{17}O_2Ti$: C, 65·0; H, 6·2; Ti, 17·3%; mol. wt. 277).

Spectral Data

The spectrum of $cp_2Ti(acac)$ was measured between 250 and 25000 cm^{-1} in KBr disk (to 4000 cm^{-1}) and tetrahydrofuran solution.

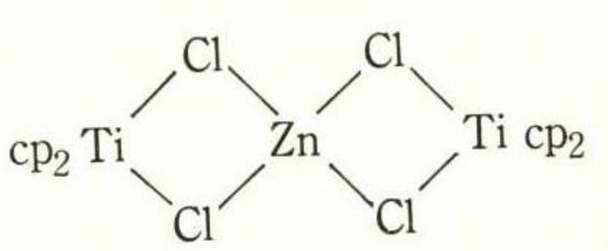
Infrared.—The main bands due to the acetylacetonato ligand are at 1583 (C=C str§), 1512 (C=O str), and 1380 cm^{-1} (C=O str), and clearly indicate that the ligand is bidentate. The cyclopentadienyl groups absorb at 3090 (C–H str), 1430 (C=C str), 1015 (C–H deform), and 785 cm^{-1} (C–H deform).

Visible spectrum.—This was run on a Cary 14 spectrophotometer; bands due to *d–d* transitions were observed at 10260sh, 13040sh, 14560 (ϵ 61), and 17240 cm^{-1} (ϵ 43). This is very similar to the spectra of other bis(cyclopentadienyl)titanium(III) compounds prepared and examined in these laboratories.[1,2] The only effect of the acetylacetonato ligand is to raise the frequency of the highest-energy *d–d* transition from 13000–14000 to 14560 cm^{-1}.

Magnetic Susceptibility

Susceptibility was measured by the Gouy method in a sealed tube over the temperature range 136–287°K. The moment is independent of temperature and close to the spin-only value for a d^1 system.

* In organic solvents (tetrahydrofuran, methanol, etc.) cp_2TiCl_2 is reduced by zinc to (II),[5] but in water the ion cp_2Ti^{III+} is present and can be precipitated by those anions which do not have insoluble zinc derivatives.



(II)

† Analyses for C and H were carried out by the Australian Microanalytical Service, Melbourne, on small pellets sealed in aluminium capsules of the type used in calorimetry.

‡ Ebulliometric in benzene.

§ Assignment by Nakamoto;[5] others assign this band to C=O and the 1512 cm^{-1} band to C=C. See ref.[6] for a discussion of these bands.

[4] Rosenblum, M., "Chemistry of the Iron Group Metallocenes." Part I. (Interscience: New York 1965.)

[5] Vonk, C. G., personal communication to Martin, H. A., and Jellinek, F., in *J. organomet. Chem.*, 1967, **8**, 115; Salzmann, J. J., *Helv. chim. Acta*, 1968, **51**(3), 526.

[6] Nakamoto, K., "Infrared Spectra of Inorganic and Co-ordination Compounds." p. 216. (John Wiley: New York 1963.)

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AUSTRALIAN JOURNAL OF CHEMISTRY

ORGANOPHOSPHORYL COMPLEXES OF ZIRCONIUM TETRACHLORIDE

By B. Kautzner* and P. C. Wailes*

[Manuscript received July 16, 1969]

Summary

A number of coordination complexes of zirconium tetrachloride with phosphoryl ligands of the type $(RO)_3PO$, $(RO)_2P(O)R'$, $ROP(O)R'_2$, and R_3PO have been prepared and characterized as complexes of the type $ZrCl_4,2L$. The shifts of the phosphoryl stretching frequency in the infrared on complex formation have been measured and are discussed with reference to the electronegativity of the substituents on the phosphorus atom.

Introduction

Phosphoryl addition compounds with metal halides have been known for some years (e.g. see[1–5]), but in the case of zirconium tetrachloride, the only complexes which have been isolated[6,7] are the phosphoryl trihalide compounds $ZrCl_4,2POCl_3$ and $[ZrCl_4,POCl_3]_n$, in which probably $n = 2$. Organophosphoryl complexes of zirconium tetrachloride have not been isolated although alkyl phosphates have been used widely in the extraction of zirconium salts from acidic aqueous solutions. For this purpose, phosphoryl compounds in general have found considerable use.[8–10]

Apart from the commonly used $(BuO)_3PO$, Nikitina *et al.*[11] have studied in solution the complexes $ZrCl_4,2(BuO)_2P(O)Bu$, $ZrCl_4,2(BuO)P(O)Bu_2$, and $ZrCl_4,2Bu_3PO$ while Umezawa and Hara[12] have carried out extraction studies on zirconium using several alkyl phosphoryl solvents. None of these workers attempted to isolate the complexes, the existence of which was inferred from infrared spectral data.

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1 Pickard, R. H., and Kenyon, J., *J. chem. Soc.*, 1906, 262.
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3 Sheldon, J. C., and Tyree, S. Y., *J. Am. chem. Soc.*, 1958, **80**, 4775.
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8 Marcus, Y., *Chem. Rev.*, 1963, **63**, 147.
9 Levitt, A., and Freund, H., *J. Am. chem. Soc.*, 1956, **78**, 1545.
10 Nikitina, G. P., and Pushlenkov, M. F., *Radiokhimiya*, 1964, **6**(3), 347.
11 Nikitina, G. P., and Pushlenkov, M. F., *Radiokhimiya*, 1963, **5**(4), 456.
12 Umezawa, H., and Hara, R., *Analytica chim. Acta*, 1961, **25**, 360.

Results and Discussion

In the work now reported, the complexes shown in Table 1 were prepared in anhydrous solvents under inert atmosphere. The P=O stretching frequency of the ligand is shown together with the shift in frequency on coordination to zirconium tetrachloride.

Table 1

PO stretching frequencies (cm^{-1}) of $ZrCl_4$ complexes

Compound	Ligand	Complex	$\Delta\nu$	Compound	Ligand	Complex	$\Delta\nu$
Phosphine oxides				Phosphonates			
$ZrCl_4,2Me_3PO$	1170	1040	130	$ZrCl_4,2MeP(O)(OEt)_2$	1240	1110	130
$ZrCl_4,2Bu_3PO$	1160	1035	125	$ZrCl_4,2PhP(O)(OEt)_2$	1245	1110	135
$ZrCl_4,2Ph_3PO$	1190	1062	128	$ZrCl_4,2PhCH_2P(O)(OEt)_2$	1240	1102	138
$ZrCl_4,2(PhCH_2)_3PO$	1180	1035	145	$ZrCl_4,2PhCH_2P(O)(OPr)_2$	1245	1115	130
Phosphinates				Phosphates			
$ZrCl_4,2Me_2P(O)OEt$	1210	1082	128	$ZrCl_4,2(MeO)_3PO$	1275	1120	155
$ZrCl_4,2Ph_2P(O)OMe$	1225	1082	143	$ZrCl_4,2(EtO)_3PO$	1265	1150	115
$ZrCl_4,2Ph_2P(O)OEt$	1225	1085	140	$ZrCl_4,2(BuO)_3PO$	1275	1150	125
$ZrCl_4,2Ph_2P(O)OPh$	1215	1085	130				

All except the phosphate complexes, $ZrCl_4,2(RO)_3PO$, are thermally stable and are not hydrolysed in moist air; cf. $ZrCl_4$, equation (1). They can be crystallized readily and give sharp melting points.

$$ZrCl_4+9H_2O \rightarrow ZrOCl_2,8H_2O+2HCl \quad (1)$$

The phosphate complexes could not be crystallized and slowly decomposed at room temperature with evolution of alkyl halide and formation of an insoluble polymeric zirconium phosphate of indeterminate composition. Pyrolysis of the initially formed complex gave approximately 2·5 moles of RCl per mole of $ZrCl_4,2(RO)_3PO$.*

In the infrared spectra of the adducts the strong P=O stretching band, normally found between 1160 and 1275 cm^{-1} in all of the ligands, is shifted to lower frequency by over 115 cm^{-1}. In the complexes, this band occurs in a frequency range with several other bands and careful examination of all spectra is necessary before assigning the band with certainty. The assignments reported in Table 1 agree with those of van der Veer and Jellinek[13] for the compounds $(Ph_3PO)_2,TiCl_4$ and $(Ph_3PO)_2,TiBr_4$, but do not substantiate the assignments of other authors.[3,5,14]

Triphenylphosphate is the only adduct which gave no apparent shift of the PO band at 1285 cm^{-1}. Some type of complex formation had taken place since the $(PhO)_3PO$, which is very soluble in carbon tetrachloride, could not be extracted from the $[ZrCl_4+2(PhO)_3PO]$ mixture using this solvent. Since tribenzylphosphate and

* The residual polymers after pyrolysis swell in benzene and absorb upwards of 16 moles of benzene per atom of zirconium. The benzene can be recovered by heating.

[13] Veer, W., van der, and Jellinek, F., *Recl Trav. chim. Pays-Bas*, 1966, **85**, 842.

[14] Osipov, O. A., Gaivoronskii, V. I., and Shvets, A. A., *Russ. J. inorg. Chem.*, 1963, **8**, 1145.

triphenylphosphine oxide behave normally, steric reasons for the triphenylphosphate exception seem to be excluded.

The reason for the decrease in the phosphoryl stretching frequency on complex formation has been discussed by Cotton *et al.*,[4] who attribute the overall lowering in bond order to a decrease in $p\pi \rightarrow d\pi$ back bonding from O→P on coordination of oxygen to metal. Back bonding from O→P is enhanced by attaching more electronegative groups to phosphorus, resulting in an increase in PO frequency in both ligand and complex. This effect can be seen in Table 2, the frequency increasing in the order phosphine oxides < phosphinates < phosphonates < phosphates.

TABLE 2

EFFECT OF ELECTRONEGATIVE GROUPS

Group	Ligand (cm^{-1})	Complex (cm^{-1})	$\Delta\nu$	Complex M.P.
Me_3PO	1170	1040	130	300°
$Me_2P(O)OEt$	1210	1082	128	113–114
$MeP(O)(OEt)_2$	1240	1110	130	55–60
$(MeO)_3PO$	1275	1120	155	liquid

A shift of 30–40 cm^{-1} is observed for each oxygen around the phosphorus atom in the ligand; in fact there is a linear correlation of PO bond order with the electronegativity of the substituents.[15] On complex formation, as the electronegativity of the substituents increases the coordinating strength becomes less. A decrease in melting points is also observed (Table 2).

Such comparisons give some idea of the relative thermal stabilities of the complexes; the stability increases from $(RO)_3PO$ to R_3PO.

It is probable that the complexes are in the *cis* form since this is the orientation of those phosphoryl complexes of other metals which have been investigated. From an X-ray crystal structure Brändén[16] found that $TiCl_4,2POCl_3$ existed as the *cis* form, and from Raman data Davies and Long[17] assigned the *cis* structure to $TiCl_4,2(BuO)_3PO$.

Although evidence based on X-ray powder patterns for a 1 : 1 complex of $ZrCl_4$ with $POCl_3$ was reported by Voitovich *et al.*,[7] this compound is probably dimeric, similar to the $(TiCl_4,POCl_3)_2$ complex which has a double chlorine bridge.[18] Osipov *et al.*[14] claim to have evidence for a 1 : 1 complex from $ZrCl_4+(BuO)_3PO$ in solution. This evidence is based on infrared bands at 1196 cm^{-1} (assigned to PO in 1 : 2 complex) and at 1148 cm^{-1} (1 : 1 complex). These assignments are not substantiated by the work reported herein, since pure $ZrCl_4,2(BuO)_3PO$ shows a PO band at 1150 cm^{-1}.* The explanation for this discrepancy lies in the instability of the phosphate complexes of zirconium tetrachloride. As mentioned above, all are unstable at room temperature, liberating alkyl chloride and forming polymeric zirconium

* Nikitina and Pushlenkov[11] found the same band at 1144 cm^{-1}.

[15] Wagner, E. L., *J. Am. chem. Soc.*, 1963, **85**, 161.

[16] Brändén, C. I., *Acta chem. scand.*, 1962, **16**, 1806.

[17] Davies, J. E. D., and Long, D. A., *J. chem. Soc.* (*A*), 1968, 2560.

[18] Brändén, C. I., and Lindquist, I., *Acta chem. scand.*, 1960, **14**, 726.

phosphates. In fact, when equimolar quantities of $ZrCl_4$ and of $(BuO)_3PO$ were mixed, over a 20-min period the PO band moved from 1130 to 1170 cm^{-1}.

From conductivity measurements in methanol, it would appear that all of the chlorides are ionized since molar conductances of all complexes ranged from 333–419 mho cm^2 $mole^{-1}$ at 10^{-3}M, i.e. an equivalent conductance of 70–90 mho cm^2 $mole^{-1}$.

Experimental

General

All manipulations of air-sensitive materials were carried out in a nitrogen-filled glove-box or in a stream of purified argon. Melting points are uncorrected. Infrared spectra were run on a Perkin–Elmer 521 spectrophotometer. Analyses were carried out by the Australian Microanalytical Service, Melbourne.

Table 3

ANALYSES

Complex	Method	M.P.	Found (%)			Calc. (%)		
			C	H	Cl	C	H	Cl
$ZrCl_4,2Me_3PO$	A	>300°	17·9	4·9	33·7	17·3	4·6	33·9
$ZrCl_4,2Bu_3PO$	A[a]	132–135	43·6	8·0	19·1	43·1	8·1	21·2
$ZrCl_4,2Ph_3PO$	A	>300	54·1	4·4	17·2	54·8	3·8	17·9
$ZrCl_4,2(PhCH_2)_3PO$	B	208–209	57·0	5·3	16·4	57·7	4·8	16·2
$ZrCl_4,2Me_2P(O)OEt$	B	113–114	19·5	4·7	29·1	20·1	4·6	29·7
$ZrCl_4,2Ph_2P(O)OMe$	A	193[b]	44·1	4·1	20·2	44·8	3·8	20·3
$ZrCl_4,2Ph_2P(O)OEt$	A	187[b]	46·4	4·4	19·4	46·2	4·2	19·5
$ZrCl_4,2Ph_2P(O)OPh$	A	217–219	52·6	4·1	17·3	52·6	3·7	17·3
$ZrCl_4,2CH_3P(O)(OEt)_2$	B	55–58	22·3	5·1	26·7	22·4	4·9	26·4
$ZrCl_4,2PhP(O)(OEt)_2$	B	121–122	37·4	4·9	21·6	36·9	4·7	21·8
$ZrCl_4,2PhCH_2P(O)(OEt)_2$	B	120–122	38·8	5·0	20·1	38·3	5·0	20·6
$ZrCl_4,2PhCH_2P(O)(OPr)_2$	B	129–130	41·2	6·0	18·8	41·8	5·7	19·0

[a] With acetone–solid CO_2 cooling. [b] Decomposition.

Materials

Phosphates.—All alkyl phosphates were commercial products, redistilled and stored over molecular sieves; $(MeO)_3PO$, b.p. 195–196°; $(EtO)_3PO$, b.p. 216°; $(BuO)_3PO$, b.p. 116–120°/2 mm.

Phosphonates.—$CH_3P(O)(OEt)_2$, $PhP(O)(OEt)_2$, $PhCH_2P(O)(OEt)_2$, and $PhCH_2P(O)(OPr)_2$ were kindly supplied by Mr A. Meisters of this Division.

Phosphinates.—These were prepared by the action of the appropriate sodium alkoxide or phenoxide on the phosphinyl chlorides $Me_2P(O)Cl$ or $Ph_2P(O)Cl$ (see[19]) in tetrahydrofuran solution. The phosphinates had the following properties: $Me_2P(O)OEt$, b.p. 75–78°/10 mm; $Ph_2P(O)OMe$, m.p. 61–63°; $Ph_2P(O)OEt$, m.p. 39–41°; $Ph_2P(O)OPh$, m.p. 135–136°.

Phosphine oxides.—Me_3PO, prepared from $POCl_3$+MeMgBr;[20] Bu_3PO, from oxidation of Bu_3P with H_2O_2;[19] $(PhCH_2)_3PO$, from $PhCH_2Cl$ and red phosphorus in air.[21] Ph_3PO was a commercial product, recrystallized from benzene, m.p. 156–157°.

[19] Houben–Weyl, "Methoden der Organischen Chemie. Vol. 12. Organische Phosphor-Verbindungen." p. 1. (Springer-Verlag: Berlin 1963.)

[20] Burg, A. B., and McKee, W. E., *Z. anorg. Chem.*, 1960, **304**, 147.

[21] Levchenko, E. S., Piven, Yu. V., and Kirsanov, A. V., *Zh. obshch. Khim.*, 1960, **30**, 1976 (*Chem. Abstr.*, 1961, **55**, 6418).

All zirconium tetrachloride was sublimed twice; first, at 500° along a glass tube at atmospheric pressure; second, under vacuum at 300°/10^{-4} mm.

Preparation of Complexes

Zirconium tetrachloride (5–10 mmole) was weighed into a 150-ml Schlenk flask in a glove-box, dissolved in 30–50 ml of dry oxygen-free tetrahydrofuran (redistilled from $LiAlH_4$), then filtered through a sintered glass frit in a stream of argon into a second Schlenk flask containing 2 mol. propn. of the phosphoryl compound dissolved in tetrahydrofuran. The solution was stirred for 4 hr. The complexes were then isolated and purified by one of two methods:

(A) The complex precipitated out of the tetrahydrofuran solution on standing.

(B) The solution was evaporated to small bulk and the solid which then precipitated, with or without the addition of petrol, was recrystallized from CCl_4–light petroleum mixtures.

Analytical results are given in Table 3. Analyses of the phosphate complexes were not carried out since all were oils prepared in 1 : 2 stoicheiometry. Their solubility in all organic solvents together with their instability, even at room temperature, prevented any attempt at purification. Under these circumstances, analyses have no significance.

Hydrides of Bis(cyclopentadienyl)zirconium

By B. KAUTZNER, P. C. WAILES,* and H. WEIGOLD
(*Division of Applied Chemistry, C.S.I.R.O., P.O. Box* 4331, *Melbourne*)

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Summary Several new hydrides of zirconium have been prepared by the action of lithium aluminium hydride on various bis(cyclopentadienyl)zirconium chlorides.

AMONG the Group IVA elements the only hydrides which have been isolated are two of zirconium, *viz.* $(\pi\text{-}C_5H_5)_2ZrH_2$ and $(\pi\text{-}C_5C_5)_2Zr(H)BH_4$, both of which were prepared by the action of trialkylamines on the bis(tetrahydroborate), $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$.[1] We report a convenient new synthesis of $(\pi\text{-}C_5H_5)_2ZrH_2$, (I) and of three new zirconium hydrides.

On addition of $LiAlH_4$ (1 mol.) in tetrahydrofuran to $(\pi\text{-}C_5H_5)_2Zr(Cl)OZr(Cl)(\pi\text{-}C_5H_5)_2$[2] in the same solvent, abstraction of both chlorine and oxygen occurs and pure (I) is slowly precipitated. From $LiAlH_4$ (0·25 mol.) and $(C_5H_5)_2ZrCl_2$, $(\pi\text{-}C_5H_5)_2Zr(H)Cl$, (II) is formed and precipitates immediately from tetrahydrofuran. The same product is obtained in a purer state when $LiAl(OBu^t)_3H$ (1 mol.) is used instead of $LiAlH_4$. Like the dihydride (I), (II) is remarkably insoluble and involatile and is undoubtedly polymeric.

When a further quantity of $LiAlH_4$ (1 mol.) in solution is added to a suspension of (II) in tetrahydrofuran, a clear solution is obtained. After removal of LiCl with benzene a new hydride, $(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$, (III) slowly deposits from solution in benzene–tetrahydrofuran.

From $(\pi\text{-}C_5H_5)_2Zr(Cl)Me$, the hydride $(\pi\text{-}C_5H_5)_2Zr(H)Me$, (IV) can be obtained using either $LiAlH_4$ or $LiAl(OBu^t)_3H$. All of these compounds have broad bands in the i.r. greatly displaced from the region normally associated with metal hydrides (*ca.* 2000 cm.$^{-1}$). The broadness of the bands together with their displacement seems to indicate bridging hydrogen.[1,3] That these bands are due to hydrides was shown by preparing the corresponding deuterides from $LiAlD_4$. The i.r. frequencies of both hydrides and deuterides are shown in the Table.

TABLE

I.r. frequencies of hydrides and deuterides

Compound	Frequency (cm.$^{-1}$, KBr disc) Zr–H	Zr–D
$(\pi\text{-}C_5H_5)_2ZrH_2$, (I)	1520, 1300	1100, 960
$(\pi\text{-}C_5H_5)_2Zr(H)Cl$, (II)	1390	1020[a]
$(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$, (III)	1425 (1790, 1700 [AlH_4])	1055 (1310, 1260 [AlD_4])
$(\pi\text{-}C_5H_5)_2Ar(H)Me$, (IV)	1500, 1310	1090, 965

[a] Overlapping with C–H deform. of $(\pi\text{-}C_5H_5)$.

All of the hydrides were characterized by analysis, i.r. and by quantitative hydrolysis with 50% aqueous H_2SO_4. Hydrogen evolved was pumped into a calibrated volume by means of a Töpler pump and accurately measured. Attempts to detect the resonance of the hydridic proton of (II), the most soluble hydride, in the ^1H n.m.r. spectrum in tetrahydrofuran have not yet been successful. Other authors have found the same difficulty with bridging hydrides.[1,3]

(*Received, July* 25*th*, 1969; *Com.* 1140.)

[1] B. D. James, R. K. Nanda, and M. G. H. Wallbridge, *Inorg. Chem.*, 1967, **6**, 1979.
[2] A. F. Reid, J. S. Shannon, J. M. Swan, and P. C. Wailes, *Austral. J. Chem.*, 1965, **18**, 173.
[3] G. E. Coates and P. D. Roberts, *J. Chem. Soc.* (*A*), 1969, 1008.

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HYDRIDO COMPLEXES OF ZIRCONIUM
I. PREPARATION

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(Received April 13th, 1970)

SUMMARY

Syntheses of $(\pi\text{-}C_5H_5)_2ZrH_2$ and of the new zirconium hydrides $(\pi\text{-}C_5H_5)_2Zr(H)Cl$, $(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$, $(\pi\text{-}C_5H_5)_2Zr(H)CH_3$ and $[(\pi\text{-}C_5H_5)_2ZrH]_2O$. $(\pi\text{-}C_5H_5)_2ZrH_2$ are described. Deuterides corresponding to all of the above hydrides have been prepared. In all of the compounds hydrido ligands bridge between neighbouring zirconium atoms so that the compounds are associated and relatively insoluble.

INTRODUCTION

The relatively recent realization of the importance of hydrido complexes of the transition metals in certain catalytic processes has helped to draw attention to this type of compound containing hydrogen as a ligand. Many transition metals form hydrido derivatives[1,2] but amongst the Group IVA elements, only three hydrides have been characterized. $(\pi\text{-}C_5H_5)_2ZrH_2$ and $(\pi\text{-}C_5H_5)_2Zr(H)BH_4$ were prepared by the action of trialkylamines on the bis(tetrahydroborate)[3], $(\pi\text{-}C_5H_5)_2Zr(BH_4)_2$, while more recently the violet, unstable $[(\pi\text{-}C_5H_5)_2TiH]_2$ has been isolated[4].

A more direct approach to the synthesis of zirconium hydrides was found while investigating the action of certain aluminium hydrides on cyclopentadienylzirconium halides. In this paper a new synthesis of $(\pi\text{-}C_5H_5)_2ZrH_2$ and of four new zirconium hydrides is described*. These hydrides show unusual reactivity towards multiply bonded compounds which will be described in later papers.

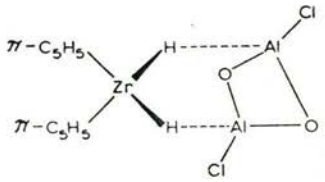
RESULTS AND DISCUSSION

The oxo-bridged compound $(\pi\text{-}C_5H_5)_2Zr(Cl)OZr(Cl)(\pi\text{-}C_5H_5)_2$[6,7] when treated with an equimolar amount of $LiAlH_4$ in tetrahydrofuran, was slowly converted to the insoluble dihydride $(\pi\text{-}C_5H_5)_2ZrH_2$, (I).

$$[(\pi\text{-}C_5H_5)_2ZrCl]_2O + LiAlH_4 \rightarrow \underset{\text{(I)}}{2(\pi\text{-}C_5H_5)_2ZrH_2} + LiCl + "[AlOCl]"_2$$

* A preliminary account of part of this work has been published[5].

The nature of the aluminium compound remaining in solution is not clear. Despite the negligible solubility of the product (I), the yield never exceeds 66% so that a by-product must be some soluble complex of zirconium and aluminium. The red colour of the reaction solution lends support to the presence of [AlOCl] since this type of compound is known to form red colours in donor solvents[8]. All of the zirconium hydrides described in this paper dissolve on adding an excess of $LiAlH_4$, so that it appears likely that soluble adducts between zirconium hydrides and aluminium compounds are readily formed and can exist in donor solvents such as tetrahydrofuran. A structure of type (II) is possible for the adduct but others in which the H, O and Cl are interchanged must also be considered. The PMR spectrum showed a broad band in the cyclopentadienyl region centred at δ 6.23 ppm. The IR spectrum of (I) is vir-



(II)

tually identical with that published by James, Nanda and Wallbridge[3]. The sharp band at 1520 and a broad strong band at 1300 cm^{-1} are associated with hydrido ligands bridging between two zirconium atoms. The extreme insolubility of this compound indicates that the bridging hydrogens form a polymeric network, the extent of which is not yet know.

The same dihydride (I) was obtained in lower yield when four moles of LiAl-(O-t-Bu)$_3$H[9] were used to reduce the oxo-bridged zirconium compound. With only two moles of LiAl(O-t-Bu)$_3$H an insoluble complex of formula $[(\pi\text{-}C_5H_5)_2ZrH]_2O \cdot (\pi\text{-}C_5H_5)_2ZrH_2$ (III), was precipitated. All of the hydridic protons of (III) could be quantitatively hydrolysed with acid, while with CH_2Cl_2 the adduct was converted to $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ and $(\pi\text{-}C_5H_5)_2ZrCl_2$, the hydridic hydrogens forming CH_3Cl with the solvent. All of these products were identified by their characteristic PMR spectra.

The IR spectrum of (III) shows three bands due to bridging hydrido groups; a very broad band centred at 1510, and sharper bands at 1385 and 1240 cm^{-1}. All of these are shifted to lower wavelengths on deuteration (Table 1).

TABLE 1

IR FREQUENCIES[a] OF HYDRIDES AND DEUTERIDES

Compound	Zr–H	Zr–D
$(\pi\text{-}C_5H_5)_2ZrH_2$ (I)	1520, 1300 (br)	1100, 960 (br)
$[(\pi\text{-}C_5H_5)_2ZrH]_2O \cdot (\pi\text{-}C_5H_5)_2ZrH_2$ (III)	1510 (br), 1385, 1240	1075 (br), 1025, 905
$(\pi\text{-}C_5H_5)_2Zr(H)Cl$ (IV)	1390 (br)	1020[b] (br)
$(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$ (V)	1425 (br)	1055 (br)
	[1790, 1700 (AlH_4)]	[1310, 1260 (AlD_4)]
$(\pi\text{-}C_5H_5)_2Zr(H)CH_3$ (VI)	1500, 1310 (br)	1090, 965 (br)

[a] Frequencies in cm^{-1}, KBr disc. [b] Overlapping with the C–H deform. of $(\pi\text{-}C_5H_5)$.

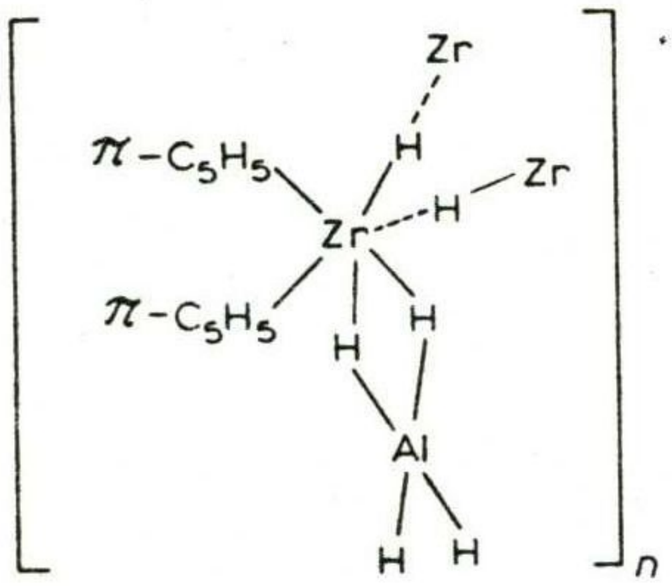
From $(\pi\text{-}C_5H_5)_2ZrCl_2$ and exactly one-quarter mole of $LiAlH_4$ or one mole of $LiAl(O\text{-}t\text{-}Bu)_3H$, the hydridochloride $(\pi\text{-}C_5H_5)_2Zr(H)Cl$ (IV) was obtained in high yield as a white solid insoluble in tetrahydrofuran. The IR spectrum of (IV) shows only one broad band in the bridging hydride region (at 1390 cm^{-1}), although its insolubility indicates a polymeric structure similar to that existing in the dihydride (I).

An interesting alternative preparation of (IV) is by magnesium metal reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$. The reaction will proceed only in tetrahydrofuran, presumably by abstraction of hydrogen from this solvent. The solution becomes deep red in colour and the hydride (IV) precipitates in about 30% yield. It is identical in every respect with the product obtained from the aluminium hydride reaction.

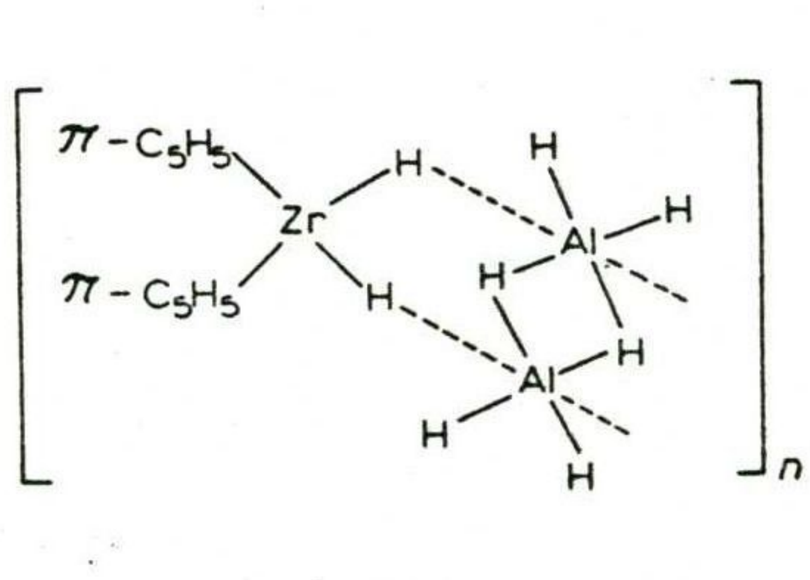
When a further quantity of $LiAlH_4$ (1 mole) was added to a suspension of $(\pi\text{-}C_5H_5)_2Zr(H)Cl$ in tetrahydrofuran a clear solution resulted. After removal of lithium chloride by addition of benzene, a new hydride, $(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$ (V), slowly precipitated from the benzene/tetrahydrofuran solution. This compound shows, in addition to the absorption band in the IR spectrum at 1425 cm^{-1} due to the bridging hydride, two more bands at 1790 and 1700 cm^{-1} due to AlH_4.

The solubility of (V) is rather greater than that of the other hydrido derivatives, but nevertheless attempts to obtain a PMR spectrum were not successful. It is to be expected that rapid exchange of all of the hydridic protons can occur[3], and this apparently destroys any resolution in the PMR spectrum. None of the other hydrides were soluble enough for PMR spectral measurements.

The aluminium complex (V) has little similarity to the boron compound of similar formula[3]. $(\pi\text{-}C_5H_5)_2Zr(H)BH_4$ is thermally stable and can be sublimed at 60° under reduced pressure; its IR spectrum does not show the band around 1400 cm^{-1} associated with bridging hydride, and the BH_4 group is believed to be bonded to zirconium by a double hydrogen bridge[3,10]. $(\pi\text{-}C_5H_5)_2Zr(H)AlH_4$ (V) on the other hand is thermally unstable and begins to decompose in solvents at 60° (see below); its IR spectrum shows a broad strong band at 1425 cm^{-1} indicating Zr–H–Zr, so that it is to some extent polymerized and therefore involatile. Although it is more convenient to regard this compound as an oligomer of the unit (Va) shown below, the possibility exists that (V) is an adduct of a zirconium hydride with an aluminium hydride, *e.g.* as in (Vb):



(Va)



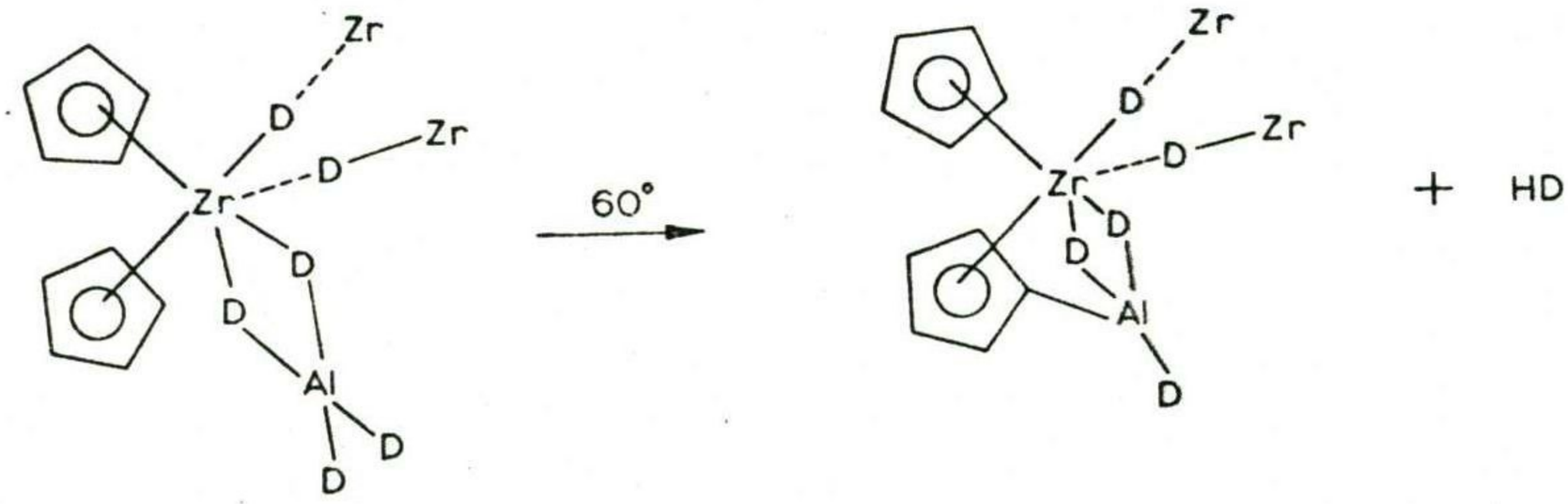
(Vb)

Dicyclopentadienylmethylzirconium chloride, $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$, prepared by the action of trimethylaluminium on $(\pi\text{-}C_5H_5)_2Zr(Cl)OZr(Cl)(\pi\text{-}C_5H_5)_2$[11], can also be converted to a hydrido compound, $(\pi\text{-}C_5H_5)_2Zr(H)CH_3$ (VI), by the action of

$LiAlH_4$ or $LiAl(O\text{-}t\text{-}Bu)_3H$. The IR spectrum of (VI) is more closely related to that of the dihydride (I) than to the other hydride spectra, since it shows broad strong bands at 1500 and 1310 cm^{-1} (Table 1).

All of the compounds described may be prepared as deuterides by using $LiAlD_4$ or $LiAl(O\text{-}t\text{-}Bu)_3D$ as reducing agents. The shapes and intensities of the IR bands are almost identical in both hydride and deuteride, but the bands due to bridging hydride are shifted to lower wavennumbers by a factor between 1/1.35 and 1/1.38 in each case on deuteration. Frequencies are shown in Table 1.

All of the hydrides are sensitive to heat and to light, turning purple or red in colour. Except for (V), this colour change is not accompanied by any loss of hydrogen or change in the IR spectrum, but pyrolysis of the aluminohydride derivative (V), which begins in a solvent at 60°, liberates one mole of hydrogen giving a deep red diamagnetic product. The band due to Zr–H–Zr is still evident in the spectrum at 1380 cm^{-1}, indicating that this part of the molecule is unchanged. If the deuterated compound $(\pi\text{-}C_5H_5)_2Zr(D)AlD_4$, is pyrolyzed in the solid state then the gas evolved is HD (identified by mass spectrometry), so that the cyclopentadienyl rings are participating and are propably bonding to the aluminium atoms; *e.g.*:



In common with many other metal hydrides, the zirconium derivatives react with chlorinated solvents, exothermally in the case of chloroform and slowly with methylene dichloride, replacing the hydrido ligand by chloride. By-products are CH_2Cl_2 (in chloroform) and CH_3Cl (in methylene dichloride), so that quantitative measurement of the PMR spectrum of the products of this reaction is a useful technique for the analysis of hydrides.

EXPERIMENTAL

General

All hydrides were assumed to be sensitive to air and were handled under argon using a Schlenk tube system, or in a nitrogen-filled glovebox. Products were analysed by ashing to ZrO_2 and by hydrolysis of a weighed sample in a vacuum line with 50% H_2SO_4, gas evolved (H_2 or D_2) being pumped into a calibrated volume by means of a Töpler pump, where it was accurately measured. Hydrolysis proved to be a better and faster indication of purity than any other analytical technique.

Materials

Standardized solutions of $LiAlH_4$ were prepared by stirring $LiAlH_4$ in purified tetrahydrofuran for some hours, filtering under argon through Celite (previously baked out at 140° and degassed by evacuation) followed by hydrolysis of an aliquot

of this solution with dilute acid on the vacuum line and accurate measurement of the hydrogen evolved. When stored under argon these standardized solutions remained unchanged for several weeks. Solutions of $LiAlD_4$ (from Merck, Sharp and Dohme Isotopic Products, Montreal) were prepared in the same way. $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ was prepared by the following adaptation of the original published method[6,7], which gives consistently high yields.

Preparation

Aniline (10 ml) and water (1.3 ml) were added to a solution of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (30 g) in methylene dichloride (250 ml) and the mixture was shaken thoroughly. A white precipitate of aniline hydrochloride formed immediately. After chilling overnight in the refrigerator, the suspension was filtered cold. At times large crystals of the product are present at this stage, which must be redissolved by addition of more CH_2Cl_2. The filtrate was evaporated to small volume and petrol (100 ml, b.p. 30–40°) was added to precipitate the product. Filtration and petrol washing gave white crystals of the oxo-bridged compound (26.5 g, 97% yield). The m.p. varies greatly with the rate of heating but if the sample in an evacuated capillary is placed in a melting point apparatus preheated to 260°, m.p's around 305° should be obtained.

Preparation of hydrides

$(\pi\text{-}C_5H_5)_2ZrH_2$ (*I*)

A clear solution of $LiAlH_4$ in tetrahydrofuran (20 ml of 1.7 molar, 34 mmoles) was added dropwise to a solution of $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ (17.7 g, 33.4 mmoles) in tetrahydrofuran (200 ml). A white precipitate slowly appeated but precipitation was not complete for several hours. The mixture was set aside overnight and then filtered giving the dihydride as an almost white micro-crystalline solid (10.1 g, 66% yield). [Found: ash (ZrO_2), 55.5; hydrolyzable H, 1.99 g-atom/mole. $C_{10}H_{12}Zr$ calcd.: ash (ZrO_2), 55.14%; hydrolyzable H, 2.00 g-atom/mole.]

$[(\pi\text{-}C_5H_5)_2ZrH]_2O \cdot (\pi\text{-}C_5H_5)_2ZrH_2]$

A solution of $LiAl(O\text{-}t\text{-}Bu)_3H$ (9.35 g, 36 mmoles) in tetrahydrofuran (50 ml) was added to $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ (9.72 g, 18 mmoles) in tetrahydrofuran (120 ml). The solution darkened appreciably and a precipitate appeared on stirring overnight. It was collected by filtration and washed with tetrahydrofuran, then pumped dry to give the pale pink complex $[(\pi\text{-}C_5H_5)_2ZrH]_2O \cdot (\pi\text{-}C_5H_5)_2ZrH_2$ (III) (2.0 g, 25% yield). [Found: C, 52.7; H, 5.0; ash (ZrO_2), 53.6; hydrolyzable H, 4.04 g-atom/mole. $C_{30}H_{34}OZr_3$ calcd.: C, 52.71; H, 5.01; ash (ZrO_2) 54.08%; hydrolyzable H, 4.00 g-atom/mole.] In CH_2Cl_2 the complex slowly dissolved; the PMR spectrum of the solution showed proton peaks due to $(\pi\text{-}C_5H_5)_2ZrCl_2$ (δ 6.41 ppm), $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ (δ 6.24 ppm) and CH_3Cl (δ 2.96 ppm) in the ratio 10/20/9 [some CH_3Cl lost due to low b.p. (−24°)].

$(\pi\text{-}C_5H_5)_2Zr(H)Cl$ (*IV*)

(*a*). $LiAl(O\text{-}t\text{-}Bu)_3H$ (28.6 g, 113 mmoles) in tetrahydrofuran (100 ml) was added slowly to a solution of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (32.9 g, 113 mmoles) in tetrahydrofuran (500 ml) with stirring. After addition was complete stirring was continued for approx. 1 h after which the product was collected by filtration and washed with tetrahydrofuran. The hydridochloride was obtained as a white solid (26.3 g, 90% yield) turning pink in light. [Found: Cl, 13.4; ash (ZrO_2), 47.0; hydrolyzable H, 1.02 g-atom/

mole. $C_{10}H_{11}ClZr$ calcd.: Cl, 13.75; ash (ZrO_2), 47.77%; hydrolyzable H, 1.00 g-atom/mole.]

(*b*). (π-$C_5H_5)_2ZrCl_2$ (17.5 g, 60 mmoles) in tetrahydrofuran (90 ml) was stirred with Grignard magnesium (0.72 g, 30 mmoles) for several days. The colour turned reddish-brown almost immediately and gradually deepened in intensity. After 3–5 days the precipitate present was collected by filtration, washed twice with tetrahydrofuran and pumped dry giving a pale pink solid (4.5 g, 30% yield) identical in every respect with the hydridochloride obtained as in (a) above. [Found: Cl, 13.3; ash (ZrO_2), 47.5; hydrolyzable H, 1.03 g-atom/mole. $C_{10}H_{11}ClZr$ calcd.: Cl, 13.75; ash (ZrO_2), 47.77%; hydrolyzable H, 1.00 g-atom/mole.]

(π-$C_5H_5)_2Zr(H)AlH_4$ (*IV*)

To a suspension of (π-$C_5H_5)_2Zr(H)Cl$ (2.05 g, 8 mmoles) in tetrahydrofuran (15 ml) was added a clear solution of $LiAlH_4$ in tetrahydrofuran (4.6 ml of 1.72 molar, 8 mmoles) with stirring. The solid dissolved to give a clear mauve-coloured solution to which was added benzene (15 ml). After 1 h precipitated LiCl was removed by filtration and another 10 ml of benzene was added to the filtrate. On chilling the aluminohydride crystallized slowly and was later collected by filtration as a white solid (0.65 g, 30% yield), very sensitive to light, heat and air. [Found: ash ($ZrO_2+\frac{1}{2}Al_2O_3$), 67.5, 69.7; hydrolyzable H, 5.01 g-atom/mole $C_{10}H_{15}AlZr$ calcd.: ash ($ZrO_2+\frac{1}{2}Al_2O_3$), 68.8%; hydrolyzable H, 5.00 g-atom/mole.]

(π-$C_5H_5)_2Zr(H)CH_3$) (*V*)

To a solution of (π-$C_5H_5)_2Zr(Cl)CH_3$ (1.3 g, 4.8 mmoles) in tetrahydrofuran (15 ml) was added dropwise a clear solution of $LiAlH_4$ in tetrahydrofuran (0.60 ml of 2.0 molar, 1.2 mmoles). The white precipitate which appeared immediately was collected after 1 h stirring and was washed with tetrahydrofuran. The hydridomethyl derivative (0.46 g, 41% yield) so obtained was also sensitive to light and hydrolyzed readily in acid giving hydrogen and methane (identified by gas IR). [Found: ash (ZrO_2), 52.6; gas on hydrolysis (H_2+CH_4), 1.98 mole/mole. $C_{11}H_{14}Zr$ calcd.: (ZrO_2), 52.0%; gas on hydrolysis (H_2+CH_4), 2.00 mole/mole.]

Deuterides

Deuterides corresponding to all of the above hydrides were prepared and characterized in exactly the same manner as above, using $LiAlD_4$ or $LiAl(O\text{-}t\text{-}Bu)_3D$ instead of $LiAlH_4$. In all cases yields were somewhat lower than with the corresponding hydride.

ACKNOWLEDGEMENT

The authors are indebted to Dr. A. J. C. Nicholson for the identification of HD by mass spectrometry.

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HYDRIDO COMPLEXES OF ZIRCONIUM
II. REACTIONS OF DICYCLOPENTADIENYLZIRCONIUM DIHYDRIDE WITH CARBOXYLIC ACIDS

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SUMMARY

Reaction between $(\pi\text{-}C_5H_5)_2ZrH_2$ and carboxylic acids can result in the formation of acylates or alkoxides depending on the mode of addition. With the carboxylic acid in excess acylates are formed; for example $\pi\text{-}C_5H_5Zr(OCOCH_3)_3$ with acetic acid and $(\pi\text{-}C_5H_5)_2Zr(OCOCF_3)_2$ with trifluoroacetic acid. When $(\pi\text{-}C_5H_5)_2ZrH_2$ is in excess, reduction of the acids occurs and leads to novel bridging alkoxides.

INTRODUCTION

The unique reactivity which many metal hydrides display towards compounds containing double or triple bonds or acidic protons is now well documented[1], but as yet the reactivity of the cyclopentadienylzirconium hydrides towards reagents of this type has not been explored. These hydrides, which are readily prepared by the methods described in the preceding paper[2], have been found to undergo reactions with a wide range of compounds, which will be described in this and subsequent papers.

RESULTS AND DISCUSSION

In reactions with carboxylic acids the dihydride, $(\pi\text{-}C_5H_5)_2ZrH_2$, was expected to give simple acylates with elimination of hydrogen, but under certain conditions the reactions took a different course.

In an attempt to prepare the diacetate, $(\pi\text{-}C_5H_5)_2Zr(OCOCH_3)_2$, by adding acetic acid to $(\pi\text{-}C_5H_5)_2ZrH_2$ in tetrahydrofuran, it was found that the amount of hydrogen evolved was always less than that required by eqn. (1):

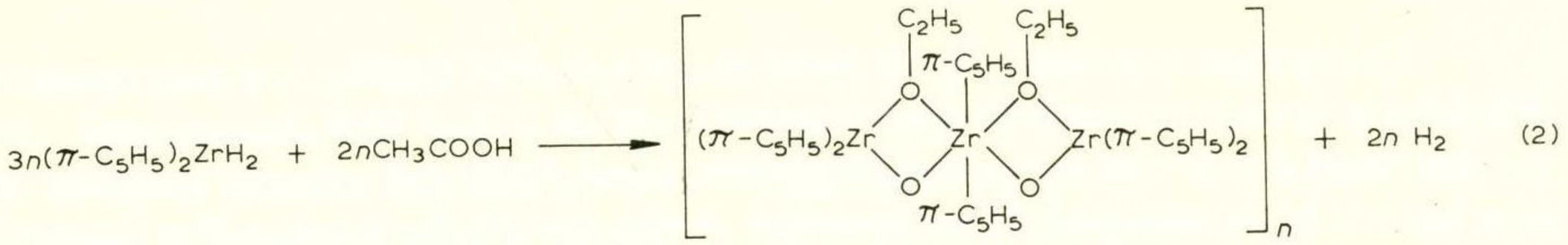
$$(\pi\text{-}C_5H_5)_2ZrH_2 + 2\ HOCOCH_3 \rightarrow (\pi\text{-}C_5H_5)_2Zr(OCOCH_3)_2 + 2\ H_2 \qquad (1)$$

Since the white product was a mixture, it was apparent that some reduction was taking place. By slow addition of $(\pi\text{-}C_5H_5)_2ZrH_2$ to a large excess of acetic acid, this reduction was eliminated and the expected amount of hydrogen was evolved, but the triacetate, $\pi\text{-}C_5H_5Zr(OCOCH_3)_3$ (II), was obtained instead of the diacetate. Removal of a cyclopentadienyl group by acetic acid was observed also by Brainina and Freid-

lina[3], who obtained (II) by heating $(\pi\text{-}C_5H_5)_2ZrCl_2$ in acetic acid at 105° for 9 h.

The IR spectrum of (II) showed three main bands in the carbonyl region, the two of highest frequency being split giving peaks at 1515, 1505, 1465, 1445 and 1395 cm^{-1}. It is apparent that acetate ligands in several different environments are present. Since the largest separation between what are presumably antisymmetric and symmetric COO^- stretching frequencies is only of the order of 120 cm^{-1}, it is probable that all of the acetate groups are symmetrically bonded, either bridging or bidentate[4]. The presence of bridging groups was suggested also by the molecular weight values which indicated some association in benzene (see Experimental). The OCO deformations of $\pi\text{-}C_5H_5Zr(OCOCH_3)_3$ were evident as strong bands at 695 and 698 cm^{-1}.

Slow addition of acetic acid to a suspension of $(\pi\text{-}C_5H_5)_2ZrH_2$ in tetrahydrofuran caused evolution of one mole of hydrogen per mole of acetic acid. The reaction was complete after addition of two moles of acetic acid per three moles of dihydride; the latter dissolved and evolution of hydrogen ceased. The product contained no hydridic protons and instead of acetate bands in the IR spectrum a strong band due to alkoxide was evident at 1135 cm^{-1}. The presence and relative abundance of ethoxy as well as cyclopentadienyl groups was established from the PMR spectrum. The protons of the cyclopentadienyl ligands gave rise to several bands in the region δ 6.08 ppm*, and the ethoxy group was observed as a quartet and triplet centred at δ 3.97 and δ 1.17 ppm, respectively. The molecular weight of the compound in boiling benzene, although varying with concentration, indicated that it contained at least three zirconium atoms. On the basis of this data the compound was formulated as the ethoxy- and oxo-bridged derivative (III), formed as in eqn. (2):



(III)

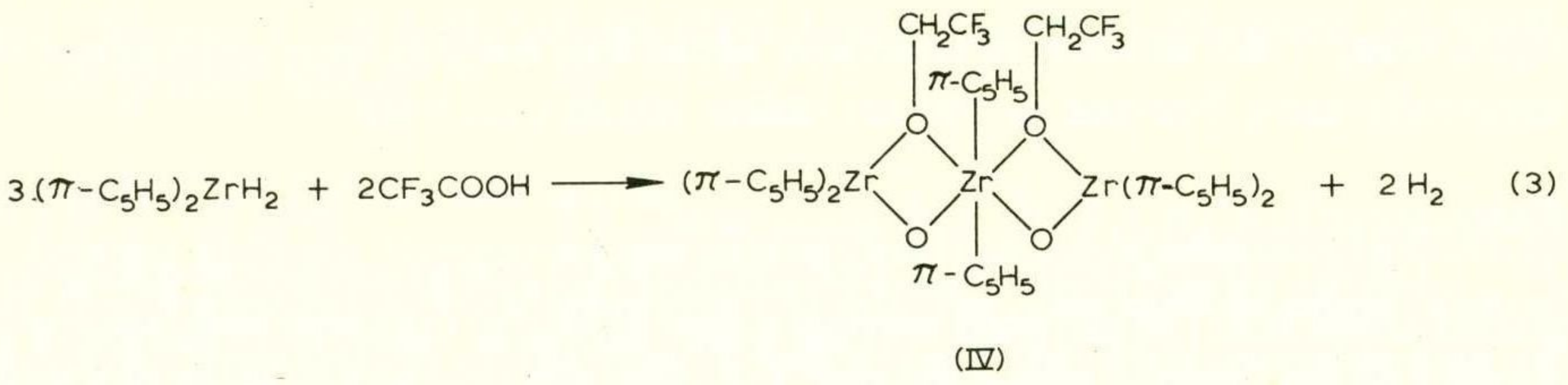
With $(\pi\text{-}C_5H_5)_2ZrD_2$ the corresponding compound containing $-CD_2CH_3$ groups was obtained. The PMR spectrum of the alkoxy group now showed only a single peak for the CH_3 at δ 1.15 ppm.

The presence of the oxygen bridges between the zirconium atoms, formed by abstraction of oxygen from the carboxyl groups during reduction, was suggested by the strong absorption band in the IR spectrum at 735 cm^{-1}. It was confirmed by treatment of (III) with a deficiency of dry gaseous HCl whereby a mixture of $(\pi\text{-}C_5H_5)_2ZrCl_2$ and $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ was obtained. Since the latter compound is converted to the former by excess HCl, its presence is confirmation of the oxygen bridge in compound (III).

With trifluoroacetic acid the corresponding fluoro-compound (IV) was obtained according to eqn. (3):

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* The multiplicity of bands in the cyclopentadienyl region of the PMR spectrum could be due, not only to the different environments of these ligands in the complex, but also to steric effects of the ethoxy groups.



(IV)

Compound (IV) is monomeric in boiling benzene. Its PMR spectrum showed only a very broad band centred at δ 5.83 ppm. The presence of the trifluoroethoxy group was confirmed by the strong absorption in the IR spectrum at 1090 cm^{-1} and a weak band at 2825 cm^{-1} due to CH_2. The Zr–O–Zr band at 730 cm^{-1} was also evident.

Reverse addition of $(\pi\text{-}C_5H_5)_2ZrH_2$ to excess trifluoroacetic acid led to the bis(trifluoroacetate), $(\pi\text{-}C_5H_5)_2Zr(OCOCF_3)_2$ (V), which was also monomeric and sublimed above 150° at 10^{-3} mm. The carbonyl region of its IR spectrum showed bands at 1725, 1620 and 1400 cm^{-1} as well as a weaker absorption at 1500 cm^{-1} which undoubtedly indicate the presence of both unidentate and bidentate coordinated trifluoroacetate[4]. This difference in reactivity between acetic and trifluoroacetic acids was noted by Brainina and Freidlina[3], who obtained similar acylates under more drastic conditions.

Benzoic acid also was reduced by the dihydride (I) with the formation of a compound similar to (III) and (IV) containing oxy and benzoxy bridges showing bands in the infrared at 735 and 1105 cm^{-1} respectively. The molecular weight of this product was too high to be measured ebulliometrically.

It would seem that a carbon atom carrying a slight residual positive charge is susceptible to attack by $(\pi\text{-}C_5H_5)_2ZrH_2$. With acetone no hydrogen was evolved and the product was the monomeric diisopropoxide (VI), formed as in eqn. (4):

$$(\pi\text{-}C_5H_5)_2ZrH_2 + 2\,(CH_3)_2CO \rightarrow (\pi\text{-}C_5H_5)_2Zr[OCH(CH_3)_2]_2 \qquad (4)$$

(VI)

The PMR spectrum of the diisopropoxide (VI) showed a singlet due to the cyclopentadienyl protons at δ 6.01 ppm together with a doublet from the methyl groups at δ 1.08 and 1.17 ppm and a C–H multiplet centred at δ 4.11 ppm.

When the preparation of (VI) from the dihydride (I) and excess isopropanol was attempted, both cyclopentadienyl groups were split off and zirconium tetraisopropoxide resulted.

EXPERIMENTAL

General

All compounds were handled in a nitrogen-filled glove-box and all reactions were carried out under argon. Zirconium was determined by ashing sulphated pellets of each compound to ZrO_2. Carbon and hydrogen analyses were performed by the Australian Microanalytical Service, C.S.I.R.O. and University of Melbourne, on pelleted samples. Difficulty was experienced in obtaining satisfactory duplicate values. even on the same sample. PMR spectra were run on a Varian A-60 instrument in

C_6D_6 using TMS as internal reference. Molecular weights were determined ebulliometrically using benzene as solvent unless stated otherwise.

Reactions of $(\pi\text{-}C_5H_5)_2ZrH_2$ *with acetic acid*

(*a*). $\pi\text{-}C_5H_5Zr(OCOCH_3)_3$. $(\pi\text{-}C_5H_5)_2ZrH_2$ (2.26 g) was added slowly to excess glacial acetic acid (16 ml) with stirring under argon. A vigorous evolution of gas occurred and the solution became warm. The clear solution was pumped to dryness, the residue was dissolved in benzene and light petroleum (50 ml, b.p. 60–80°) was then added. White crystalline $\pi\text{-}C_5H_5Zr(OCOCH_3)_3$ (1.35 g, 40% yield) precipitated and was washed with petrol and pumped dry. The PMR spectrum showed two sharp peaks at δ 6.26 (C_5H_5) and δ 1.73 (CH_3) ppm in the intensity ratio 5/9.

Found: C, 39.9; H, 4.6; ash (ZrO_2), 37.8; mol.wt., 420 reducing to 320 after 1 h boiling; ebulliometric in THF 370. $C_{11}H_{14}O_6Zr$ calcd.: C, 39.62; H, 4.23; ash (ZrO_2), 36.95%; mol.wt., 333.]

(*b*). *Preparation of compound* (*III*). A standardized solution of acetic acid in tetrahydrofuran (6.10×10^{-3} *M*) was added slowly to a suspension of $(\pi\text{-}C_5H_5)_2ZrH_2$ (2.20 g) in THF (100 ml) until the hydride dissolved and gas evolution ceased (after 28.5 ml, *i.e.* acid/hydride = 2/3; gas evolved = 2 moles). The solution was filtered under argon, pumped to dryness and the residue was washed with a little petrol (solubility was quite high) giving a white crystalline product. The PMR spectrum showed a complex of peaks centred at δ 6.08 ppm (C_5H_5), and a quartet (δ 3.97 ppm, *J* 6.8 Hz) and triplet (δ 1.17 ppm, *J* 6.8 Hz) due to ethoxy, the ratio of the integrated intensities being 30/4/6.

Found: C, 50.1; H, 5.0; ash (ZrO_2), 46.9, 47.0; mol.wt., 765–1280 with increasing concentration. $C_{30}H_{40}O_4Zr_3$ calcd.: C, 51.90; H, 5.13; ash (ZrO_2), 47.0%; mol.wt., 786.] From $(\pi\text{-}C_5H_5)_2ZrD_2$ a corresponding compound was obtained, the PMR spectrum of which showed a multiplet at δ 6.08 ppm (C_5H_5) and a broad singlet due to CH_3 of the CH_3CD_2 groups at δ 1.15 ppm, in the ratio 30/6.

Reactions of $(\pi\text{-}C_5H_5)_2ZrH_2$ *with trifluoroacetic acid*

(*a*). $(\pi\text{-}C_5H_5)_2Zr(OCOCF_3)_2$. $(\pi\text{-}C_5H_5)_2ZrH_2$ (1.09 g) was added to excess trifluoroacetic acid (10 g) in tetrahydrofuran (70 ml) and worked up as in (*a*) of the preceding experiment, giving $(\pi\text{-}C_5H_5)_2Zr(OCOCF_3)_2$. [Found: C, 39.1; H, 2.6; ash (ZrO_2), 28.0; mol.wt., 472. $C_{14}H_{10}F_6O_4Zr$ calcd.: C, 37.55; H, 2.25; ash (ZrO_2), 27.54%; mol.wt., 447.]

(*b*). *Preparation of compound* (*IV*). As in (*b*) of the preceding experiment, a standardized solution of CF_3COOH in tetrahydrofuran (0.1756 *M*) was titrated into a suspension of $(\pi\text{-}C_5H_5)_2ZrH_2$ (1.78 g) in tetrahydrofuran (70 ml). 31.5 ml was added before a clear solution was obtained, corresponding to the ratio acid/hydride = 2/3. The clear solution was worked up as before giving (IV) as a cream-coloured solid. [Found: C, 44.6; H, 4.0; ash (ZrO_2), 40.1; mol.wt., 933. $C_{34}H_{34}F_6O_4Zr_3$ calcd.: C, 45.66; H, 3.83; ash (ZrO_2), 41.34%; mol.wt., 894.]

Reaction of $(\pi\text{-}C_5H_5)_2ZrH_2$ *with benzoic acid*

A solution of benzoic acid in tetrahydrofuran (0.251 *M*) was titrated into a suspension of $(\pi\text{-}C_5H_5)_2ZrH_2$ (1.22 g) in tetrahydrofuran (70 ml). As for the other acids the ratio acid/hydride = 2/3. The mol. wt. of the white product was too high to be de-

termined. [Found: C, 55.7; H, 5.0; ash (ZrO_2), 41.1. $C_{44}H_{44}O_4Zr_3$ calcd.: C, 58.03; H, 4.9; ash (ZrO_2), 40.61%.]

Reaction of $(\pi\text{-}C_5H_5)_2ZrH_2$ *with acetone*

Acetone (0.75 ml, 10 mmoles) was added slowly to a suspension of $(\pi\text{-}C_5H_5)_2ZrH_2$ (1.12 g, 5 mmoles) in tetrahydrofuran (70 ml). The dihydride dissolved without gas evolution. Evaporation of the clear solution gave the white isopropoxide, $(\pi\text{-}C_5H_5)_2Zr(O\text{-}i\text{-}Pr)_2$, which sublimed around $150°/10^{-3}$ mm but was never obtained completely pure. The PMR spectrum showed peaks at δ 6.01 ppm (C_5H_5), a multiplet centred at δ 4.11 ppm (J 5.8 Hz) and a doublet centred at δ 1.13 ppm (J 6.0 Hz) with integrated intensities in the ratio 5/1/6. [Found: C, 54.8; H, 6.9; ash (ZrO_2), 37.6; mol. wt., 393. $C_{16}H_{24}O_2Zr$ calcd.: C, 56.56; H, 7.12; ash (ZrO_2), 36.27%; mol. wt., 340.]

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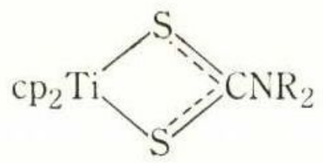
DITHIOCARBAMATES OF TITANIUM(III)

By R. S. P. Coutts,* P. C. Wailes,* and J. V. Kingston†

[Manuscript received October 29, 1969]

Summary

Several *N*,*N*-dialkyldithiocarbamates of bis(cyclopentadienyl)titanium(III) have been prepared from cp_2TiCl (cp = π-cyclopentadienyl) and sodium dialkyldithiocarbamates under inert atmosphere. The bright green air-sensitive compounds are paramagnetic with one unpaired electron per titanium atom. Their formulation as monomeric, symmetrical bidentate chelate complexes



has been established from spectral, magnetic, and molecular weight data.

Introduction

Although the literature on metal dithiocarbamates is extensive, there are very few such complexes of the early transition metals. As early as 1934 Dermer and Fernelius prepared the titanium(IV) dithiocarbamates, $Ti[-SC(S)NR_2]_4$ (R = n-C_4H_9 and $C_6H_5CH_2$) from titanium tetrachloride and the dithiocarbamic acids.[1] Thirty years later, Bradley prepared several titanium(IV) complexes of the same type by insertion of CS_2 into $Ti(NR_2)_4$,[2] but dithiocarbamates of titanium(III) were unknown before the work now reported.‡

In 1958, Chatt pointed out[4] that those transition metals to the left of the periodic table (type A) form their most stable complexes with nitrogen-, oxygen-, and fluorine-containing ligands, while type B show a greater affinity for phosphorus, sulphur, and chlorine. Although titanium is an early transition metal, its designation as type A is in doubt since it has been shown to form stable complexes with all six types of ligands. Complexes with many different types of sulphur-containing ligands

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‡ A preliminary account of this work has already been published.[3]

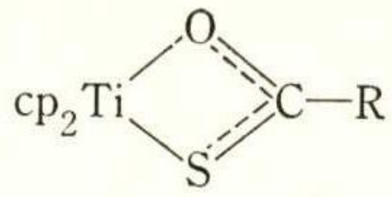
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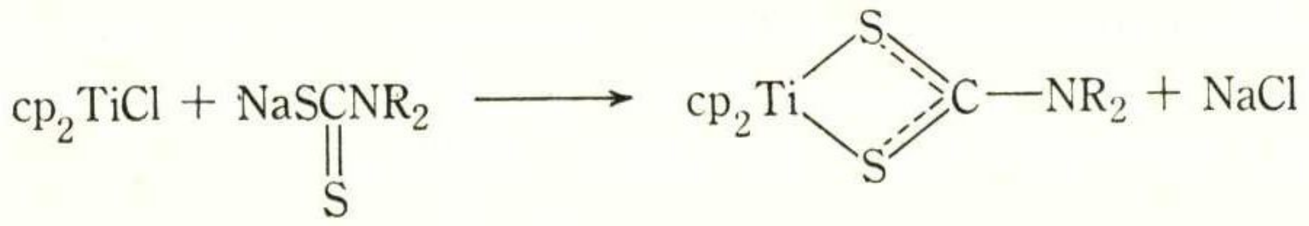
in particular are known, e.g. cp_2TiS_x (where $x = 2$, 3, 4,[5] and 5[6]), $cp_2Ti(SH)_2$,[7] $cp_2Ti(SR)_2$,[8–10] $cp_2Ti(Cl)SR$,[8] and[11]



but no organotitanium(III) compounds with two sulphurs attached were known. Accordingly, the dialkyldithiocarbamates of cp_2Ti^{III} were prepared to examine the stability of such complexes with variation in oxidation state.

Results and Discussion

The dialkyldithiocarbamates were obtained as deep green solids by addition of cp_2TiCl[12] in air-free water to sodium dialkyldithiocarbamates in the same solvent:



(1)

As the chain length R increases the melting point drops until at R = n-C_5H_{11} the complex is an oil. At room temperature, the parent compound (1; R = H) was not appreciably soluble in organic solvents, probably because of association by hydrogen bonding. As a result, it was not possible to determine the molecular weight of the parent, but solubility increased with chain length and ebulliometric measurements on the higher homologues showed that all are monomeric. Four members of the series, R = CH_3, C_2H_5, n-C_5H_{11}; $R_2 = -(CH_2)_5-$, could be purified by sublimation under vacuum but the remaining members could not be sublimed because of decomposition (see Table 1).

In the infrared some of the absorption bands due to the dithiocarbamato ligand are masked by cyclopentadienyl absorption bands, but several assignments are possible. The "thioureide" band (C–N) near 1500 cm^{-1} is very characteristic of dithiocarbamates. The frequency of this band lies between that for C–N (1250–1350 cm^{-1}) and C=N (1640–1690 cm^{-1}), which suggests that this bond has some double bond character, the amount of which increases up to R = C_2H_5 and then remains fairly constant (see Table 2).

In a comparison of the spectra of metal dithiocarbamates with ester-type derivatives, Bonati and Ugo[13] showed that the spectra were almost identical, except

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in the region 980 ± 70 cm^{-1}, where only one intense band was found in the metal derivatives and two in the esters.[14] One of the two bands was therefore assigned to uncomplexed C=S. This assignment was supported by the recent infrared study of the stretching frequencies of many organic compounds[15] and by recent work on

TABLE 1

PHYSICAL AND ANALYTICAL DATA

Compound	Colour	M.P. (°C)	Subl. Temp. (°C, 10^{-3}mm)	Analyses (%)[a]	Ti	C	H	N	Mol. Wt.[b]
(1; R = H)	pale green	165 (dec.)	dec.	Found:	17·9	49·9	4·7	4·9	—
				Calc.:	17·7	48·9	4·5	5·2	270
(1; R = CH_3)	blue green	194–196	140	Found:	16·1	52·3	5·4	4·8	310
				Calc.:	16·1	52·4	5·4	4·7	298
(1; R = C_2H_5)	deep green	117–118	120	Found:	14·7	54·3	6·3	4·3	317
				Calc.:	14·7	55·2	6·2	4·3	326
(1; R = n-C_3H_7)	deep green	56–58	100	Found:	13·3	56·4	7·0	4·4	335
				Calc.:	13·5	57·6	6·8	4·0	354
(1; R = n-C_4H_9)	deep green	43–44	dec.	Found:[c]	12·5	—	—	—	365
				Calc.:	12·5	59·7	7·4	3·7	382
(1; R = n-C_5H_{11})	deep green	oil	dec.	Found:	11·9	59·6	7·9	—	—
				Calc.:	11·7	61·4	7·9	3·3	410
(1; R_2 = –$(CH_2)_5$–)	deep green	160 (dec.)	180	Found:	14·1	56·8	6·1	4·1	332
				Calc.:	14·2	56·8	6·0	4·1	338

[a] See Experimental.
[b] Ebulliometric in tetrahydrofuran.
[c] Could not be pelleted satisfactorily due to low m.p. and waxy nature.

TABLE 2

SPECTRAL DATA (cm^{-1})

Infrared spectra in KBr disk; visible spectra in tetrahydrofuran

Compound	I.R. Bands ν(CN)[a]	ν(CNC)	ν(CS)	Visible Spectra (ϵ)		
(1; R = H)	1390	—	860	—	16000 (110)	13330 (60)
(1; R = CH_3)	1500	1135	975	21740 (140)	16340 (82)	13330 (43)
(1; R = C_2H_5)	1480	1140	990	21550 (176)	16310 (79)	13330 (43)
(1; R = n-C_3H_7)	1475	1140	980	21510 (158)	16450 (76)	13330 (41)
(1; R = n-C_4H_9)	1480	1140	980	21410 (179)	16390 (87)	13330 (47)
(1; R = n-C_5H_{11})	1475	1140	985	21410 (188)	16530 (94)	13330 (51)
(1; R_2 = –$(CH_2)_5$–)	1480	1135	985	21370 (140)	16420 (78)	13330 (43)

$Ru(NO)(S_2CNEt_2)_3$. The spectrum of this dithiocarbamate has one extra infrared band in the 970–980 cm^{-1} region and an X-ray structure study has shown that one unchelated dithiocarbamato group is present.[16]

In the dithiocarbamatotitanium compounds (1) only one band is present in the C–S region, at 860 cm^{-1} for the parent derivative (1; R = H), and at 980 ± 5 cm^{-1} for

[14] Chatt, J., Duncanson, L. A., and Venanzi, L. M., *Suom. Kemi.*, 1956, 75.
[15] Jensen, K. A., and Nielson, P. H. *Acta chem. scand.*, 1966, **20**, 597.
[16] Domenicano, A., Vaciago, A., Zambouelli, L., Loader, P. L., and Venanzi, L. M., *Chem. Commun.*, 1966, 476.

all others (Table 2). It is assumed from this evidence that the C–S bonds are most likely equivalent. The strong band around 1140 cm^{-1} is assigned to C–N–C; the frequencies for the various homologues are set out in Table 2.

The infrared bands associated with the cyclopentadienyl rings are consistently found at 3100 (C–H stretch), 1445 (C–C stretch), 1010 (C–H in-plane bending), and 790 cm^{-1} (C–H out-of-plane bending).

TABLE 3

MAGNETIC PROPERTIES

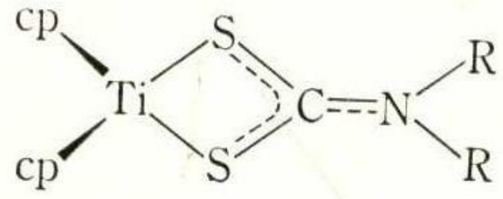
χ'_M, ligand corrections, and T.I.P. in CGS units; μ_{eff} in B.M.

T (°K)	$10^6\chi'_M$	μ_{eff}
$cp_2TiS_2CNH_2$		
319	1140	1·71
286·5	1241	1·69
263	1393	1·72
233	1534	1·70
205·5	1724	1·69
177·5	1971	1·68
146	2331	1·66
116	2896	1·65
109·5	3115	1·66
78	4282	1·64
ligand corr. 138×10^{-6}; θ −12°; T.I.P. 140×10^{-6}; μ_{eff} (corr.) 1·62		
$cp_2TiS_2CN(CH_3)_2$		
328	1101	1·71
291	1223	1·69
292	1209	1·69
265	1375	1·71
204·5	1783	1·72
172	2041	1·68
111	3101	1·67
109	3211	1·68
ligand corr. 162×10^{-6}; θ −6°; T.I.P. 80×10^{-6}; μ_{eff} (corr.) 1·65		
$cp_2TiS_2CN(C_2H_5)_2$		
322	1192	1·76
291	1308	1·74
263	1468	1·76
233	1653	1·76
204	1884	1·76
165	2257	1·73
112	3218	1·70
90	3833	1·67
ligand corr. 185×10^{-6}; θ −12°; T.I.P. 100×10^{-6}; μ_{eff} (corr.) 1·69		
$cp_2TiS_2CN(C_3H_7)_2$		
320·5	1102	1·69
293	1221	1·70
263	1352	1·69
233	1548	1·71
204·5	1782	1·71
172	2066	1·69
150	2383	1·70
131	2474	1·62
111	2889	1·61
104·5	3128	1·62
92·5	3473	1·61
ligand corr. 219×10^{-6}; θ −20°; T.I.P. 100×10^{-6}; μ_{eff} (corr.) 1·62		
$cp_2TiS_2CN(C_4H_9)$		
292	993	1·53
273	1036	1·51
238	1130	1·47
227	1218	1·49
192	1425	1·49
165	1636	1·48
113	2439	1·51
105	2543	1·47
ligand corr. 253×10^{-6}; θ −5°; T.I.P. 80×10^{-6}; μ_{eff} (corr.) 1·45 (low μ_{eff} values are due to waxy nature of compound which prevented even packing)		
$cp_2TiS_2CN(CH_2)_5$		
319	1246	1·79
291	1348	1·78
292·5	1371	1·80
265	1491	1·79
233	1699	1·79
204·5	1898	1·79
177·5	2196	1·77
150	2613	1·78
105	3263	1·66
ligand corr. 210×10^{-6}; θ −8°; T.I.P. 100×10^{-6}; μ_{eff} (corr.) 1·71		

In the visible region the positions of the bands and their optical densities are remarkably consistent. Their frequencies, their optical density values, and the fact that they disappear when oxygen is introduced, all support their assignment as *d–d* transitions.

The magnetic susceptibilities of the complexes were measured over the temperature range 80–320°K. With decreasing temperature, a decrease in the uncorrected magnetic moment was evident but on applying a correction for temperature-indepen-

dent paramagnetism (T.I.P.), a Curie–Weiss law was followed, the moment being substantially independent of temperature. The Weiss constant values are small ($\theta < 20°$) and in fact have little effect on the room temperature moments (Table 3). The dithiocarbamates are therefore magnetically dilute with no interaction between titanium atoms. The magnetic and spectral properties, together with molecular weight values and their solubility in non-polar solvents all support the symmetrical, bidentate structure:



The dithiocarbamates are therefore in the same class as the carboxylates,[17] thiocarboxylates,[11] and sulphate[18] in which the chelating group forms a four-membered ring with the trivalent titanium.

Experimental

General

Manipulations of air-sensitive materials were carried out in a nitrogen-filled glove-box or in vacuum, and all reactions were effected in a stream of purified argon using a Schlenk tube system.[19] Melting points were determined in evacuated capillaries and are uncorrected. Infrared spectra were run in KBr disks protected by pure KBr pressed on either side of the sample, on a Perkin–Elmer 521 spectrophotometer. Visible spectra were measured in tetrahydrofuran solution on a Beckman DK2 spectrophotometer. Magnetic susceptibilities were determined by the Gouy method and molecular weight values were obtained in a Gallenkamp ebulliometer modified to take a 3·5-ml cell.

Analyses

Titanium was estimated by ashing a sulphated pellet of the sample. Carbon, hydrogen, and nitrogen were determined by the Australian Microanalytical Service by burning weighed pellets sealed in aluminium capsules.

Materials

cp_2TiCl was prepared from titanium trichloride and magnesium cyclopentadienide in tetrahydrofuran.[12] The sodium dialkyldithiocarbamates, NaS_2CNR_2, were prepared by shaking together equimolar amounts of the appropriate secondary amine, aqueous sodium hydroxide solution, and excess of carbon disulphide, keeping the temperature below 10° during addition of CS_2. The solutions were reduced to dryness and the resulting salts were recrystallized from an ethanol–ether mixture. The parent dithiocarbamate (R = H) was prepared as an ammonium salt by bubbling ammonia into a solution of CS_2 in ethanol.

Preparation of Titanium Dithiocarbamates

cp_2TiCl (2·1 g, 10 mmole) was weighed into a 100-ml Schlenk flask in the glove-box, then dissolved in air-free water (40 ml). A tube with a sintered-glass filter was attached and in a stream of argon the blue solution was filtered into a solution of the sodium salt of the dithiocarbamate (10 mmole). The dithiocarbamatotitanium derivative which precipitated immediately

[17] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1967, **20**, 1579.
[18] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 1181.
[19] Herzog, S., and Dehnert, J., *Z. Chemie, Lpz.*, 1964, **4**, 1.

was filtered by reversing the flow of argon and pushing the supernatant liquid back into the first flask. The precipitate was washed with air-free water from a hypodermic syringe, then pumped dry and sublimed if necessary.

Physical properties and analytical data are given in Table 1.

Acknowledgment

The authors would like to thank the Stauffer Chemical Co. for a gift of $TiCl_3$.

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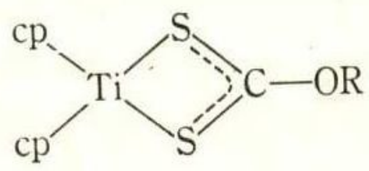
XANTHATES OF TITANIUM(III)

By R. S. P. Coutts,* P. C. Wailes,* and J. V. Kingston†

[Manuscript received October 29, 1969]

Summary

The first xanthates of titanium have been prepared from cp_2TiCl (cp = π-cyclopentadienyl) and NaS_2COR (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, and n-C_5H_{11}) in air-free water under inert atmosphere. The trivalent titanium complexes are blue in colour, monomeric, and extremely sensitive to oxygen, with one unpaired electron per titanium atom. They are believed to be of the form



with bidentate xanthato ligands, analogous to the corresponding dithiocarbamates.

Introduction

The apparent anomaly of titanium, an early transition metal, forming numerous stable complexes with sulphur-containing ligands has been discussed in the preceding paper[1] and will not be elaborated on here. No xanthates of titanium in any valence form have been prepared and reported in the literature since the first unsuccessful attempt by Grossman in 1906.[2] In view of the ability of the $(cp_2Ti^{III})^+$ cation to form the stable four-coordinate dithiocarbamato complexes described in the preceding paper, its reactions with various xanthates were investigated.

Results and Discussion

The usual method for preparing sodium xanthates from sodium hydroxide, an alcohol, and carbon disulphide was found to be unsatisfactory owing to the presence of undesirable by-products such as sulphide, sulphate, sulphite, thiosulphate, and trithiocarbonate,[3,4] all of which interfered in the subsequent reaction. Accordingly, all xanthates were prepared under argon from sodium, the alcohol, and carbon disulphide by the method described in the Experimental section. Under these

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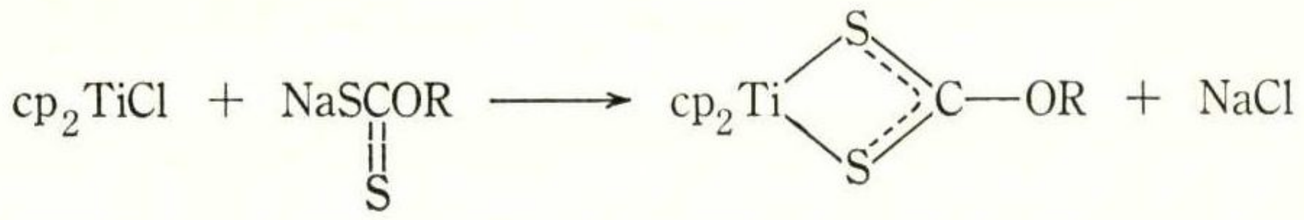
[1] Coutts, R. S. P., Wailes, P. C., and Kingston, J. V., *Aust. J. Chem.*, 1970, **23**, 463.

[2] Grossman, A., *Öst. ChemZtg*, 1906, **30**, 907.

[3] Hirschkind, W., (to Great Western Electrochemical Co.), U.S. Pat. 2,024,923 (1935).

[4] Danilov, S. N., Grad, N. M., and Geine, E. I., *Zh. obshch. Khim.*, 1949, **19**, 826.

conditions, high-purity sodium xanthates were obtained. When air-free aqueous solutions of the sodium xanthate and of cp_2TiCl were mixed the blue titanium xanthates precipitated immediately.



(1)

These complexes are among the most sensitive to oxygen of any handled in these Laboratories and extreme care was necessary to preserve them in the three-valent state. Exposure to traces of oxygen caused an immediate colour change to orange-yellow and loss of paramagnetism. The nature of the malodorous oxidation products is apparently complex since some loss of ligand occurred, and was not investigated further.

Derivatives of the parent xanthic acid (1; R = H) are not known, so that the first member of the series is the methyl derivative. All are insoluble in water but very soluble in most organic solvents. With increase in chain length up to butyl, the melting point drops in much the same way as most aliphatic derivatives. Although less stable thermally than the corresponding dithiocarbamates, the xanthates (with the exception of the propyl) could all be purified by sublimation, although with some decomposition. Despite several attempts the propyl derivative could not be sublimed before decomposition was complete.

Determination of molecular weights in tetrahydrofuran under argon showed that all are monomeric (Table 1). The variation of magnetic susceptibility with temperature showed no evidence of spin–spin interaction between titanium atoms. As with the dithiocarbamates, there is some lowering of the moment with temperature, but this effect is virtually removed when a correction for temperature-independent paramagnetism (T.I.P.) is applied. The Curie–Weiss law is followed, the moment being independent of temperature and close to the spin-only value for a d' system (Table 2).

Assignment of structure to metal xanthates from infrared data is not always reliable. All xanthates have four characteristic bands[5] which in the titanium(III) compounds under discussion occur around 1250, 1100, 1020, and 550 cm^{-1}. The exact assignment of these bands has been the subject of some controversy but it seems clear that they are mixed bands, due to C=S, C–S, C–O, and R–O, which are highly coupled and sensitive to environmental changes.

A normal coordinate analysis of nickel(II) ethyl xanthate by Agarwala *et al.*[6] indicates that the 1250 cm^{-1} band has about 90% contribution from C–O–R stretch and 10% from C=S stretch. The band at 1100 cm^{-1} is mainly a combination of C–O, R–O, and C=S stretching modes. The band at 1020 cm^{-1} has a single major contribution of 60% from C=S stretch and the highly coupled band around 550 cm^{-1} obtains 95% of its total from C–O, C=S, and C–S stretch.

[5] Watt, G. W., and McCormick, B. J., *Spectrochim. Acta*, 1965, **21**, 753.
[6] Agarwala, U., Lakshmi, and Rao, P. B., *Inorg. chim. Acta*, 1968, **2**, 337.

TABLE 1

PHYSICAL AND ANALYTICAL DATA

Compound	Colour	M.P. (°C)	Subl. Temp. (°C, 10^{-3} mm)	Analyses (%)[a]	Ti	C	H	Mol. Wt.[b]
(1; R = CH_3)	light blue	135–136	130	Found:	17·0	50·3	4·4	292
				Calc.:	16·8	50·5	4·6	285
(1; R = C_2H_5)	bright blue	127–128	120	Found:	16·2	52·7	5·4	297
				Calc.:	16·0	52·2	5·1	299
(1; R = n-C_3H_7)[c]	bright blue	108–110	dec.	Found:	15·1	50·0	5·4	321
				Calc.:	15·3	53·7	5·5	313
(1; R = n-C_4H_9)	dark blue	60–65 (dec.)	60	Found:	14·8	53·9	6·3	331
				Calc.:	14·6	55·1	5·9	327
(1; R = n-C_5H_{11})	dark blue	101–103	100	Found:	13·9	56·3	6·4	339
				Calc.:	14·0	56·3	6·2	341

[a] See Experimental.

[b] Ebulliometric in tetrahydrofuran.

[c] This compound could not be purified by sublimation.

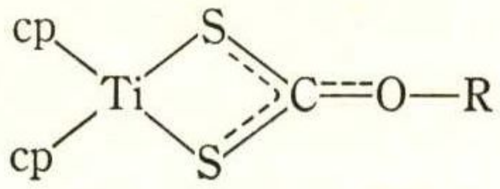
TABLE 2

MAGNETIC PROPERTIES

χ'_m, ligand correction, and T.I.P. in CGS units; μ_{eff} in B.M.

T (°K)	$10^6\chi'_m$	μ_{eff}
$cp_2TiS_2COCH_3$		
289	1150	1·74
262	1293	1·75
234	1463	1·75
207	1683	1·75
172	1961	1·71
142	2343	1·69
112	2965	1·68
100	3285	1·64
ligand corr. 154×10^{-6}; θ −18°; T.I.P. 200×10^{-6}; μ_{eff} (corr.) 1·62		
$cp_2TiS_2COC_2H_5$		
290	1148	1·64
256	1308	1·66
227	1455	1·63
196	1639	1·61
165	1908	1·59
136	2285	1·59
107	2876	1·57
ligand corr. 166×10^{-6}; θ −16°; T.I.P. 140×10^{-6}; μ_{eff} (corr.) 1·54		
$cp_2TiS_2COC_3H_7$		
288	1097	1·60
256	1227	1·59
238	1388	1·63
210	1561	1·63
175	1802	1·60
152	2192	1·64
113	2635	1·55
105	3060	1·61
ligand corr. 188×10^{-6}; θ −8°; T.I.P. 0, μ_{eff} (corr.) 1·61		
$cp_2TiS_2COC_4H_9$		
291	1294	1·74
263	1413	1·73
235	1594	1·74
204	1803	1·72
172	2092	1·70
142	2489	1·69
112	3100	1·67
105	3289	1·67
ligand corr. 200×10^{-6}; θ −16°; T.I.P. 160×10^{-6}; μ_{eff} (corr.) 1·64		
$cp_2TiS_2COC_5H_{11}$		
288	1333	1·76
264	1467	1·77
235	1639	1·76
204	1855	1·75
174	2129	1·73
145	2527	1·72
113	3124	1·69
107	3384	1·71
ligand corr. 212×10^{-6}; θ −18°; T.I.P. 200×10^{-6}; μ_{eff} (corr.) 1·64		

In these circumstances, infrared spectra are of little help in determining whether the xanthato ligands are mono- or bi-dentate. Both molecular weight and magnetic data indicate isolated titanium atoms in monomeric complexes, so that bridging xanthato groups can be excluded. By analogy with the dithiocarbamates described in the preceding paper,[1] and in view of the known tendency of titanium in all cp_2Ti^{III} compounds to adopt a coordination number of at least four, the bidentate structure below is proposed for these complexes:



The degree of symmetry of the four-membered ring cannot be determined from the evidence available, but it is expected that the bond order of C---O will be less than that of C=N in the dithiocarbamates, due to the lower electron-releasing character of OR groups compared with NR_2.[5,7,8]

TABLE 3

SPECTRAL DATA (cm^{-1})

Compound	Infrared[a]				Visible Spectra (ϵ)[b]		
(1; R = CH_3)	1210	1120	1040	470	18520 (126)	16390 (82)	14290 (55)
(1; R = C_2H_5)	1205	1115	1040	445	18590 (111)	16530 (74)	14290 (47)
(1; R = C_3H_7)	1205	1120	1045	475	18540 (115)	16530 (77)	14290 (49)
(1; R = C_4H_9)	1205	1125	1050	490	18520 (132)	16530 (86)	14290 (53)
(1; R = C_5H_{11})	1205	1120	1040	495	18590 (128)	16610 (85)	14290 (52)

[a] See text for assignments. [b] In tetrahydrofuran solution.

The visible spectrum of each of the xanthates in tetrahydrofuran solution shows three bands at the frequencies shown in Table 3. These frequencies span a narrower range than those of the dithiocarbamates although the central band is almost identical in frequency and intensity in both types of complex. On exposure to dry oxygen, all three bands of the xanthates disappear so that all must be due to *d–d* transitions.

The xanthates and dithiocarbamates can be added to the growing list of complexes of bis(cyclopentadienyl)titanium with sulphur-containing ligands. On this basis, titanium cannot be classified as either type A or type B metal (for explanation of these terms see[1]) since it possesses the characteristics of both.

EXPERIMENTAL

All of the general remarks from the preceding paper apply here.

Materials

cp_2TiCl was prepared from titanium trichloride and magnesium cyclopentadienide in tetrahydrofuran.[9] Sodium xanthates NaS_2COR (R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, n-C_5H_{11})

[7] Huseby, S., *Acta chem. scand.*, 1967, **21**, 42.
[8] Chatt, J., Duncanson, L. A., and Venanzi, L. M., *Suom. Kemi.*, 1956, 75.
[9] Reid, A. F., and Wailes, P. C., *Aust. J. Chem.*, 1965, **18**, 9.

were prepared by dissolving sodium metal in the anhydrous alcohol under argon and adding excess CS_2 to the resultant solution cooled to 10°. After several hours at room temperature, the solvent was removed under vacuum and the pale yellow residue was used without further purification.

Preparation of Titanium Xanthates

The method of preparation from cp_2TiCl (2·1 g, 10 mmole) and the appropriate sodium xanthate (10 mmole) in air-free water under argon was the same as described in the preceding paper[1] for the dithiocarbamates.

Physical properties and analytical data are given in Table 1.

Acknowledgment

The authors would like to thank the Stauffer Chemical Company for a gift of titanium(III) chloride.

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THE REACTIONS OF DICYCLOPENTADIENYLTITANIUM WITH ALUMINIUM ALKYLS

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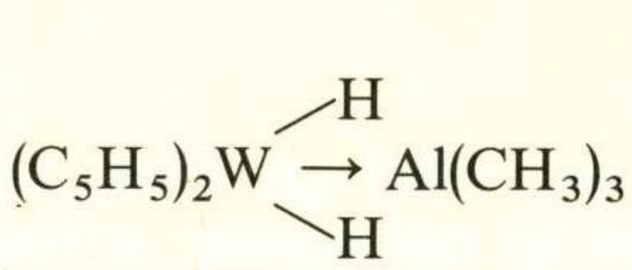
(Received May 11th, 1970)

SUMMARY

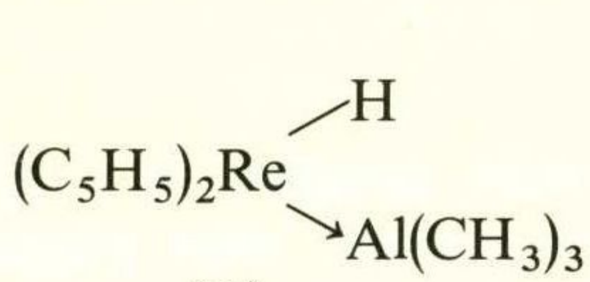
When dicyclopentadienyltitanium (titanocene) is warmed with triethylaluminium, ethane is eliminated and a red diamagnetic complex is obtained. It is believed to be identical with the compound $[C_5H_5TiC_5H_4Al(C_2H_5)_2]_2$ isolated by Natta and co-workers from the reaction between $(C_5H_5)_2TiCl$ and $Al_2(C_2H_5)_6$. The corresponding methyl derivative has also been isolated.

INTRODUCTION

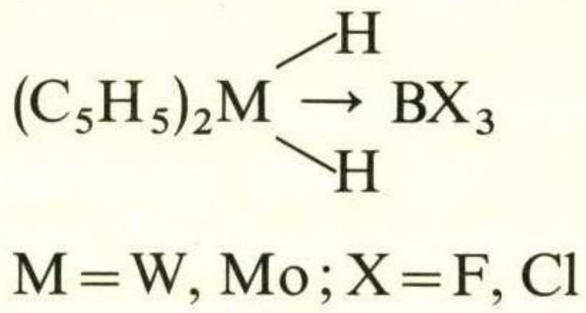
Certain dicyclopentadienylmetal compounds with non-bonding electrons have been shown to form donor–acceptor complexes with electron-deficient compounds. Examples of such complexes are (I)[1], (II)[1] and (III)[2] in which transition metal derivatives form donor bonds with compounds of Group III elements.



(I)



(II)



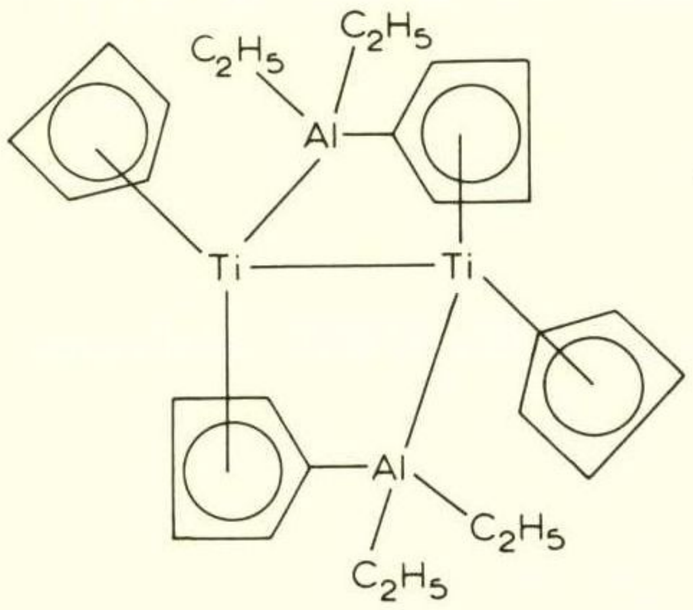
M = W, Mo; X = F, Cl

(III)

RESULTS AND DISCUSSION

In exploring the possible donor properties of dicyclopentadienyltitanium (titanocene), its reactions with aluminium alkyls were examined. Instead of donor–acceptor compounds being obtained, an alkane was eliminated and crimson coloured diamagnetic complexes were isolated. On the basis of analyses, molecular weight determination and hydrolysis experiments, the product from triethylaluminium and dicyclopentadienyltitanium fits closely a formula like $[(C_5H_5)_2TiAl(C_2H_5)_2]_2$. In all of its physical properties this compound appears to be identical with that isolated by Natta and co-workers[3] from the reaction between $(\pi\text{-}C_5H_5)_2TiCl$ and $Al_2(C_2H_5)_6$. An X-ray crystal structure determination of Natta's compound by Corradini and Sirigu[4] confirmed structure (IV), in which the aluminium atoms are bonded to ti-

tanium and also to one of the cyclopentadienyl ligands on the neighbouring titanium atom.



(IV)

The ethane obtained in the reaction now described is no doubt evolved when the Al–C_5H_4 bond is formed. It is interesting to note that this begins at room temperature. The formula of the complex should be amended therefore to $[C_5H_5TiC_5H_4Al(C_2H_5)_2]_2$.

From dicyclopentadienyltitanium and trimethylaluminium a similar diamagnetic complex was isolated after evolution of methane. This compound is red-brown in colour, dimeric in benzene and somewhat less soluble than the corresponding ethyl derivative. It is assumed to be the methyl analogue of (IV).

The corresponding reactions with dicyclopentadienylzirconium (zirconocene) were not so well defined. With triethyl- or -trimethylaluminium and dicyclopentadienylzirconium in both cases a mixture of a red and a green product was obtained, together with the corresponding alkane. The red compounds were found to be approximately trimeric in boiling benzene whereas the green derivatives were too insoluble for molecular weight determinations.

EXPERIMENTAL

General remarks

All solid materials were handled in a nitrogen-filled glovebox. Dicyclopentadienyltitanium[4] and -zirconium[6] were prepared by the method of Watt and collaborators. Aluminium alkyls were used without purification and were syringed into the reaction tube under purified argon. All solvents were purified by distillation under nitrogen from $LiAlH_4$. M.p.'s were determined in evacuated capillaries and are uncorrected. Molecular weights were measured ebulliometrically in benzene. Hydrolysis of the products to give a quantitative yield of alkane was carried out with methanol followed by acid, to avoid the formation of hydrogen and alkenes.[7]

Dicyclopentadienyltitanium with triethylaluminium

Triethylaluminium (3.0 ml, 20 mmole) was added to a suspension of dicyclopentadienyltitanium (3.6 g, 20 mmole) in toluene (8 ml) contained in a reaction tube topped by a Fischer and Porter threaded valve. A purple colour developed almost immediately. The valve was sealed with the Teflon stem and the tube was then heated to 70° for several days. The course of the reaction was followed by measuring periodically the gas evolved by pumping it into a calibrated volume on a vacuum line using

a Töpler pump. At 70° the reaction was 50% complete after 1 day; at 100° the reaction was complete in 20 h. Gas evolved (432 ml at N.T.P., 19.4 mmole) was condensable and showed an IR spectrum identical with that of ethane. After removal of solvent from the tube the residue was continuously extracted with benzene under argon for 1–2 h, giving a purple-red product in near-quantitative yield, m.p. 172–173°. Natta *et al.*[3] found m.p. 169–170°. [Found: ash ($TiO_2 + 0.5Al_2O_3$), 50.1; ethane (by hydrol.), 40.6 mmole); mol.wt., 496. $C_{28}H_{38}Al_2Ti_2$ calcd.: ash, 49.9%; ethane (by hydrol.), 40.0 mmole; mol.wt., 524.] The compound is essentially diamagnetic, having a T.I.P. of 150–250 cgs units between room temperature and 85° K.

Dicyclopentadienyltitanium with trimethylaluminium

From $(C_5H_5)_2Ti$ (20 mmole) and $Al_2(C_2H_5)_6$ (20 mmole) heated in toluene as above, a red-brown product was obtained, m.p. >320°, with evolution of methane (20 mmole). (Found: ash, 55.5; mol.wt., 481. $C_{24}H_{30}Al_2Ti_2$ calcd.: ash, 55.85%; mol.wt., 468.)

The compound is diamagnetic, with a T.I.P. of 70–80 cgs units between room temperature and 85° K.

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AZIDO DERIVATIVES OF BIS(CYCLOPENTADIENYL)ZIRCONIUM AND BIS(CYCLOPENTADIENYL)TITANIUM

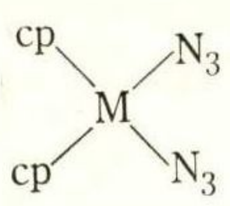
By R. S. P. Coutts* and P. C. Wailes*

[Manuscript received November 17, 1970]

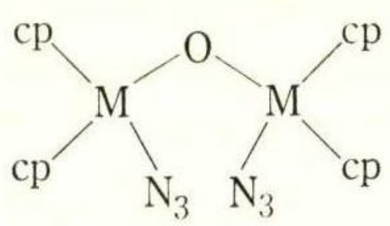
The preparation of the bis-azido derivatives $cp_2Ti(N_3)_2$ and $cp_2Zr(N_3)_2$ (cp = π-cyclopentadienyl) has been claimed by Thayer.[1,2] The compounds were apparently formed by the action of HN_3 on the corresponding dichlorides in a chloroform–water mixture. Details of these preparations have not been published, although an alternative synthesis of $cp_2Ti(N_3)_2$ from the dichloride and NaN_3 in boiling acetone was published by Langford and Aplington[3] in 1965. In our experience the use of aqueous systems in the preparation of pseudohalogen derivatives of titanium(IV) and zirconium(IV) generally leads to bridged oxide species.[4] Although the presence of excess HN_3 may prevent the formation of these oxides, it was considered desirable to reinvestigate the preparation of these compounds, and also the preparation of the corresponding titanium(III) derivative, cp_2TiN_3.

Titanium(IV) *and Zirconium*(IV)

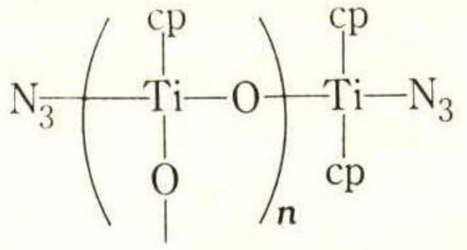
When aqueous solutions of sodium azide and cp_2TiCl_2 were mixed, a yellow-orange solid precipitated, but the p.m.r. spectrum clearly showed this to be a mixture of products. Separation by extraction with diethyl ether gave the diazide (1; M = Ti) (70%) as an orange-coloured crystalline solid, and left a yellow residue consisting



(1)



(2)



(3)

mostly of the oxygen-bridged derivative (2; M = Ti) together with a small amount of a more insoluble polymeric material. This is probably (3), analogous to the polymer obtained from the corresponding chloride.[5] In air the oxide (2) was slowly converted into the polymer (3). As a result (2) was never obtained completely pure.

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[1] Thayer, J. S., personal communication.
[2] Thayer, J. S., *Organomet. Chem. Rev.*, 1966, **1**, 157.
[3] Langford, C. H., and Aplington, J. P., *J. organomet. Chem.*, 1965, **4**, 271.
[4] Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1966, **19**, 2069.
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From cp_2ZrCl_2 and NaN_3 in water a quantitative yield of the oxygen-bridged compound (2; M = Zr) was obtained. Anhydrous conditions were required before the diazide could be prepared. Thus from dry tetrahydrofuran containing a trace of $AlCl_3$ (1; M = Zr) was isolated as a pale yellow crystalline solid. In the same way the pure titanium diazide (1; M = Ti) could be prepared.

The thermal stability of the diazides of both titanium and zirconium was found to be surprisingly high; in fact both could be sublimed under vacuum at the temperatures shown in Table 1. Even the oxygen-bridged zirconium azide was volatile at 250° although the corresponding titanium compound decomposed. In boiling tetrahydrofuran both diazides were monomeric. They were moderately stable in air but hydrolysed slowly in the presence of moisture giving oxygen-bridged species.

TABLE 1

PHYSICAL PROPERTIES OF AZIDES

Compound	Colour	M.P. (°C)	T_S[a] (°C)	N.M.R. (δ) $CDCl_3$	N.M.R. (δ) THF	Infrared Data (cm^{-1}, KBr disk) N_3	Infrared Data (cm^{-1}, KBr disk) Cyclopentadiene
$cp_2Ti(N_3)_2$	orange	145–146	200	6·31	6·51	2070, 2040, 1332	3075, 1425, 1080, 835
$(cp_2TiN_3)_2O$	deep yellow	300 (dec.)	—	6·16	6·35	2060, 1325	3100, 1420, 1010, 1005 824, 814[b]
$cp_2Zr(N_3)_2$	pale yellow	123	140	6·35	6·53	2075, 1350	3050, 1420, 1080, 810
$(cp_2ZrN_3)_2O$	colourless	268 (dec.)	250	—	6·41	2070, 1338, 1328	3040, 1420, 1070, 810[c]

[a] Sublimation temperature at 10^{-3} mm. [b] TiOTi band at 720 cm^{-1}. [c] ZrOZr band at 735 cm^{-1}.

In their mass spectra both $cp_2Ti(N_3)_2$ and $cp_2Zr(N_3)_2$ showed molecular ions and successive loss of N_3, cp, and N_2, with some disruption of the C_5H_5 rings to give fragments such as C_3H_3, C_2H_2, and C_2H. The most intense peaks of each spectrum corresponded to $cp_2Ti^+N_3$ or $cp_2Zr^+N_3$.

In the mass spectra of the oxygen-bridged compounds (2), all of the intense peaks contained both metal atoms bridged by oxygen, which is good indication of the strength of this bridge. Here again, successive loss of N_3, N_2, and cp was evident, the most intense peak in the case of the zirconium derivative being M^+—cp. This behaviour is analogous to that of the corresponding chloro compound $(cp_2ZrCl)_2O$.[6]

The infrared spectra of organometallic azides have been discussed by Thayer.[2] The two strongest bands, the asymmetric and symmetric NNN stretch, occur around 2000 and 1300 cm^{-1} respectively. The frequencies of these bands in the titanium and zirconium azides are shown in Table 1 together with the main bands due to the cyclopentadienyl ligands.

Titanium(III)

In previous attempts in these Laboratories[7] to prepare the titanium(III) azide cp_2TiN_3 from cp_2TiCl and NaN_3, air-free water was used as solvent. The initially formed product was red-brown, but this decomposed immediately liberating nitrogen and giving insoluble yellow products. Extensive hydrolysis of both azido and cyclopentadienyl ligands occurred since the yellow product, although varying somewhat

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[7] Coutts, R. S. P., and Wailes, P. C., *Inorg. nucl. Chem. Lett.*, 1967, **3**, 1.

in composition from one experiment to another, analysed approximately for $cpTiNO_2$. An azide band was present in the infrared spectrum, so that it is probable that the material is a polymer terminated by azide, somewhat similar to (3).

In anhydrous tetrahydrofuran a red-brown product was formed on stirring NaN_3 with cp_2TiCl at room temperature under argon. The solubility of this material in organic solvents was similar to that of NaN_3 and a complete separation could not be effected. However, with lithium azide in the same solvent reaction occurred readily at room temperature with liberation of nitrogen giving a red-brown polymeric product of approximate composition $[cp_2TiN_2]_n$. Ebulliometric measurements in tetrahydrofuran, although not conclusive due to low solubility, indicated that $n = 3$. The compound was not a complex of molecular nitrogen; no gas was evolved on either acid hydrolysis or on treatment with α,α-bipyridyl. In addition infrared bands at 2060 and, in particular, at 1335 cm^{-1} clearly indicate the presence of azido groups. It is probable that the compound cp_2TiN_3 is unstable under the conditions of the experiment and breaks down with polymerization. This type of behaviour is common with azides, although generally occurring at a higher temperature through a nitrene intermediate, and has been discussed by Thayer.[2] The magnetic susceptibility of the product was measured, χ_{Ti} varying from 273×10^{-6} to 372×10^{-6} CGS units over the temperature range 360–100°K, so that the compound was virtually diamagnetic.

In dimethylformamide as solvent, cp_2TiCl and NaN_3 gave a green solid which, from the infrared spectrum, appeared to be the dimethylformamide solvate of cp_2TiN_3, but the compound was exceptionally unstable and could not be kept at room temperature.

Anhydrous HN_3 in benzene also reacted with cp_2TiCl; nitrogen was evolved but evolution ceased after one-half mole of HN_3 had been added. The red-brown product was apparently $(cp_2TiCl)_2NH$, analogous to $(cp_2TiCl)_2NR$ formed by the reaction of cp_2TiCl with organic azides.[8] Also present, no matter how slowly the HN_3 was added, was a small quantity of $cp_2Ti(N_3)_2$. This diazide was the sole product when excess HN_3 was added to cp_2TiCl.

Experimental

All solid compounds were handled in a nitrogen-filled glove-box and all reactions were carried out under purified argon. Molecular weights were determined ebulliometrically. All solvents were purified by distillation under argon from $LiAlH_4$.

Analyses

Metals were determined by ashing sulphated pellets of each sample. Carbon, hydrogen, and nitrogen were determined by the Australian Microanalytical Service, on pelleted samples sealed in aluminium capsules.

$cp_2Ti(N_3)_2$.—(Found: C, 46·4; H, 4·1; N, 31·6; Ti, 18·3. Calc. for $C_{10}H_{10}N_6Ti$: C, 45·8; H, 3·9; N, 32·0; Ti, 18·3%).

$cp_2Zr(N_3)_2$.—(Found: C, 39·4; H, 3·4; N, 27·1; Zr, 29·6; mol. wt. (THF), 330. Calc. for $C_{10}H_{10}N_6Zr$: C, 39·4; H, 3·3; N, 27·5; Zr, 29·9%; mol. wt., 305).

$(cp_2ZrCl)_2O$.—(Found: C, 43·8; H, 3·9; N, 15·5; Zr, 33·5. Calc. for $C_{20}H_{20}N_6OZr_2$: C, 44·3; H, 3·7; N, 15·5; Zr, 33·6%). The compound was too insoluble for determination of molecular weight.

[8] Coutts, R. S. P., and Surtees, J. R., *Aust. J. Chem.*, 1965, **19**, 387.

Reaction of LiN_3 with cp_2TiCl

LiN_3 (250 mg, 5 mmol) and cp_2TiCl (1·06 g, 5 mmol) were stirred together in tetrahydrofuran (40 ml). Gas evolved was measured by pumping into a calibrated volume with a Töpler pump (Found: N_2, 2·5 mmol). The red-brown solution was reduced to low volume, benzene was added, and the precipitated inorganic material was filtered off. The filtrate was again reduced in volume and light petroleum was added giving a red-brown precipitate (Found: C, 55·6; H, 5·2; N, 13·8; Ti, 23·0; mol. wt. (THF), 640. Calc. for $C_{30}H_{30}N_6Ti_3$ ($[cp_2TiN_2]_3$): C, 58·2; H, 4·9; N, 13·6; Ti, 23·2%; mol. wt., 618).

Reaction of HN_3 with cp_2TiCl

Anhydrous HN_3 in benzene (1·9 ml of 1·3M) was added dropwise to a stirred solution of cp_2TiCl (1·06 g, 5 mmol) in benzene (20 ml). Gas evolved was measured as above (Found: N_2, 2·3 mmol; gas chromatography showed the absence of H_2). The red-brown solution was pumped to low volume and light petroleum added to precipitate the product (Found: C, 53·1; H, 4·6; Cl, 15·1; N, 5·4; Ti, 21·2; mol. wt. (THF), 420. Calc. for $C_{20}H_{21}Cl_2NTi_2$ ($[cp_2TiCl]_2NH$): C, 54·3; H, 4·8; Cl, 16·0; N, 3·2; Ti, 21·7%; mol. wt., 442).

Acknowledgment

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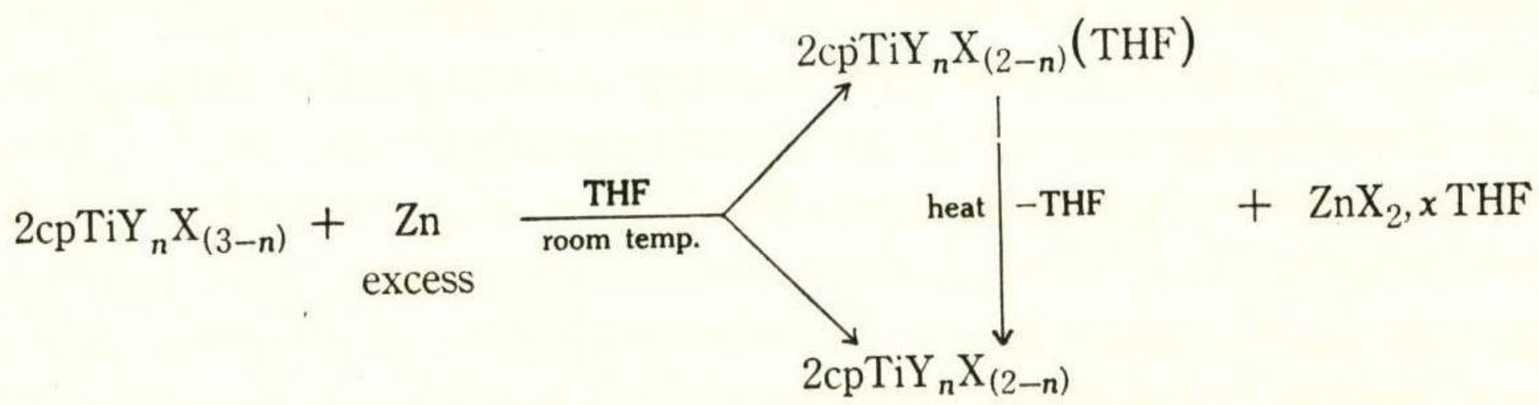
MONOCYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

By R. S. P. Coutts,* R. L. Martin,† and P. C. Wailes*

[Manuscript received December 15, 1970]

Although organotitanium(III) chemistry has expanded rapidly over the last decade, more than 85% of all compounds reported have contained the bis(cyclopentadienyl)titanium(III) moiety.[1] At present the literature contains only six references to mono(cyclopentadienyl)titanium(III) derivatives.[1–6] Our objective in this area of organotitanium chemistry has been to synthesize a variety of new compounds of this type and to establish the preferred coordination number, and hence bonding modes.

We report here a versatile general method of synthesis which leads to the isolation of several classes of mono(cyclopentadienyl)titanium(III) derivatives. Unlike previous synthetic methods[3,5,6] extremely mild reaction conditions are employed, namely the reduction of a suitable organotitanium(IV) compound by means of zinc dust in tetrahydrofuran at room temperature under anaerobic conditions. In some instances the reduction, which is usually complete within 1 hr, leads to the formation of stable, intermediate solvates, as shown in Scheme 1.



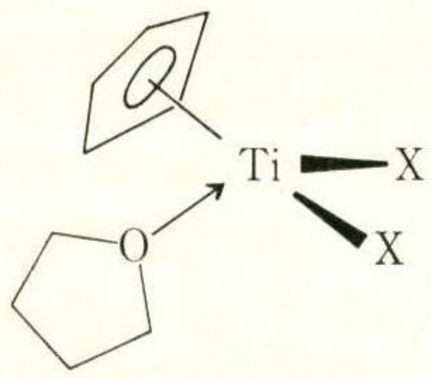
Scheme 1.—Products of zinc reduction. For $n = 0$, X = Cl, Br, I, OMe, OEt, but not OPr^i. For $n = 1$, X = Cl or Br, Y = OR or SR.

In the case where $n = 0$ and X = Cl, Br, or I, blue or green crystalline complexes were isolated which analysed for $cpTiX_2(THF)$. The chloride complex was thermally unstable and tended to lose the THF ligand in working up the product. As a result, it was necessary to remove excess solvent by pumping under high vacuum at temperatures below 0°. The composition of the sky-blue crystals so obtained varied from

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preparation to preparation with respect to the amount of residual solvent. The sample used for characterization analysed for $[cpTiCl_2(THF)],\frac{1}{2}THF$. The magnetic data showed the compounds to be magnetically dilute following the Curie–Weiss law. Ebulliometric molecular weight measurements in THF indicated that the complexes were monomeric. Infrared results confirmed that the cyclopentadienyl ligand was π-bonded and that the ether molecule was complexed to the metal, since the ν_{COC} (asym) band which occurs in THF at 1070 cm^{-1} was shifted to 1040 ± 5 cm^{-1} by coordination. The complexes can best be represented by a pseudotetrahedral stereochemistry.



X = Cl, Br, I

Pyrolysis of these complexes at 120–150° under high vacuum provided the highly coloured compounds $cpTiX_2$ (X = Cl, Br, I). These are insoluble in non-polar solvents but dissolve in coordinating solvents. Complexes are readily formed with ethers, alcohols, amines, and alkyl cyanides as well as the normal chelating agents such as dipyridyl, *o*-phenylenediamine, etc. Some of these complexes will be described in a future publication. The halides showed interesting magnetic behaviour indicated by θ values of *c.* +20°K using the expression

$$\mu_e = 2{\cdot}83\sqrt{\chi_A(T + \theta)}$$

Further investigation is in progress and will be reported at a later date. Some degree of association must be expected in these compounds to satisfy both a coordination number greater than three, and the observed physical properties.

When $n = 0$ and X = OMe or OEt (but not OPr^i) red-brown products were obtained which analysed for $cpTi(OR)_2$. These compounds were extremely sensitive to oxygen and moisture and were sufficiently soluble for molecular weight determinations. The dimethoxide was found to be tetrameric in boiling tetrahydrofuran.

When $n = 1$ and X = Cl a range of Y groups was examined including Y = OMe, OEt, and SPh. Polymeric, sparingly soluble products were obtained corresponding to $[cpTiCl(Y)]_n$. When X = Br the reduction proceeded as evidenced by the usual colour changes, but the products isolated could not be identified from elementary analyses as the expected $[cpTiBr(Y)]_n$.

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HYDRIDO COMPLEXES OF ZIRCONIUM
III. REACTIONS WITH ACETYLENES TO GIVE ALKENYLZIRCONIUM DERIVATIVES

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(Received October 6th, 1970)

SUMMARY

The zirconium hydride $(C_5H_5)_2Zr(H)Cl$ reacts with both mono and disubstituted acetylenes by addition of Zr–H across the triple bond. Generally *trans*-alkenyl derivatives result although in some cases mixtures of isomers are formed. With monosubstituted acetylenes $(C_5H_5)_2ZrH_2$ behaves similarly giving di(*trans*-alkenyl)-zirconium compounds, but with diarylacetylenes hydrogen is evolved and tetra-arylbutadiene complexes result.

INTRODUCTION

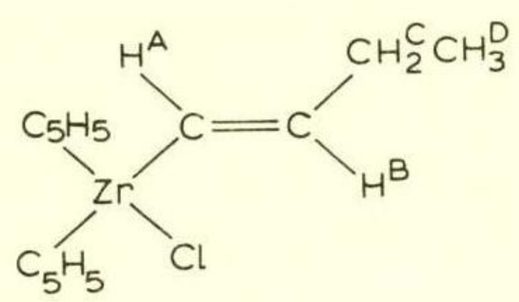
In Parts I[1] and II[2] the preparations of several derivatives of zirconium with bridging hydrido ligands were reported, as well as their reactions with carboxylic acids and ketones. These hydrides react also with acetylenes and olefins giving highly coloured alkenyl- and alkylzirconium derivatives which are extremely sensitive to oxygen and to water. In this paper the reactions of $(C_5H_5)_2ZrH_2$ and $(C_5H_5)_2Zr(H)Cl$ with mono- and disubstituted acetylenes are described.

RESULTS AND DISCUSSION

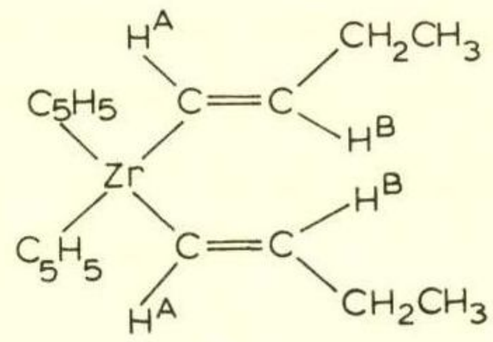
Despite the insolubility of $(C_5H_5)_2ZrH_2$ and $(C_5H_5)_2Zr(H)Cl$, both hydrides dissolved readily when boiled in benzene in the presence of acetylenes, the colour darkening to reddish-brown or black. In most cases the reaction was complete in several minutes. Dry acetylene reacted rapidly giving black solid products, but the composition of these was somewhat variable. Better results were obtained with substituted acetylenes.

From $(C_5H_5)_2Zr(H)Cl$ and 1-butyne a pale brown oily product was obtained, the infrared spectrum of which showed a C=C stretching band at 1560 cm^{-1} and no triple bond absorption. The PMR spectrum confirmed structure (I), the H^A proton being evident as one half of an AB quartet at δ 6.74 (J_{AB} 18 Hz) in which each signal was further split into a triplet ($J \sim 2$ Hz) by long range allylic coupling to the CH_2 of the ethyl group. The large AB coupling (J 18 Hz) indicated that the double bond was *trans*. The broadened quintet and triplet due to H^C and H^D were centred at δ 1.93

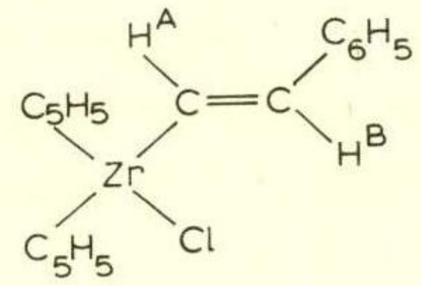
(J 7.2 Hz) and 0.90 (J 7.6 Hz) respectively. H^B was obscured by several small sharp peaks around the major cyclopentadienyl resonance at δ 5.92. These were probably due to small amounts of other isomeric forms.



(I)



(II)



(III)

When $(C_5H_5)_2Zr(D)Cl$ was used instead of the hydride, the infrared spectrum of the product (I, $H^B = D$) showed the C=C stretch at 1525 cm^{-1}. The ethyl resonances in the PMR spectrum occurred now as a broadened quartet centred at δ 1.96 (J 8 Hz) and a triplet at δ 0.92 (J 8 Hz), but H^A showed as a broad band at δ 6.72 split into a multiplet by weak coupling with deuterium and with the allylic protons. Irradiation of this band and consequent sharpening of the CH_2 quartet at δ 1.96 demonstrated the weak coupling of H^A with the CH_2 protons.

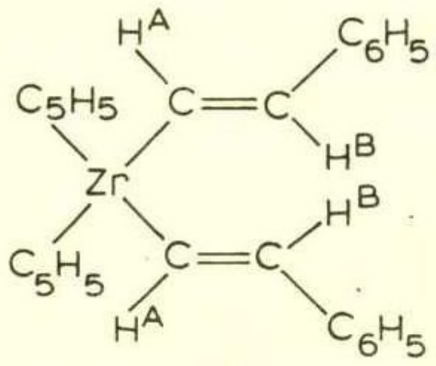
From the dihydride $(C_5H_5)_2ZrH_2$ and 1-butyne an oil was obtained, showing a broad absorption in the C=C stretch region of the infrared (1580 cm^{-1}) and broad multiplets in the PMR spectrum due to C_2H_5 at δ 1.00 and 2.25 and due to C_5H_5 at δ 5.90. The resonances due to H^A and H^B were split and distributed under the C_5H_5 band. It would appear from analysis that the product has structure (II) but the complicated PMR spectrum indicates the presence of isomers and extensive interference between the cyclopentadienyl and the 1-butenyl ligands.

Phenylacetylene behaved similarly with both hydrides, although in all cases the double bond stretching frequency around 1580 cm^{-1} in the infrared spectrum was masked by the aromatic absorption in this area. The product from $(C_5H_5)_2Zr(H)Cl$ and $C_6H_5C{\equiv}CH$ was a viscous oil, the PMR spectrum of which showed extensive splitting of all of the proton resonances. The C_5H_5 occurred as a multiplet centred at δ 5.76 and the C_6H_5 as a multiplet at δ 7.21. Protons H^A and H^B [structure (III)] could not be detected, but in the spectrum of the corresponding compound (III), $H^B = D$) from $(C_5H_5)_2Zr(D)Cl$, H^A showed as a peak at δ 7.62, split into a triplet by small coupling with deuterium (J 3 Hz).

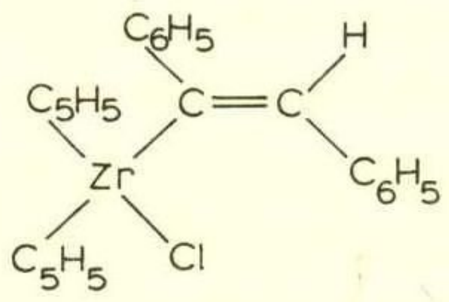
From $(C_5H_5)_2ZrH_2$ and $C_6H_5C{\equiv}CH$ in the molar ratio 1/2, a black solid corresponding to structure (IV) was obtained. This was monomeric in boiling benzene; protons H^A and H^B could not be detected in the PMR spectrum since they were masked by multiplets at δ 5.78 (C_5H_5) and 6.98 (C_6H_5). A similar black product (IV, $H^B = D$) was obtained from $(C_5H_5)_2ZrD_2$, showing a substantially unchanged PMR spectrum. The C_5H_5 peak was a strong sharp singlet at δ 5.78 accompanied by several very small sharp bands at δ 6.07, 5.96, 5.71, 5.63, 5.48, 5.26 and 5.12. It seems likely that the compound is 90% of one isomer, the rest being a mixture of the other possible isomers.

A by-product from this reaction was a green solid, insoluble in benzene, tetrahydrofuran, dimethyl sulphoxide and other solvents, and showing a strong sharp band in the infrared spectrum at 1825 cm^{-1} indicative of a co-ordinated triple bond. Analysis indicated the loss of a cyclopentadienyl ligand giving a polymeric product of the type $(C_5H_5ZrC{\equiv}CC_6H_5)_n$. Loss of a cyclopentadiene in this way occurs readily and was observed often in reactions with disubstituted acetylenes.

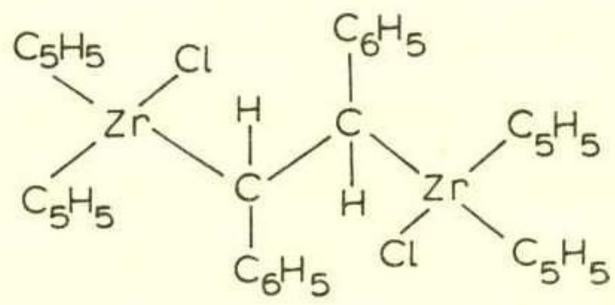
With disubstituted acetylenes the two hydrides reacted in different ways; the hydridochloride added across the multiple bond and the dihydride eliminated hydrogen forming olefin complexes. Thus from $(C_5H_5)_2Zr(H)Cl$ and diphenylacetylene (tolan) in equimolar quantities an orange solid (V) was obtained, which was monomeric in boiling benzene.



(IV)



(V)



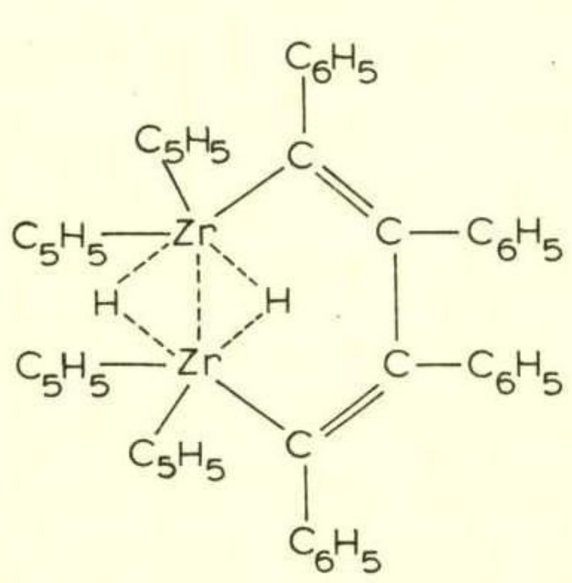
(VI)

Integrated intensities of the PMR peaks of (V) indicated that the proton on the double-bonded carbon was hidden under the multiplet due to C_6H_5 at δ 6.76. The similarity of this multiplet to that of *trans*-stilbene indicated that the major part of the product was the *trans*-adduct. Two sharp bands due to the cyclopentadienyl ligands were present at δ 5.90 and 5.77 in the intensity ratio 3/1, so that 25% *cis*-isomer could be present.

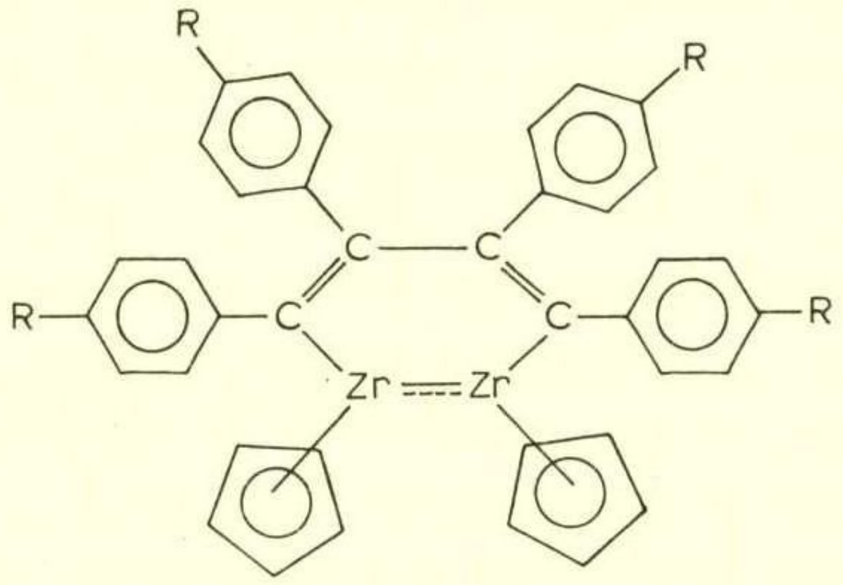
From $(C_5H_5)_2Zr(H)Cl$ and tolan in the molar ratio 2/1, a crimson-coloured solid was obtained containing no double bond. Addition of the second mole of hydride had apparently occurred giving the saturated compound (VI), which was extremely soluble in organic solvents.

The phenyl peak of (VI) in the PMR spectrum was again split into a multiplet centred at δ 6.76 and in the cyclopentadienyl region were two strong sharp bands (δ 5.90 and 5.78) together with two weaker sharp bands (δ 5.85 and 5.60). Since structure (VI) has two asymmetric centres the possibility of *threo* and *erythro* forms arises and the resonance bands between δ 5.60 and 5.90 may be connected with these, but no definite assignments have been made.

Reactions of the dihydride $(C_5H_5)_2ZrH_2$ with diphenyl- and di-*p*-tolylacetylene were characterized by the evolution of hydrogen and the loss of one cyclopentadienyl ligand from each zirconium atom on prolonged heating at 80°. When the mixture was boiled in benzene until the hydride had just dissolved, the product isolated at this stage corresponded to $[(C_5H_5)_2ZrH_n \cdot C_6H_5C{\equiv}CC_6H_5]_2$ in analysis and molecular weight. After heating the solution for a longer period the products isolated contained less carbon, and after one hour or more at 80° the product corresponded to $(C_5H_5\text{-}Zr \cdot C_6H_5C{\equiv}CC_6H_5)_2$. Treatment of the monocyclopentadienyl product with acetone



(VII)



(VIII A) R = H
(VIII B) R = CH_3

gave large colourless crystals of *cis, cis*-1,2,3,4-tetraphenylbutadiene.

These results indicate the formation of an initial complex, for which structure (VII) is a reasonable possibility, since not all of the hydrogen has been lost at this stage.

Both cyclopentadienyl groups were still present on each zirconium and showed a single resonance line in the PMR spectrum. Complete hydrogen evolution was a slow process which probably paralleled the loss of one cyclopentadienyl ligand from each zirconium atom to give what is believed to be the dizirconabenzene complex (VIII).

The product (VIIIA) from diphenylacetylene and the dihydride or dideuteride showed a singlet cyclopentadienyl resonance at δ 6.00 and a multiplet due to the phenyl groups with at least eight bands between δ 6.64 and 7.10. The PMR spectrum of the di-*p*-tolylacetylene compound (VIIIB) showed two methyl peaks of equal intensity at δ 1.75 and 1.96, a sharp singlet at δ 5.94 due to the cyclopentadienyl protons and two multiplets due to the two AA′BB′ systems of the phenyl rings (Fig. 1). To satisfy the coordination requirements of the zirconium it is probable that a double bond exists between the metal atoms.

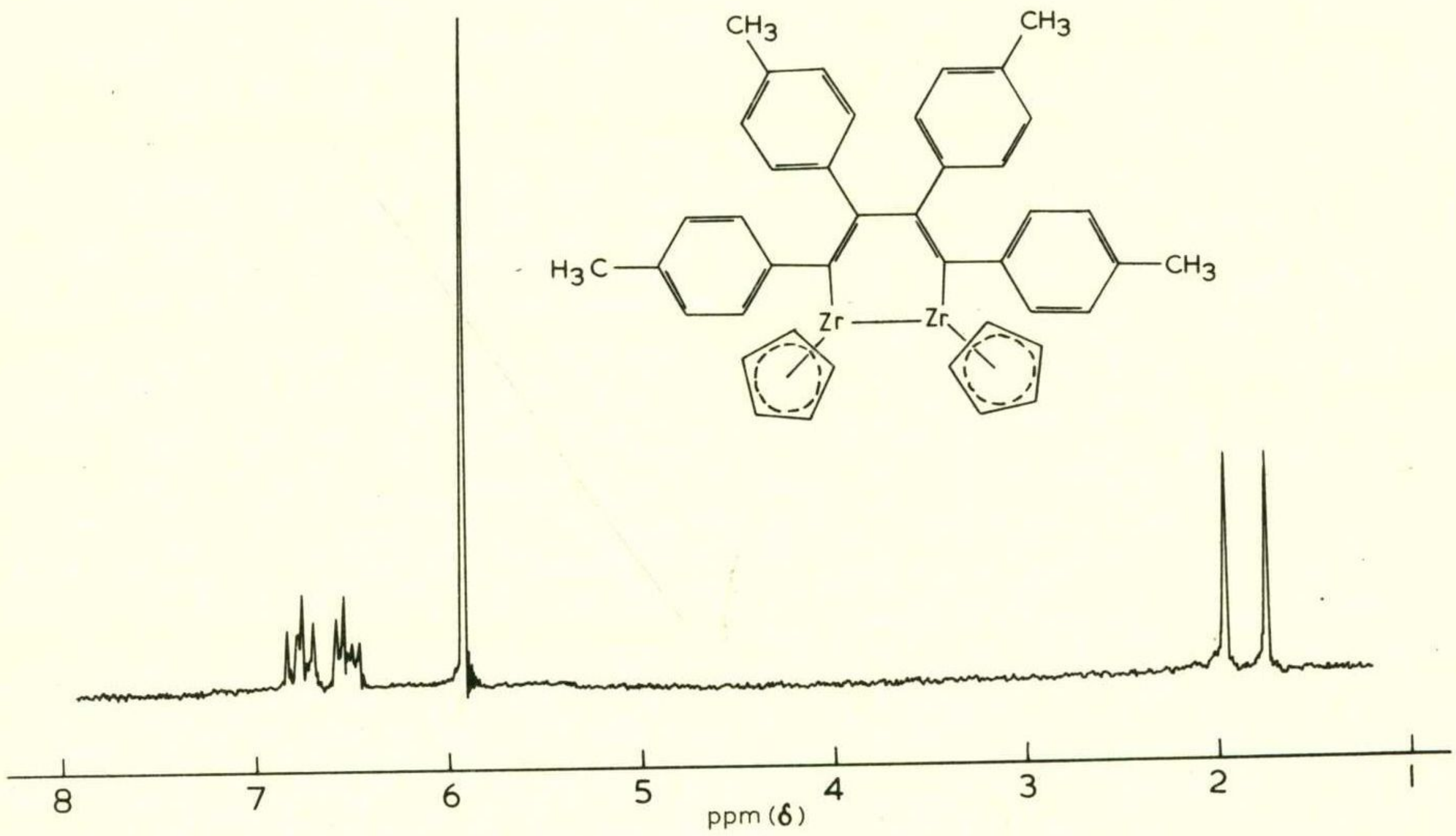


Fig. 1. PMR spectrum of compound (VIIIB) in deuterobenzene.

PMR spectra

The PMR spectra of many of the compounds just described were characterized by a multiplicity of resonance bands in both the cyclopentadienyl and the phenyl regions. Since most of the alkenes were *trans*-isomers, multiplets of the type shown by *trans*-stilbene would be expected. Multiplets in the cyclopentadienyl region are probably due to the formation of isomeric forms of the alkenes attached to zirconium, although the possibility of steric interference between the substituent on the alkene and the cyclopentadienyl ligands should not be overlooked[3,4]. Consideration of the possible molecular conformations of most of the products shows that such interference is possible. Only in one class of complex, namely the tetraarylbutadiene compounds, is interference not possible and in these cases single PMR resonance bands were observed for the cyclopentadienyl protons.

EXPERIMENTAL

General

All solid compounds were handled in a nitrogen-filled glovebox and all reactions were carried out under purified argon in a Schlenk tube system. Molecular weights were determined ebulliometrically in a Gallenkamp ebulliometer modified to take a 3-ml cell with N_2 inlet. PMR spectra were measured on a Varian HA 100 instrument in C_6D_6. Infrared spectra were run on a Perkin–Elmer 137 spectrophotometer calibrated with polystyrene.

Materials

Zirconium hydrides were prepared as described in Part I of this series[1]. 1-Butyne, phenylacetylene and diphenylacetylene were commercial prodducts; phenylacetylene was distilled before use, the others were used without further treatment. Di-*p*-tolylacetylene was prepared from 4,4′-dimethylbenzil[5].

Analyses

Zirconium was determined by ignition to the oxide. Carbon and hydrogen were determined by the Australian Microanalytical Service, on pelleted samples sealed in aluminium capsules. In those cases in which the products were oils, encapsulation was not possible and analyses for carbon and hydrogen could not be determined.

Reaction of acetylenes with zirconium hydrides

General reaction. The hydride (5 mmole) and the acetylene (5 or 10 mmoles as required) were refluxed in benzene (50 ml) until the hydride dissolved. In the case of 1-butyne the gas was bubbled through the refluxing benzene. The solution, usually red-brown or black, was then filtered, solvent was removed under reduced pressure and the product was washed with petrol several times. Those products which were oils or low-melting solids could generally not be purified beyond this stage owing to their extreme sensitivity to heat, oxygen and moisture.

$(C_5H_5)_2Zr(Cl)CH{=}CHC_2H_5$. From $(C_5H_5)_2Zr(H)Cl$ and $C_2H_5C{\equiv}CH$, a yellow-brown oil. (Found: Zr, 29.5. $C_{14}H_{17}ClZr$ calcd.: Zr, 29.23%.)

$(C_5H_5)_2Zr(Cl)CH{=}CHC_6H_5$. From $(C_5H_5)_2Zr(H)Cl$ and $C_6H_5C{\equiv}CH$, a brown-black low-melting solid which could not be purified further. (Found: C, 62.5; H, 5.4; Zr, 24.9. $C_{18}H_{17}ClZr$ calcd.: C, 60.06; H, 4.76; Zr, 25.3%.)

$(C_5H_5)_2Zr(CH{=}CHC_2H_5)_2$. From $(C_5H_5)_2ZrH_2$ and $C_2H_5C{\equiv}CH$, brown-black oil. (Found: Zr, 28.3. $C_{18}H_{24}Zr$ calcd.: Zr, 27.50%.)

$(C_5H_5)_2Zr(CH{=}CHC_6H_5)_2$. From $(C_5H_5)_2ZrH_2$ and $C_6H_5C{\equiv}CH$, black solid. (Found: C, 72.3; H, 5.3; Zr, 21.3; mol.wt., 436. $C_{26}H_{24}Zr$ calcd.: C, 73.03; H, 5.66; Zr, 21.33%; mol.wt., 428.)

Compound (*V*). From $(C_5H_5)_2Zr(H)Cl$ and $C_6H_5C{\equiv}CC_6H_5$, an orange solid. (Found: C, 66.3; H, 4.5; Zr, 21.1; mol.wt., 465. $C_{24}H_{21}ClZr$ calcd.: C, 66.12; H, 4.85; Zr, 20.91%; mol.wt., 436.)

Compound (*VI*). From $(C_5H_5)_2Zr(H)Cl$ (2 moles) and $C_6H_5C{\equiv}CC_6H_5$, a crimson solid which was never obtained completely pure. [Found: C, 60.7; H, 4.6; Zr, 24.8. $C_{34}H_{32}Cl_2Zr_2$ calcd.: C, 58.84; H, 4.65; Zr, 26.28%.)

Compound (*VII*). From $(C_5H_5)_2ZrH_2$ and $C_6H_5C{\equiv}CC_6H_5$, a brown-black

solid. (Found: C, 71.3; H, 5.5; Zr, 21.8; mol.wt., 825. $[C_{24}H_{21}Zr]_2$ calcd.: C, 71.96; H, 5.28; Zr, 22.77%; mol.wt., 801.)

Compound (*VIIIA*). From $(C_5H_5)_2ZrH_2$ and $C_6H_5C{\equiv}CC_6H_5$, red-brown solid. (Found: C, 67.8; H, 5.4; Zr, 24.9; mol.wt., 668. $[C_{19}H_{15}Zr]_2$ calcd.: C, 68.21; H, 4.52; Zr, 27.27%; mol.wt., 669.)

When the product was dissolved in air-free acetone and set aside for two days, long colourless needles of *cis,cis*-1,2,3,4-tetraphenylbutadiene, m.p. 185°, were deposited. (Found: C, 93.9; H, 6.3. $C_{28}H_{22}$ calcd.: C, 93.82; H, 6.18%.)

Compound (*VIIIB*). From $(C_5H_5)_2ZrH_2$ and $CH_3C_6H_4C{\equiv}CC_6H_4CH_3$, red-brown solid. (Found: C, 68.9; H, 5.3; Zr, 25.5; mol.wt., 650. $[C_{21}H_{19}Zr]_2$ calcd.: C, 69.55; H, 5.27; Zr, 25.16%; mol.wt., 725.)

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PREPARATION OF LOW OXIDATION STATE CYCLOPENTADIENYL COMPLEXES OF TITANIUM AND ZIRCONIUM
I. COMPOUNDS OF ZIRCONIUM

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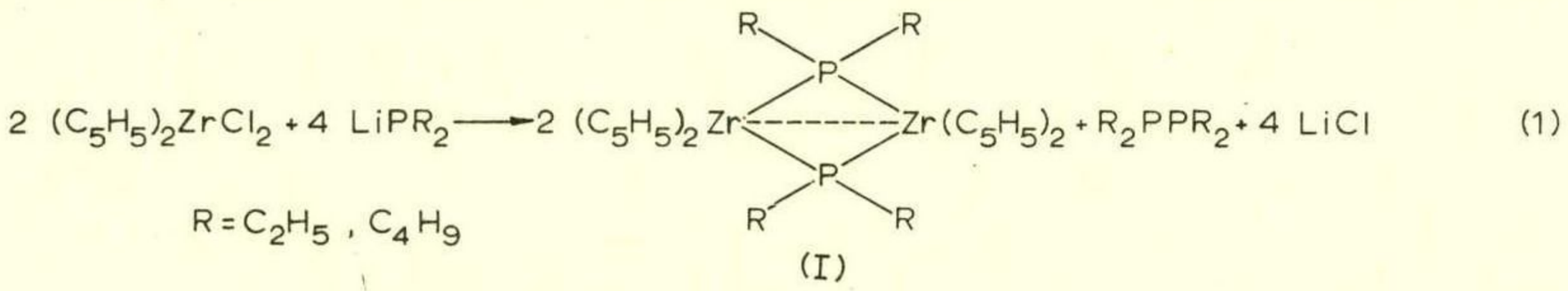
(Received October 26th, 1970)

SUMMARY

Low oxidation state zirconium complexes have been obtained by controlled reduction of zirconium(IV) halogen compounds. Those prepared were the zirconium-(III) compounds $[(C_5H_5)_2ZrCl]_n$ and $[(C_5H_5)_2Zr]_2O$, and the complex $(C_5H_5)_2Zr\cdot$ Bipy. The latter was also obtained from the reaction between $(C_5H_5)_2Zr$ and 2,2′-bipyridine. These low oxidation state zirconium compounds are often complexed with aromatic hydrocarbons such as benzene or naphthalene.

INTRODUCTION

Reduction of dicyclopentadienyltitanium dichloride, $(\pi\text{-}C_5H_5)_2TiCl_2$, with a variety of reagents has lead to numerous complexes of both titanium(II) and titanium-(III)[1]. In the case of zirconium, although zirconocene can be obtained by vigorous reduction of the corresponding zirconium(IV) compound[2], $(\pi\text{-}C_5H_5)_2ZrCl_2$, many of the milder reducing agents are ineffective. The only known cyclopentadienyl-zirconium(III) compounds are the phosphides(I), prepared by Issleib and Häckert[3] from $(\pi\text{-}C_5H_5)_2ZrCl_2$ and lithium dialkylphosphides [eqn. (1)]:



In this and subsequent papers, preparations of several new zirconium(II) and zirconium(III) compounds, as well as titanium(II) and titanium(III) compounds will be described. Several workers have speculated on the types of cyclopentadienyl groups, either σ- or π-bonded, which exist in some low oxidation state titanium complexes[4-6]. Cotton *et al.*[7] have shown that the cyclopentadienyl groups in $(C_5H_5)_4Ti$ are fluxional and at low temperatures in $C_6D_5CD_3$ two of the cyclopentadienyl ligands are σ-bonded and two are π-bonded. For the corresponding zirconium compound, $(C_5H_5)_4Zr$, it was established by X-ray analysis that one of the ligands is σ-bonded[8].

Further evidence for the existence of both σ- and π-bonded cyclopentadienyl groups on zirconium is given in this paper.

RESULTS AND DISCUSSION

By reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with the disodium salt of 2,2′-bipyridine in tetrahydrofuran, $(C_5H_5)_2Zr\cdot Bipy$ (II) was obtained as a purple solid, moderately soluble in benzene and very soluble in tetrahydrofuran, in which it is monomeric. The major peaks in the mass spectrum of this complex could be assigned to the parent compound, 2,2′-bipyridine and cyclopentadiene fragments. The magnetic susceptibility was very low, χ_{Zr} being approximately 100×10^{-6} cgs units in the temperature range 356 to 99° K (μ_{eff} varied from 0.44 BM at 356° to 0.34 BM at 99° K). As in the corresponding titanium compound[9] there appears to be a strong antiferromagnetic interaction due to the spin coupling between the zirconium ion and the radical anion of 2,2′-bipyridine.

Reaction of zirconocene with 2,2′-bipyridine in toluene, followed by extraction with benzene gave the purple complex $(C_5H_5)_2Zr\cdot Bipy\cdot C_6H_6$ (III). The high intensity of the peak in the mass spectrum at *m/e* 78, relative to that of $(C_5H_5)_2Zr\cdot Bipy$, was good indication of the presence of benzene. Compound (III) is monomeric in both boiling benzene and boiling tetrahydrofuran, indicating that the benzene is held firmly in the complex. The magnetic moment decreases from 1.24 BM at 352° K to 0.73 BM at 94° K, so that (III) is antiferromagnetic. On heating under vacuum to 100° the benzene was expelled from the complex giving $(C_5H_5)_2Zr\cdot Bipy$ (II).

Reduction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with an equimolar amount of monosodium 2,2′-bipyridine gave a purple-coloured, extremely air-sensitive compound. Approximately one-half of the bipyridine could be sublimed out of the reaction mixture leaving a product which analyzed approximately for $[(C_5H_5)_2ZrCl]_2\cdot Bipy$ (IV). This complex was extremely air-sensitive and unstable in solution, and could not be analyzed satisfactorily.

Previous attempts to prepare the zirconium(III) compound, $(C_5H_5)_2ZrCl$, in these laboratories from $ZrCl_3$ had not been successful. Two other methods were now tried; namely, reduction of $(C_5H_5)_2ZrCl_2$, and equilibration of this compound with $(C_5H_5)_2Zr$. Reduction of $(C_5H_5)_2ZrCl_2$ with one equivalent of sodium, either as its amalgam or as sodium naphthalide, led in all cases to a small amount of a red, diamagnetic product which always had high chloride (*e.g.* 14.3–15.1 % instead of 13.79 %) and low metal (46.4–47.3 % ash instead of 47.97 %) analyses, suggesting that some dichloride was present. The mass spectrum showed peaks as high as *m/e* 460, indicating the polymeric nature of the product. Determination of the molecular weight in boiling tetrahydrofuran gave inconsistent results, different preparations varying between 430 and 846.

An alternative route to $(C_5H_5)_2ZrCl$ was by equilibration of zirconocene with the corresponding dichloride. When equimolar amounts of $(C_5H_5)_2Zr$ and $(C_5H_5)_2ZrCl_2$ were heated together in toluene, the solution turned red after a short time and a green precipitate formed. The small amount of soluble red product after benzene extraction was the benzene adduct $[(C_5H_5)_2ZrCl]_2\cdot C_6H_6$ (V), while the major part of the product was the olive-green insoluble polymer $[(C_5H_5)_2ZrCl]_n$ (VI). This compound was diamagnetic (χ_M varied from 8×10^{-6} to 20×10^{-6} cgs units between

ambient and liquid nitrogen temperature). In air the red benzene complex decomposed slowly whereas the green compound was pyrophoric. Because of this extreme sensitivity to oxygen it was not possible to obtain a mass spectrum of (VI) free of oxide peaks. The highest mass number, *m/e* 570, probably arose from the trimer $(C_5H_5 \cdot ZrCl)_3$ but no other information on the molecular weight of this complex could be obtained.

We suggest that the difference between the green and red forms of $[(C_5H_5)_2ZrCl]_n$ may be accounted for by postulating the presence of both σ- and π-bonded cyclopentadienyl groups in the green form derived from $(C_5H_5)_2Zr$. The splittings of the bands at 1040 and 1400 cm^{-1} in the infrared spectrum of green $(C_5H_5)_2ZrCl$ tend to confirm this (Fig. 1). It is of interest to draw an analogy with the titanium case.



Fig. 1. Infrared spectrum of $(C_5H_5ZrCl)_n$ (KBr disc).

Salzmann and Mosimann[4] found that treatment of titanocene with dry gaseous HCl did not yield the expected green $(C_5H_5)_2TiCl$ or the red $(C_5H_5)_2TiCl_2$, but gave instead a red form of $(C_5H_5)_2TiCl$ and an insoluble green form of $(C_5H_5)_2TiCl_2$. These compounds contained both σ- and π-bonded cyclopentadienyl groups.

In like manner we found that treatment of zirconocene with dry HCl did not lead to the known $(C_6H_5)_2ZrCl_2$, but instead a pale green compound was obtained showing an infrared spectrum very similar to that of green $(C_5H_5)_2TiCl_2$, with multiple cyclopentadienyl bands at 1005, 1055 (CH deform ||) and 1370, 1405 and 1440 cm^{-1} (C–C stretch).

This postulate of both σ- and π-bonded cyclopentadienyl ligands in zirconocene would explain also the two products from its reaction with aluminium triethyl or trimethyl[10]. Each of these reactions yielded two products of similar composition, the major one being green, insoluble and containing, we propose, both σ- and π-bonded cyclopentadienyl ligands. The minor product was red and soluble with both cyclopentadienyl groups π-bonded. There would appear to be some interconversion since this di-π compound must be formed from the σ, π compound during the reaction.

Another zirconium(III) complex can be obtained by reduction of the oxygen bridged compound $[(C_5H_5)_2ZrCl]_2O$[11] with one equivalent of sodium naphthalide. The naphthalene complex $\{[(C_5H_5)_2Zr]_2O\}_2 \cdot C_{10}H_8$ (VII) was obtained as a dark brown solid. Attempts to sublime the naphthalene from this complex by heating at 110° under vacuum for 5 h failed, suggesting that the naphthalene is held quite strongly by the zirconium compound. The PMR spectrum in deuterobenzene showed the proton bands of the naphthalene in the same positions as those of free naphthalene.

The cyclopentadienyl band at δ 5.88 was broad indicating that the compound was weakly paramagnetic. Molecular weight values in boiling tetrahydrofuran were around 20% low, showing that some dissociation was occurring under the conditions of the determination. It is not possible to say what part the naphthalene plays in the bonding of the molecule. It may be bridging two $[(C_5H_5)_2Zr]_2O$ groups or it could be bonded to the dimer $\{[(C_5H_5)_2Zr]_2O\}_2$.

EXPERIMENTAL

General

All solid materials were handled in a nitrogen filled glovebox and all reactions were carried out under purified argon. All solvents were purified by distillation under argon from $LiAlH_4$. Molecular weights were measured ebulliometrically under argon in a 3 ml cell. PMR spectra were measured on a Varian A60 or HA100 instrument. $(C_5H_5)_2Zr$ was prepared by the method of Watt and Drummond[2] and $[(C_5H_5)_2ZrCl]_2O$ was prepared from $(C_5H_5)_2ZrCl_2$ and aniline[11].

Analyses

Zirconium was determined by ashing sulphated pellets of each compound to ZrO_2. Carbon and hydrogen analyses were performed by the Australian Microanalytical Service, C.S.I.R.O. and University of Melbourne, on pelleted samples sealed in aluminium capsules. With low oxidation state zirconium compounds difficulty was generally experienced in obtaining satisfactory duplicate values.

$(C_5H_5)_2Zr \cdot Bipy$

Sodium (0.46 g, 20 mmole) was dissolved in a solution of 2,2′-bipyridine (1.56 g, 10 mmole) in tetrahydrofuran (40 ml). On addition of $(C_5H_5)_2ZrCl_2$ (2.92 g, 10 mmole) a purple coloured solution was obtained. Evaporation of solvent and extraction of the residue with benzene gave $(C_5H_5)_2Zr \cdot Bipy$ (2.72 g, 72% yield) as a purple solid. (Found: N, 7.5; ZrO_2, 33.5%; mol.wt. in THF, 382. $C_{20}H_{18}N_2Zr$ calcd.: N, 7.42; ZrO_2, 32.56%; mol.wt., 378.)

$(C_5H_5)_2Zr \cdot Bipy \cdot C_6H_6$

$(C_5H_5)_2Zr$ (2.2 g, 10 mmole) and 2,2′-bipyridine (1.56 g, 10 mmole) were heated together in toluene (15 ml) in a sealed tube at 150° for 25 h. The colour turned to purple and a solid precipitated. Solvent was removed under vacuum and the residue was extracted with benzene, to give the purple benzene complex in near quantitative yield. In a sealed m.p. tube the compound melted at 260–265°. When placed in the melting point apparatus at 260°C it melted immediately with frothing. (Found: ZrO_2, 27.1%; mol.wt. in benzene, 440; in THF, 452. $C_{26}H_{24}N_2Zr$ calcd.: ZrO_2, 27.05%; mol.wt., 456.)

On heating at 100–120° under vacuum for several hours $(C_5H_5)_2Zr \cdot Bipy$ was obtained. (Found: C, 63.5; H, 4.8; N, 6.6. $C_{20}H_{18}N_2Zr$ calcd.: C, 63.62; H, 4.80; N, 7.42%.)

$[(C_5H_5)_2ZrCl]_n$ *and* $[(C_5H_5)_2ZrCl]_2 \cdot C_6H_6$

$(C_5H_5)_2Zr$ (6.0 g, 27.1 mmole) and $(C_5H_5)_2ZrCl_2$ (7.93 g, 27.1 mmole) were

heated together in toluene (75 ml) for 45 h. The solution turned red-brown in colour and a large amount of precipitate was always present. Solvent was removed under reduced pressure and the residue was extracted in a Soxhlet apparatus under argon with tetrahydrofuran for 20 h. The residue in the thimble was olive-green $[(C_5H_5)_2ZrCl]_n$. (Found: Cl, 13.8; ZrO_2, 48.1. $C_{10}H_{10}ClZr$ calcd.: Cl, 13.79; ZrO_2, 47.94%.) The red tetrahydrofuran solution was evaporated to dryness and the red-brown residue was extracted once again with tetrahydrofuran for 1–2 h. The evaporated extract was extracted with light petroleum (b.p. 60–80°) to remove a small amount of oily material, then the residue was extracted with benzene, in which it was very soluble. Removal of solvent under reduced pressure gave red $[(C_5H_5)_2ZrCl]_2 \cdot C_6H_6$. (Found: C, 48.6; H, 3.9; ZrO_2, 42.3; mol.wt. in benzene, 606. $C_{26}H_{26}Cl_2Zr_2$ calcd.: C, 52.73; H, 4.43; ZrO_2, 41.62%; mol.wt., 592.)

$\{[(C_5H_5)_2Zr]_2O\}_2 \cdot C_{10}H_8$

A solution of sodium naphthalide [from 0.69 g (30 mmole) sodium and 10% excess of naphthalene] in tetrahydrofuran (40 ml) was added slowly to a solution of $[(C_5H_5)_2ZrCl]_2O$ (7.95 g, 15 mmole) in tetrahydrofuran (80 ml). The solution was warmed at 60° for 1 h, evaporated to dryness and the residue was extracted continuously with light petroleum for 3 h to remove excess naphthalene. The residue was then extracted into tetrahydrofuran and the product isolated by evaporation of solvent followed by heating under high vacuum at 110° for 5 h. Dark brown $\{[(C_5H_5)_2Zr]_2O\}_2 \cdot C_{10}H_8$ was obtained. (Found: C, 56.2; H, 4.6; ZrO_2, 46.7; mol.wt. in THF, 828. $C_{50}H_{48}O_2Zr_4$ calcd.: C, 57.41; H, 4.62; ZrO_2, 47.12%; mol.wt., 1047.)

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MONOCYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

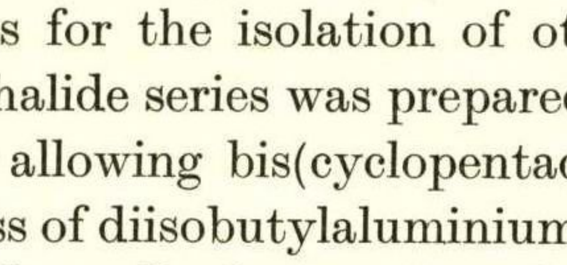
I. HALIDES AND THEIR TETRAHYDROFURAN COMPLEXES

By R. S. P. Coutts,*† R. L. Martin,† and P. C. Wailes*

[Manuscript received June 24, 1971]

Abstract

The halides of monocyclopentadienyltitanium(III) with the general formula $cpTiX_2$ (where X = Cl, Br, and I; and cp = π-cyclopentadienyl) have been prepared by pyrolysis from their tetrahydrofuran complexes ($cpTiX_2$,THF). The THF complexes were prepared from the appropriate cyclopentadienyltitanium(IV) trihalide by reduction in THF. They are believed to be monomers of the form shown below, involving a pseudo-tetrahedral stereochemistry about the central titanium atom:



X = Cl, Br, I

Introduction

At the commencement of this project in 1969 only one compound had been reported in the literature which contained the monocyclopentadienyltitanium(III) moiety[1] ($cpTi^{III}$). Our objective was to synthesize a variety of new compounds of this type and to establish the preferred coordination number, stereochemistry, and hence bonding modes of the $cpTi^{III}$ moiety. The synthesis of the halides seemed a suitable starting point for our investigations, since it was hoped that these would provide reactive intermediates for the isolation of other derivatives.

The first member of the halide series was prepared accidentally by Bartlett and Seidel[1] some ten years ago by allowing bis(cyclopentadienyl)titanium(IV) dichloride, cp_2TiCl_2, to react with an excess of diisobutylaluminium chloride in a toluene–heptane solvent heated to 50° for 3 hr. Normally the reaction of cp_2TiCl_2 with organoaluminium compounds under similar conditions leads to bimetallic complexes (now well known as Ziegler–Natta catalysts) with retention of the bis(cyclopentadienyl)titanium moiety. These workers suggested that the structure of solid $cpTiCl_2$ was a chlorine-bridged dimer, or even a higher polymer, since it is generally insoluble in non-polar solvents. The possibility of obtaining evidence for spin–spin interaction, due to the associated nature of the chloride, by a magnetic investigation was not attempted

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[1] Bartlett, P. D., and Seidel, B., *J. Am. chem. Soc.*, 1961, **83**, 581.

until 1968.[2] Although the compound appeared to behave as a nearly magnetically dilute compound following the Curie–Weiss law [$\chi(T-\theta) = \text{constant}$], it showed a finite Weiss constant (θ) of +17°K consistent with some form of association. Accordingly, the extent of association of $[\text{cpTiCl}_2]_n$ remains unresolved, and requires an extension of the magnetic susceptibility studies to temperatures down to that of liquid helium (4°K).

The present paper describes the preparation, characterization, and properties of the halides and THF complexes of the cpTi^{III} moiety. Electronic and vibrational spectra in conjunction with magnetic susceptibility determinations down to liquid nitrogen temperature (80°K) are discussed in relation to the possible structures of these compounds.

Results and Discussion

(*a*) *Preparation and Properties of the Halides and Complexes*

The complexes were formed by a general method of synthesis reported earlier.[3] In these preparations the cyclopentadienyltitanium(IV) trihalide was dissolved in dry, oxygen-free tetrahydrofuran and an excess of degassed zinc dust was added with stirring. Immediately the yellow-orange solutions changed colour to green. The proposed reaction is shown below:

$$2\text{cpTiX}_3 + \text{Zn(excess)} \xrightarrow[\text{room temp.}]{\text{THF}} 2\text{cpTiX}_2,\text{THF} + \text{ZnX}_2,2\text{THF}$$

After stirring for 2 hr at room temperature the unchanged zinc was filtered off, and the filtrate evaporated to low bulk. Crystals usually formed at this stage. In the case of bromide and iodide the products were then washed with diethyl ether to remove the adhering zinc halide etherate. The products were then pumped dry and found to analyse for the 1 : 1 complexes cpTiX_2,THF (see Table 1).

Table 1

Physical and analytical data

Molecular weight determinations in THF

Compound	Colour	Found (%) Ti	Hal	C	H	Calc. (%) Ti	Hal	C	H	Mol. Wt. Found	Calc.
$(\text{cpTiCl}_2,\text{THF}),\frac{1}{2}\text{THF}$	sky-blue	16·4	24·1	45·1	5·7	16·4	24·3	45·2	5·9	318	292
$\text{cpTiBr}_2,\text{THF}$	blue-green	14·1	46·0	30·4	3·8	13·9	46·3	31·3	3·8	365	345
$\text{cpTiI}_2,\text{THF}$	blue-green	10·8	[a]	26·8	3·6	10·9	57·9	24·6	3·0	431	439
cpTiCl_2	mauve	26·0	38·1	32·5	2·7	26·0	38·6	32·7	2·7		
cpTiBr_2	dark blue	17·8	57·7	21·7	2·0	17·6	58·6	22·0	1·9		

[a] Iodide determinations gave low values due to loss of free iodine.

In the case of the chloride complex, the sky-blue crystals formed were unstable and if washed with diethyl ether or even benzene, they started to lose THF to form the mauve cpTiCl_2. However, it was found that if the crystals were filtered and washed rapidly with THF to remove the zinc chloride etherate and then pumped under

[2] Canty, A. J., Coutts, R. S. P., and Wailes, P. C., *Aust. J. Chem.*, 1968, **21**, 807.
[3] Coutts, R. S. P., Martin, R. L., and Wailes, P. C., *Aust. J. Chem.*, 1971, **24**, 1079.

vacuum (*c.* 10^{-4} mmHg) at 0°C, decomposition did not take place; however, the crystals retained some solvent in excess of the desired 1 : 1 stoicheiometry, the amount varying from preparation to preparation. These crystals were characterized by selecting one such preparation. Elementary analysis and molecular weight determination showed that, for the sample chosen, half a mole of lattice THF was present. This was verified by dissolving a sample in methanol, bubbling in dry oxygen, and then running its n.m.r. spectrum. Integration of the peaks due to the protons of the cp ligand and those due to the protons of THF were in the ratio 5 : 12 confirming that the formula of the original titanium(III) complex was ($cpTiCl_2$,THF),$\frac{1}{2}$THF (Table 1).

The complexes were insoluble in non-polar solvents but in THF it was shown ebulliometrically that the compounds were monomeric (Table 1).

The halides were prepared from the complexes by pyrolysis under vacuum. Although the chloride complex showed itself to be thermally unstable at room temperature it was not until the temperature was raised to *c.* 120° at a pressure of *c.* 10^{-4} mmHg that the last trace of coordinated THF was removed. The THF was more strongly bonded in the case of the bromide complex and required a temperature of *c.* 150° for decomposition. Analytical data from several different preparations of $cpTiI_2$ indicated that decomposition started before all the ligand could be removed so that satisfactory analytical data could not be obtained. This is in keeping with the data available on the cyclopentadienyltitanium(IV) trihalides. The chloride is moisture sensitive, but the iodide is moisture, heat, and light sensitive. One might expect a similar trend in the lower valent monocyclopentadienyltitanium(III) dihalides plus the increased hazard of oxygen sensitivity.

Molecular weights for the halides could not be carried out in non-polar solvents due to lack of solubility. The use of coordinating solvents would offer no evidence in support of polymeric structure, as complexation takes place with degradation of the polymer.

As stated above, all the compounds reported are extremely sensitive to air; the halides in particular inflamed spontaneously even when exposed in a densely packed form. Controlled oxidation of all compounds gave bright yellow to orange coloured titanium(IV) compounds of unknown composition.

(*b*) *Infrared Spectra* (*4000–600 cm*$^{-1}$)

The spectra of the $cpTiX_2$ halides in the rock salt region are closely similar as the metal–halogen stretching frequencies fall below 600 cm^{-1}. This similarity is consistent with the presence of the common $cpTi^{III}$ moiety. Thus all the compounds showed bands associated with the π-C_5H_5 ring.[4] These occurred at 810, 860, 1015, 1435, and 3100 cm^{-1} and are assigned to CH out-of-plane deformation (symmetrical and unsymmetrical); CH in-plane deformation; CC in-plane skeletal stretch; and CH in-plane stretch, respectively.

In addition to the above bands, the spectra of the THF complexes contained the characteristic absorptions of tetrahydrofuran. In particular, the peak associated

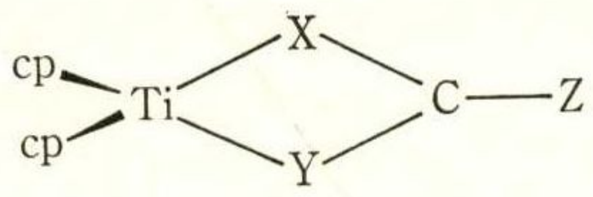
[4] Fritz, H. P., *Adv. organomet. Chem.*, 1964, **1**, 239.

with COC antisymmetric stretching mode showed the expected frequency decrease,[5] due to complexation, through oxygen, with the metal. This band, which occurs in the free ligand at 1070 cm^{-1}, was shifted to 1035 ± 5 cm^{-1} by coordination.

(c) *Electronic Spectra (30000–7000 cm^{-1})*

Visible spectra have been measured for the complexes, both as solids and in THF solutions. Unfortunately, tetrahedral complexes are known for only a few of the ions of the first transition series. The interpretation of their spectra is complicated by certain features which have been adequately discussed elsewhere.[6,7] It suffices to say that the intensities of absorption bands are high partly because of d–p mixing, and the distinction between ligand field and charge transfer bands is generally difficult.

Several classes of organotitanium(III) compounds have been synthesized[8–11] which have a pseudotetrahedral stereochemistry, the point symmetry being C_{2v} or lower. It is interesting to note that in all these compounds bands occur in three distinct regions: 16000–17500, 13000–14000, and 10000–11000 cm^{-1}, and extinction coefficients, when reported, are high (ϵ_{max} 40–110). The two bands at lower energy are shoulders with the lower being very weak. All the compounds are believed to have the general structure (1).



(1)

X = O, S
Y = O, S
Z = R, OR, NR_2

In the cases where X = Y = S and Z = OR[10] or NR_2,[11] a band at *c.* 10000 cm^{-1} was not detected experimentally although resolution of the spectra into the minimum number of Gaussian components with an analogue computer,[12] suggested that such a band may well be present.

An isoelectronic spectrum to Ti^{III} is that of V^{IV}, and recently some work on the magnetic and spectral properties for monomeric vanadium(IV) compounds has shown that considerable distortions are present in the expected tetrahedral configurations.[13,14] In the tetrakis(dialkylamino)vanadium(IV) compounds, absorption bands in the electronic spectra occurred at 13300 cm^{-1} as a shoulder and between 17400–17900 cm^{-1}. These data agree well with those reported in the titanium(III) cyclopentadienyl systems.

[5] Kern, R. J., *J. inorg. nucl. Chem.*, 1962, **24**, 1105.
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[13] Holloway, C. E., Mabbs, F. E., and Smail, W. R., *J. chem. Soc.* (*A*), 1968, 2980.
[14] Alyea, E. C., and Bradley, D. C., *J. chem. Soc.* (*A*), 1969, 2330.

The absorption spectra in THF solution of the complexes under investigation are almost identical with the solid state diffuse reflectance spectra of the complexes (Table 2) indicating that the same absorbing species exists in solution and in the solid state (Fig. 1). Bands occurred in the general region of 15500, 13300, and 10000 cm^{-1}, with extinction coefficients in the range 60–150. This pattern closely resembles the spectra of the compounds discussed above, considering that the increased non-equivalence of the ligands probably lowers the symmetry yet further. It would appear that the electronic spectral data can be attributed to a distorted tetrahedral environment. The iodide complex has two bands at *c.* 17000 and *c.* 20000 with high extinction coefficients most likely due to charge transfer bands.

TABLE 2

ELECTRONIC SPECTRAL DATA (cm^{-1})

Compound	State	Charge Transfer Bands			Ligand Field Bands		
$cpTiCl_2$,THF	solid	25000			15600	—	10000sh b
	soln	—			15100[a]	—	11200[b]
$cpTiBr_2$,THF	solid	25000sh vw			15400	13300sh w	—
	soln	25000			14500[c]	13100sh	10500sh vw[d]
$cpTiI_2$,THF	solid		20300	16700	15100	13200sh w	9500sh
	soln	23800	20200	17200	15400	12900sh w	—
$cpTiCl_2$	solid	26000	19600		—	14100sh	9600
$cpTiBr_2$	solid	27800	17200		—	13400sh	9600

[a] ϵ_{max} 74. [b] ϵ_{max} 62. [c] ϵ_{max} 156. [d] Approximate.

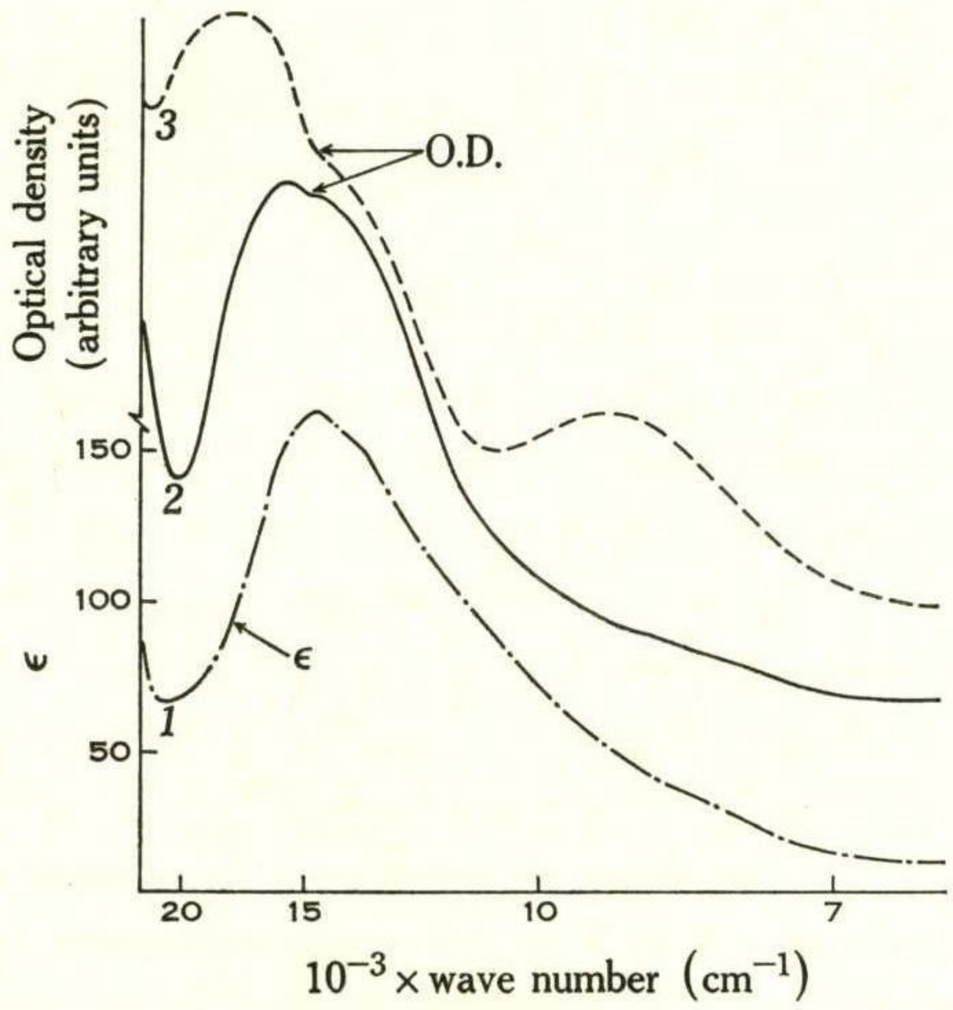
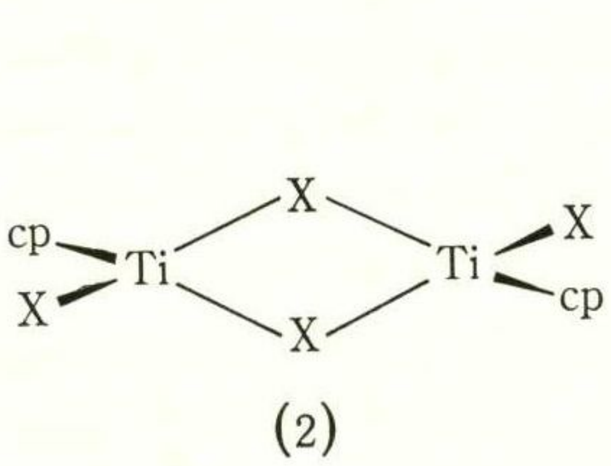


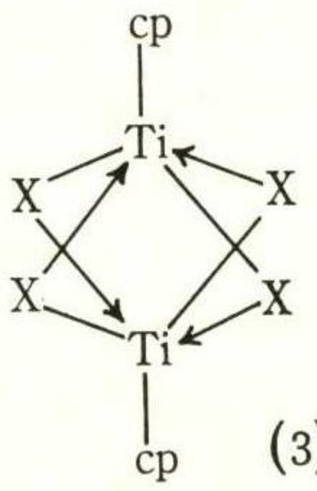
Fig. 1.—Electronic spectra.
1, $cpTiBr_2$,THF (solution);
2, $cpTiBr_2$,THF (solid);
3, $cpTiBr_2$ (solid).

The spectra of the halides, $cpTiX_2$, were run in the solid state by reflectance. In the case of the chloride and bromide, strong peaks were observed at 19600 (chloride) and 17200 cm^{-1} (bromide); as well each compound had an associated shoulder in the ligand field region at 14100 (chloride) and 13400 cm^{-1} (bromide). At lower energy

the spectrum of the chloride showed a band at 9600 cm^{-1}, that of the bromide one at 9000 cm^{-1} (see Fig. 1). The degree of association is unknown, as is the mode of bonding, thus little can be said about the spectra which is not pure conjecture. Bartlett and Seidel proposed dimer formation for the chloride but offered no suggestions as to how the dimer was bound. Two alternate proposals are offered below:



(2)



(3)

If the halides were in a tetrahedral environment (structure (2)) we might expect spectral data similar to the THF complexes, but this is not the case as evident from Figure 1 where we see the complexes have their highest d–d bands at *c.* 15500 cm^{-1} whereas the halides have bands between 17–20000 cm^{-1} which may or may not be d–d transitions but certainly have no counterpart in the spectra of the complexes. Magnetically, structure (2) would suggest a close analogy to the bis(cyclopentadienyl)-titanium(III) chloride dimer which shows antiferromagnetic behaviour[15] through the double halide bridge. It will be seen later that no decrease of μ_{eff} with decreasing temperature is observed. The alternative, structure (3), offers a potentially square-pyramidal arrangement and this low symmetry system may explain the peak positions in the electronic spectra being at higher energies.

(*d*) *Magnetic Properties*

The variation of magnetic susceptibility with temperature over the range 100–300°K was examined. In the case of the THF complexes (Table 3) the Curie–Weiss law was obeyed with a Weiss constant (θ) between −22°K to −30°K [using the formula $\mu_{eff} = 2{\cdot}83\sqrt{\chi_A(T-\theta)}$] and a temperature-independent paramagnetism (t.i.p.) of *c.* 250 $cm^3\ mol^{-1}$. These data, as well as the resultant values of μ_{eff}, are consistent with a magnetically dilute structure containing one unpaired electron per titanium atom. The low value of μ_{eff} for the iodide is probably due to the partial decomposition of the sample as indicated by the poor analysis.

If a pseudo-tetrahedral stereochemistry is involved, the ^2E ground term gives rise to a t.i.p. of $\chi(\text{t.i.p.}) = 4N\beta^2/10Dq$ if electron delocalization is ignored.[6] Extrapolation of the present data gives χ(t.i.p.) *c.* 250×10^{-6} $cm^3\ mol^{-1}$ from which we obtain $10Dq$ *c.* 4000 cm^{-1}. Even though this is a crude estimate, it suggests that either the absorption bands in the optical spectra (cf. Table 2) are not d–d in their origin, or alternatively, that the stereochemistry is not pseudo-tetrahedral. It should be noted that a t.i.p. term of this size will introduce an appreciable temperature dependence into the magnetic moment since it contributes more than 15% of the total susceptibility at room temperature.

[15] Martin, R. L., and Winter, G., *J. chem. Soc.*, 1965, 4709.

With the solid state magnetic study consistent with a monomeric nature of the complexes, as first indicated by solution molecular weight determinations, and the spectral evidence supporting complexation through the ethereal oxygen atom, as well as the presence of a π-bonded cyclopentadienyl ligand, we propose that the complexes

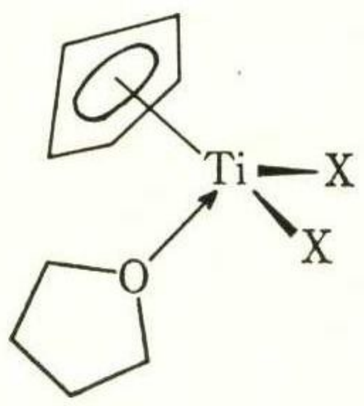
TABLE 3

MAGNETIC DATA FOR COMPLEXES

$(cpTiCl_2,THF),\frac{1}{2}THF$[a]			$cpTiBr_2,THF$[b]			$cpTiI_2,THF$[c]		
T (°K)	$10^6\chi'_M$	μ_{eff}	T (°K)	$10^6\chi'_M$	μ_{eff}	T (°K)	$10^6\chi'_M$	μ_{eff}
293	1510	1·89	292	1346	1·74	293	887	1·45
264	1675	1·89	264	1506	1·79	264	995	1·46
234	1864	1·88	234	1676	1·78	234	1175	1·49
203	2083	1·85	204	1891	1·76	205	1237	1·43
171	2389	1·82	172	2181	1·74	172	1432	1·41
147	2827	1·83	141	2582	1·82	141	1668	1·38
112	3462	1·77	122	3292	1·80	112	2070	1·37
						104	2221	1·37

[a] Ligand correction -106×10^{-6} cm^3 mol^{-1}, θ -30°K, t.i.p. 350×10^{-6} cm^3 mol^{-1}.
[b] Ligand correction -167×10^{-6} cm^3 mol^{-1}, θ -22°K, t.i.p. 250×10^{-6} cm^3 mol^{-1}.
[c] Ligand correction -195×10^{-6} cm^3 mol^{-1}, θ -25°K, t.i.p. 220×10^{-6} cm^3 mol^{-1}.

of the halides probably contain titanium(III) atoms in a pseudo-tetrahedral stereochemistry as shown:



X = Cl, Br, I

The halides displayed interesting magnetic behaviour (Table 4). As mentioned in the Introduction, $cpTiCl_2$ appeared to behave as a magnetically dilute compound,[2] although it had a positive value for its Weiss constant and no observable t.i.p. Examination of the bromide showed that μ_{eff} increased with decreasing temperature, and also had a positive value for the Weiss constant. Re-examination of the data for the chloride shows in fact a similar trend (before the correction for θ was applied) but the effect was not as pronounced. Unfortunately, the iodide could not be prepared sufficiently pure to warrant a magnetic study.

From this preliminary magnetic data it would appear that the halides, as might be expected from their physical properties, are associated in some way. A plot of $1/\chi_M$ against T showed Curie–Weiss law behaviour over most of the range examined, indicating that yet lower temperatures are required before the Curie point is obtained. In the bromide case the deviation at lower temperatures was more evident. It must be stressed that an extension of the temperature range to liquid helium temperature is now required to provide sufficient data to elucidate the nature of the exchange

interaction occurring between neighbouring titanium atoms and to confirm the above provisional comments on stereochemistry and association. It is hoped to perform these magnetic measurements at helium temperature in the near future.

TABLE 4

MAGNETIC DATA FOR HALIDES

cpTiCl$_2$			cpTiBr$_2$		
T (°K)	$10^6\chi'_M$	μ_{eff}	T (°K)	$10^6\chi'_M$	μ_{eff}
322	1149	1·73	293	1314	1·76
298	1260	1·74	264	1509	1·79
273	1383	1·75	234	1728	1·81
247	1533	1·75	205	2033	1·83
220	1730	1·75	173	2442	1·85
190	2028	1·75	142	3044	1·87
158	2502	1·79	107	4305	1·93
121	3403	1·83			

EXPERIMENTAL

General

Manipulations of air-sensitive materials were carried out in a nitrogen-filled glove-box or in vacuum, and all reactions were effected in a stream of purified argon using a Schlenk tube system.[16] Infrared spectra were run in KBr disks protected by pure KBr pressed on either side of the sample, on a Perkin–Elmer 521 spectrophotometer. Visible spectra were measured in tetrahydrofuran solution in a Beckman DK2 spectrophotometer or in the solid state by using a reflectance attachment on a Beckman DK 2A spectrophotometer. Magnetic susceptibilities were determined by the Gouy method and molecular weight values obtained in a Gallenkamp ebulliometer modified to take a 3·5-ml cell.

Analyses

Titanium was estimated by ashing a hydrolysed, sulphated pellet of the sample. Halides were determined by the Volhard method. Carbon and hydrogen were determined by the Australian Microanalytical Service, Melbourne, by burning weighed pellets sealed in aluminium capsules.

Materials

The cyclopentadienyltitanium(IV) halides were prepared from the trialkoxides by reaction with acyl halides.[17]

ACKNOWLEDGMENTS

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SULPHUR DIOXIDE INSERTION REACTIONS WITH DICYCLOPENTADIENYLTITANIUM AND -ZIRCONIUM ALKYL AND ARYL COMPOUNDS

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SUMMARY

Sulphur dioxide was found to react in the expected manner with alkyl- and aryldicyclopentadienyltitanium compounds to yield the red monomeric *O*-sulphinates $(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2$, $(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)Cl$, and $(\pi\text{-}C_5H_5)_2Ti(O_2SC_6H_5)_2$. With dicyclopentadienylzirconium compounds, the sulphur dioxide inserts into the zirconium–alkyl bond and also into the zirconium–cyclopentadienyl bond in certain cases, even though the cyclopentadienyl group is π-bonded to zirconium. The preparations of the *O*-sulphinates $[\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)Cl]_n$, $[\pi\text{-}C_5H_5(C_5H_5SO_2)ZrO]_n$ and $[\pi\text{-}C_5H_5(C_5H_5SO_2)ZrSO_3]_n$ are reported.

INTRODUCTION

While alkyl and aryl derivatives of Zr and especially Ti have been known for some time, the reactivity of these compounds towards sulphur dioxide has never been studied. In this paper the reactions of SO_2 with several dicyclopentadienyl compounds of Ti^{IV} and Zr^{IV} are reported.

RESULTS AND DISCUSSION

(*a*). *Titanium compounds*

The reaction of solid $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ and SO_2 at solid CO_2/EtOH temtemperatures is too vigorous and results in a large amount of decomposition of the dimethyl compound. To moderate the reaction, the alkyltitanium was dissolved in light petroleum or in CH_2Cl_2 and gaseous SO_2 condensed into the solution.

When light petroleum is used as solvent, the product precipitates as a dark red oil which slowly solidifies on standing. On the basis of elemental analysis, molecular weight in chloroform, and NMR spectrum, the product was considered to be dicyclopentadienyltitanium bis(methanesulphinate) formed according to eqn. (1).

$$(\pi\text{-}C_5H_5)_2Ti(CH_3)_2 + 2\,SO_2 \xrightarrow[\text{solvent}]{-78^\circ} (\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2 \qquad (1)$$

With dichloromethane as solvent, the product, which is very soluble in this solvent, may be obtained as an orange-red solid after removing the dichloromethane

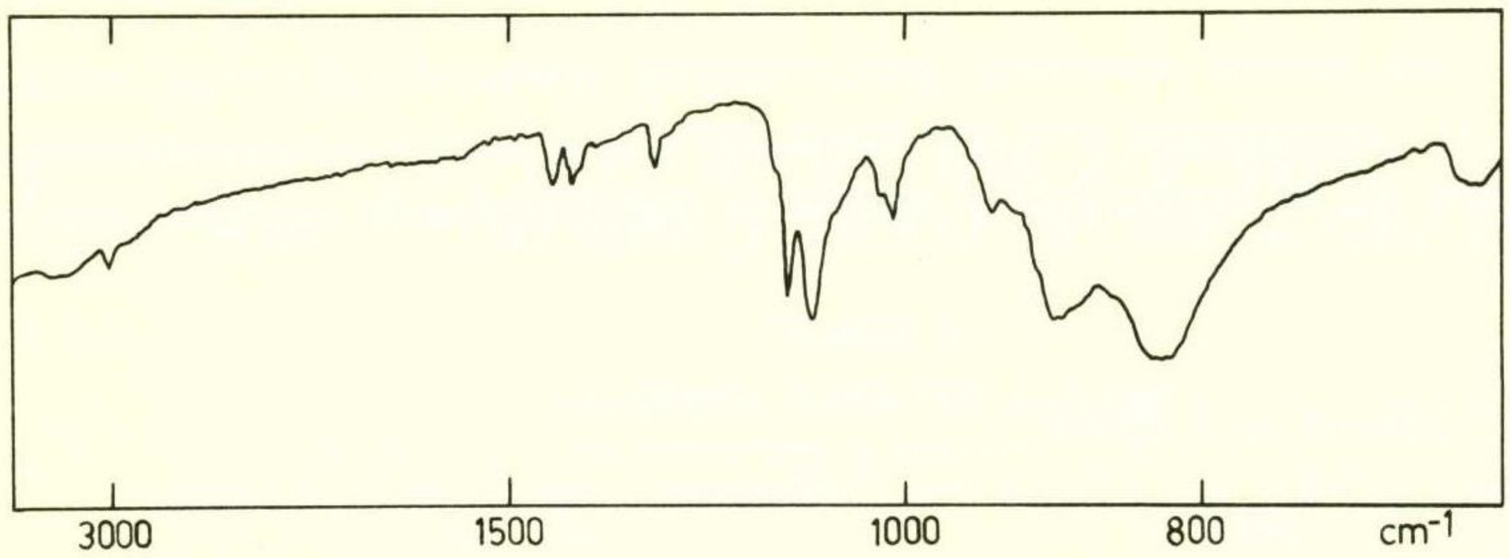


Fig. 1. IR spectrum of $(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2$ (KCl disc).

under reduced pressure. The IR spectrum of this compound (and in fact all other compounds investigated) in the SO_2 absorption region is similar in either KCl mull, chloroform or nujol. The peaks which can be assigned to the sulphinate moiety are found at 1115, 1090 and 885 cm^{-1}, indicating that the methanesulphinate groups are *O*-bonded to titanium[1] (Fig. 1). This of course is not unexpected in view of the high affinity which Ti shows for oxygen. The relatively large separation in the energy of the S–O stretching vibrations suggests that the sulphinate may not be symmetrically bound through both oxygens to the metal.

Reaction of $(\pi\text{-}C_5H_5)_2Ti(CH_3)Cl$ with SO_2 is much less vigorous and hence can be carried out by condensation of the SO_2 on to solid $(\pi\text{-}C_5H_5)_2Ti(CH_3)Cl$ cooled in a solid CO_2/ethanol bath. The product, which was shown to be dicyclopentadienylmonochlorotitanium methanesulphinate was isolated after evaporation of SO_2 as a red oil which solidified slowly on standing. Again, as in the dimethyl case above, if the reaction is carried out in CH_2Cl_2 the product is obtained as an orange-red solid.

The bands in the IR spectrum at 1090, 1070 and 872 cm^{-1} could be assigned to the S–O stretching vibrations. On this basis the compound was considered to be an *O*-sulphinate. The NMR spectrum in $CDCl_3$ of the compound prepared in CH_2Cl_2 was interesting in that the C_5H_5 and the methyl peaks were both split, the bands being at δ 6.62 and 6.55 ppm for the C_5H_5 and at δ 2.43 and 2.48 ppm for the methyl. The intensities of the C_5H_5 and CH_3 bands at lower field were approximately 50% of those of the higher field bands and this intensity ratio was consistent from preparation to preparation in SO_2 or in CH_2Cl_2. The ratio of the integrated intensities of the two sets of bands was C_5H_5/CH_3 9.6/3, which together with elemental analyses and a monomeric molecular weight in chloroform, is in good agreement with the suggested formula $(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)Cl$. In view of these results it seems likely that two isomers are present, possibly and *O*,*O*′-sulphinate as well as an *O*-sulphinate.

An equilibrium of the type:

$$2\,(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)Cl \rightleftarrows (\pi\text{-}C_5H_5)_2TiCl_2 + (\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2$$

can be discounted since only two C_5H_5 absorptions were found.

SO_2 will also insert into $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ to form the red bis(benzenesulphinato) compound. Insertion will not occur in dichloromethane as solvent at solid CO_2/EtOH temperatures, but only on allowing the solution to warm up to room temperature. The compound is monomeric in chloroform. The NMR spectrum in C_6D_6 has a sharp C_5H_5 singlet at δ 6.11 ppm (intensity 10) and two complex multiplets due to the phenyl groups, one centred at δ 7.78 ppm (intensity 4) and the other at

δ 7.10 ppm (intensity 6) which can be ascribed to the *ortho* and *meta* + *para* hydrogens respectively of the phenyl groups. The IR spectrum of the compound has two bands in the S–O asym. stretching region at 1092 and 1060 cm^{-1}, and a broad shoulder centred at approximately 880 cm^{-1} on the high energy side of the strong π-C_5H_5 band at 815 cm^{-1}.

(*b*). *Zirconium compounds*

At the time of this investigation there were no known organometallic sulphinato compounds of zirconium. Recently Lindner *et al.*[2] prepared $(\pi\text{-}C_5H_5)_2Zr(O_2SCH_3)_2$ by the reaction of CH_3SO_2Na with $(\pi\text{-}C_5H_5)_2ZrCl_2$ in THF. They suggest, on the basis of the S–O absorptions in the IR that it is an *O,O'*-sulphinato complex. When the reaction was carried out in boiling ethanol for 12 h, the cyclopentadienyls were displaced from the zirconium giving $Zr(O_2SCH_3)_4$. This of course is not surprising as the cyclopentadienyl groups on zirconium are relatively labile. Their lability is highly dependent on the nature of the other groups attached to the zirconium. The more electron donating the group, the higher the ionicity of the π-C_5H_5–Zr bond and hence the higher the lability of the cyclopentadienyls. Thus, $(\pi\text{-}C_5H_5)_2ZrCl_2$ is stable to moisture and may be refluxed with methanol for some hours without appreciable decomposition. However after 1 h in boiling ethanol $(\pi\text{-}C_5H_5)_2Zr(OCOCH_3)_2$★ is converted quantitatively to $(EtO)_2Zr(OCOCH_3)_2$. Similarly, $(\pi\text{-}C_5H_5)_2Zr(O\text{-}i\text{-}Pr)_2$ will dissolve in cold isopropanol to give $Zr(O\text{-}i\text{-}Pr)_4$[3].

The difference in behaviour of $(C_5H_5)_2ZrH_2$ with acetic acid to form π-C_5H_5-$Zr(OCOCH_3)_3$, and with trifluoroacetic acid to give $(\pi\text{-}C_5H_5)_2Zr(OCOCF_3)_2$ can also be rationalised on the basis of the higher basicity of the acetato group over the trifluoroacetato group[3].

Thus, we believe that the ethanol plays an important part in the reaction of $(\pi\text{-}C_5H_5)_2ZrCl_2$ with CH_3SO_2Na. The reaction:

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 4\ CH_3SO_2Na \xrightarrow[12\ h]{\text{Reflux in EtOH,}} Zr(O_2SCH_3)_4 + 2\ NaCl + 2\ NaC_5H_5$$

is probably more correctly considered as being a series of reactions, namely:

$$(\pi\text{-}C_5H_5)_2ZrCl_2 + 2\ CH_3SO_2Na \rightarrow (\pi\text{-}C_5H_5)_2Zr(O_2SCH_3)_2 + 2\ NaCl$$
$$(\pi\text{-}C_5H_5)_2Zr(O_2SCH_3)_2 + 2\ C_2H_5OH \rightarrow (C_2H_5O)_2Zr(O_2SCH_3)_2 + 2\ C_5H_6$$
$$(C_2H_5O)_2Zr(O_2SCH_3)_2 + 2\ (CH_3SO_2)Na \rightarrow Zr(O_2SCH_3)_4 + 2\ C_2H_5ONa$$

The majority of the C_5H_6 generally escapes from the reaction mixture as the monomer has a boiling point of only 42°. Certainly, C_5H_5Na is not stable in ethanol.

In this study we attempted to insert SO_2 into Zr–C bonds rather than using the ligand exchange reactions such as Lindner *et al.* used. Further, if the ionicity of the C_5H_5–Zr band is increased on forming the sulphinato compound, as postulated above, it may well be possible to insert a further SO_2 group between the zirconium and the π-C_5H_5 groups, a process which appears not to have been observed before.

When $(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$ was treated with SO_2, the expected product (π-

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★ Prepared by refluxing $(\pi\text{-}C_5H_5)_2ZrCl_2$ with excess $NaOCOCH_3$ in benzene and then recrystallizing it from a benzene/light petroleum solution; NMR, π-C_5H_5, δ 6.32 ppm; CH_3, δ 2.03 ppm in $CDCl_3$.

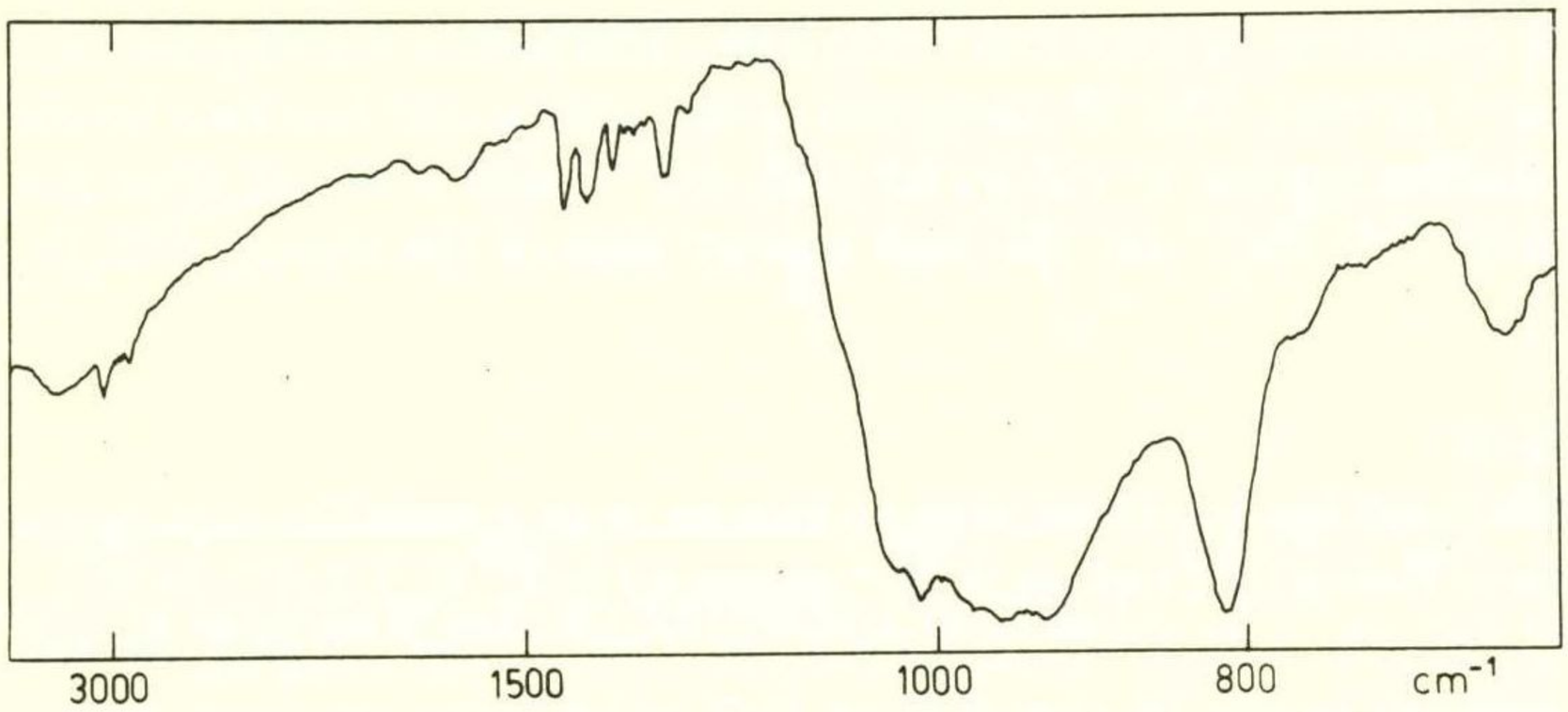


Fig. 2. IR spectrum of π-$C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)Cl$ (KCl disc).

$C_5H_5)_2Zr(O_2SCH_3)Cl$ was not obtained. Instead, a pale yellow product analysing for $(\pi$-$C_5H_5)_2Zr(CH_3)Cl \cdot 2\,SO_2$, and which we believe is π-$C_5H_5(C_5H_5SO_2)Zr$-$(O_2SCH_3)Cl$ was obtained. Both sulphinato groups appear to be oxygen-bonded as the S–O stretching absorptions are all strong, the maxima occurring at 1041, 980 (sh), 955 and 925 cm^{-1}. No other strong absorption which may be associated with an S–O moiety were observed in the IR spectrum (Fig. 2).*

It would appear that the reaction involves firstly the insertion of an SO_2 group between the metal and the methyl group to form $(\pi$-$C_5H_5)_2Zr(O_2SCH_3)Cl$. Now, the ionicity of the C_5H_5–Zr bond is increased sufficiently to allow the SO_2 to react across it, the electrophilic sulphur reacting with the C_5H_5 and the oxygens with the zirconium. This reaction of course, parallels the reaction pathway of the ionic C_5H_5–Zr bond with, for example, ethanol or acetic acid.

TABLE 1

NMR POSITIONS OF THE C_5H_5 PROTONS IN SOME ZIRCONIUM COMPOUNDS

	δ (ppm) in $CDCl_3$	δ (ppm) in C_6D_6
$(\pi$-$C_5H_5)_2ZrCl_2$	6.52	5.83
$(\pi$-$C_5H_5)_2Zr(OC_6H_5)_2$	6.35	5.88
$(\pi$-$C_5H_5)_2Zr(OCH_3)Cl$	6.35	
$(\pi$-$C_5H_5)_2Zr$(O-i-Pr)Cl	6.33	6.00
$(\pi$-$C_5H_5)_2Zr(OC_2H_5)Cl$	6.32	5.90
$[(\pi$-$C_5H_5)_2ZrCl]_2O$	6.28	5.89
$(\pi$-$C_5H_5)_2Zr(CH_3)Cl$	6.27	5.73
$(\pi$-$C_5H_5)_2Zr$(O-i-Pr)$_2$	6.17	5.95

Since $(\pi$-$C_5H_5)_2ZrCl_2$ is reasonably stable to ethanol and water, and only reacts with acetic acid under refluxing conditions[4] when the side products are removed from the reaction medium, it was considered unlikely that the cyclopentadienyl groups in $(\pi$-$C_5H_5)_2ZrCl_2$ were sufficiently reactive to insert SO_2. This was

* The possibility of SO_2 addition to the cyclopentadienyl ring was considered and discarded, largely on the basis of the IR spectral evidence. Any type of addition would, we believe, cause IR absorption different to that observed.

in fact found to be the case, as the $(\pi\text{-}C_5H_5)_2ZrCl_2$ could be recovered unchanged from liquid SO_2 at room temperature after periods exceeding 10 days.

The position of the cyclopentadienyl peak in the spectrum of $(\pi\text{-}C_5H_5)_2TiX_2$ type compounds has been used as a guide to the ionicity of the metal–C_5H_5 bond[5]. This can also be applied to cyclopentadienyl zirconium compounds. However, it should be pointed out that the NMR spectra in perdeutero benzene (and presumably other aromatic solvents) cannot be used as a guide to the ionicity of the Zr–C_5H_5 bond. C_6D_6 (see Table 1) has a drastic effect on the position of the C_5H_5 bands, moving them upfield. The bridged oxide $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ has the C_5H_5 absorption at δ 6.24 ppm while $(\pi\text{-}C_5H_5)_2ZrCl_2$ absorbs at δ 6.41 ppm in the same solvent, *viz.* dichloromethane. Accordingly this bridged oxide was treated with SO_2.

When SO_2 was bubbled through a methylene dichloride solution of $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ an insoluble white precipitate analyzing for $(C_5H_5)_2ZrO_3S$ was formed, together with the soluble $(\pi\text{-}C_5H_5)_2ZrCl_2$. The sulphur-containing compound had a strong band at 708 cm^{-1} in the IR which can be assigned to a Zr–O–Zr stretching vibration. This band occurs at 750–775 cm^{-1} in the bridged oxide. On treatment of this compound with acid, no sulphur dioxide is evolved, so that the compound is not a sulphite, but in fact an oxygen-bridged zirconium compound. The bands in the IR that are associated with the SO_2 stretching vibrations occur at 1157 cm^{-1} and at 918 and 902 cm^{-1} (see Fig. 3). The large separation between the bands would suggest that the SO_2 group is present in the complex as an unsymmetrically bonded *O*-sulphinate which is possibly bridging to another zirconium atom through the sulphur. This possibility was suggested by Chatt and Mingos[6] to explain IR absorption at 1200 and 950 cm^{-1} in certain platinum compounds. We believe therefore that the SO_2 has inserted between the Zr and what was initially a π-bonded-C_5H_5.

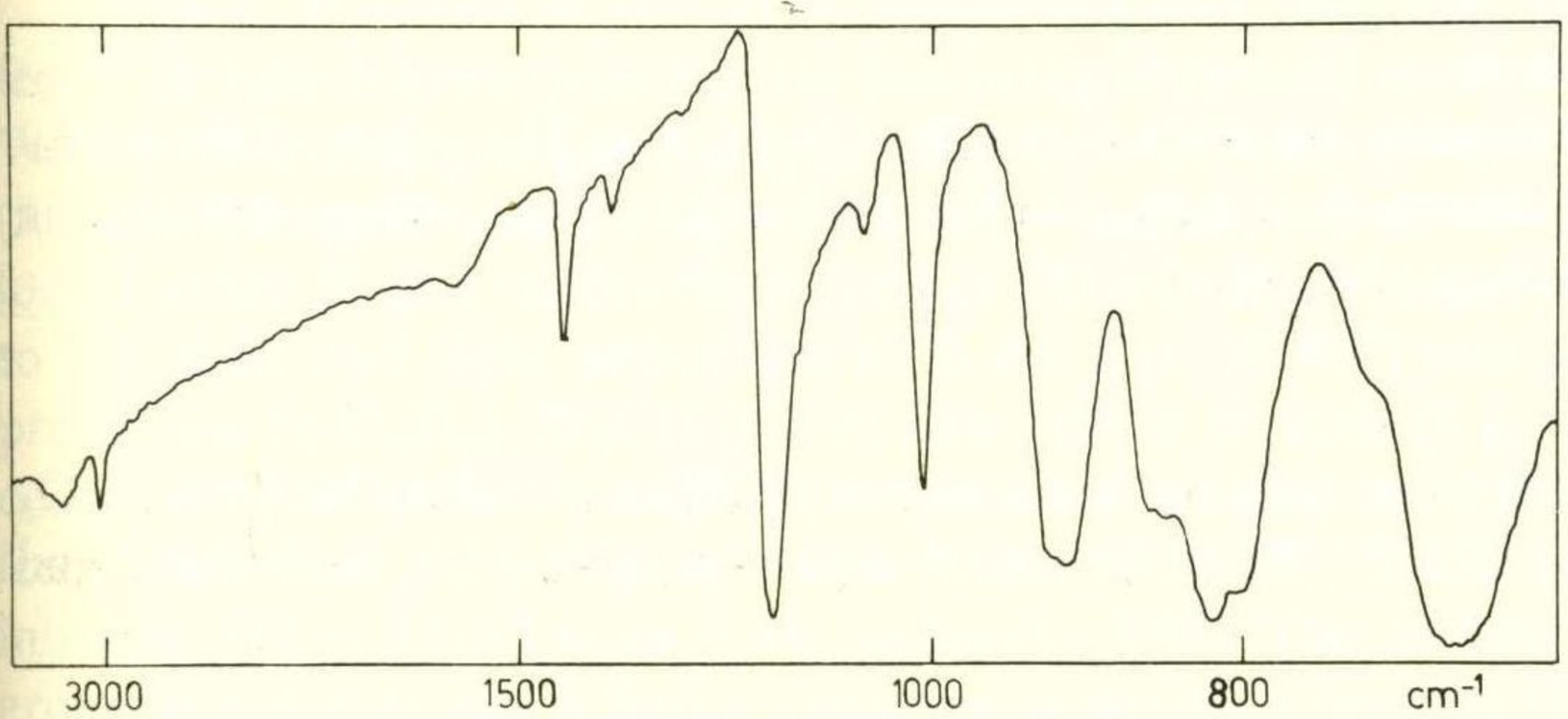


Fig. 3. IR spectrum of $[\pi\text{-}C_5H_5(C_5H_5SO_2)ZrO]_n$ (KCl disc).

The reaction for the formation of this bridged oxide sulphinato complex may be written as:

$$n\,[(\pi\text{-}C_5H_5)_2ZrCl]_2O + n\,SO_2 \rightarrow [(\pi\text{-}C_5H_5)(C_5H_5SO_2)\,ZrO]_n + n(\pi\text{-}C_5H_5)_2ZrCl_2$$

This sulphinato complex will react further with SO_2 at room temperature over a period of several days, forming a compound which analyzes for $(C_5H_5)_2ZrO \cdot 2\,SO_2$. This compound, insoluble in liquid SO_2, does not have an IR band which can be associated with the Zr–O–Zr moiety. Furthermore, on treatment with acid, it is decomposed liberating SO_2. The IR spectrum now shows one very broad and intense

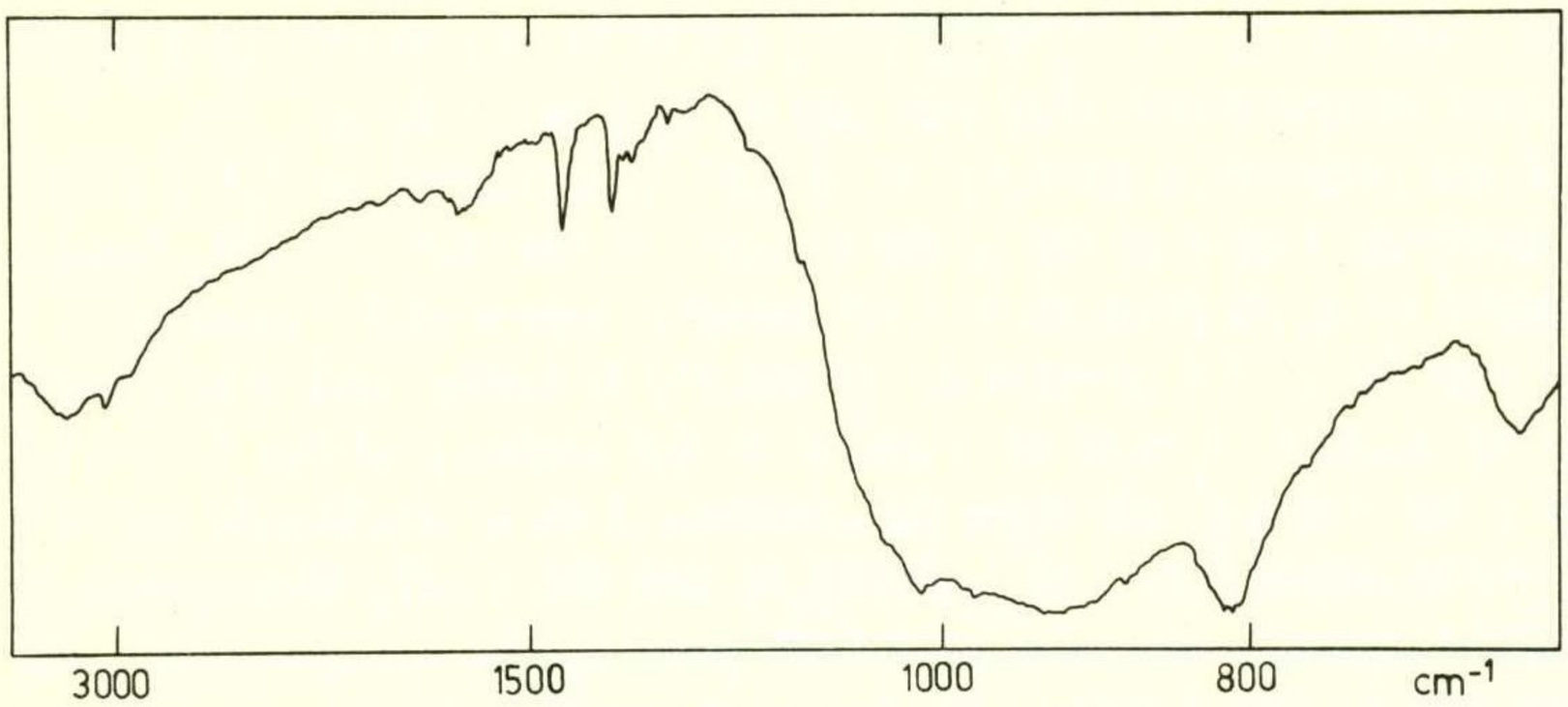


Fig. 4. IR spectrum of $[\pi\text{-}C_5H_5(C_5H_5SO_2)ZrSO_3]_n$ (KCl disc).

band between 1100 and 850 cm^{-1} which may be assigned to S–O stretches (Fig. 4). We therefore consider the compound to be a sulphite and the sulphinato group to be bidentate through the oxygens. Thus the reaction of the sulphinato oxide compound with SO_2 can be written as:

$$[(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrO]_n + n\ SO_2 \rightarrow \frac{n}{m}[(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrSO_3]_m$$

It was not possible to insert an SO_2 molecule between the second π-C_5H_5 group and the metal even by allowing the reactants to stand at room temperature for up to 10 days.

We are continuing our investigations of SO_2 insertions including into Ti–OR and Zr–OR bonds.

EXPERIMENTAL

NMR

The NMR spectra were measured on either the Varian HA 100 or T60 instruments using tetramethylsilane as internal calibrant in all solvents except benzene in which hexamethyldisiloxane was used.

Solvents

C_6D_6 was distilled from $LiAlH_4$ under argon; $CDCl_3$ was distilled from P_2O_5 under argon as was the CH_2Cl_2 after first washing it with Na_2CO_3 and water and drying with $CaCl_2$.

General

All reactions were carried out under Ar or N_2; $(\pi\text{-}C_5H_5)_2ZrCl_2$ was obtained from Arapahoe Chemicals, Inc.; $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ was prepared by the previously published method[7]. The SO_2 was obtained from BDH. Reactions with SO_2 at room temp. were carried out in a tube containing a magnetic stirring bar and sealed with a threaded glass valve with Teflon stem. Analyses were carried out by the Australian Microanalytical Service.

Preparations

$(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$. This was prepared by the method of Clauss and Bestian[8] with minor modifications. The methyllithium solution was added over less than 5 min

to $(\pi\text{-}C_5H_5)_2TiCl_2$ (11.5 g) suspended in ether (70 ml) and cooled in ice. The NMR spectrum of the product in C_6D_6 showed peaks at δ 5.65 (C_5H_5) and 0.02 ppm (CH_3).

$(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)_2$. Sulphur dioxide was bubbled into a solution of $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ (2 g) in CH_2Cl_2 cooled in a solid CO_2/EtOH bath. The colour deepened to red but no precipitate was formed even at $-78°$. Removal of SO_2 and solvent gave the bis(methanesulphinate) as an orange-red solid. (Found: C, 40.3; H, 4.8; S, 19.4; Ti, 14.2; mol.wt. ebulliometric in $CHCl_3$, 322. $C_{12}H_{16}O_4S_2Ti$ calcd.: C, 42.89; H, 4.80; S, 19.07; Ti, 14.24%; mol.wt., 336.3.) NMR, $\pi\text{-}C_5H_5$, δ 6.57 ppm; CH_3, δ 2.48 ppm in $CDCl_3$.

$(\pi\text{-}C_5H_5)_2Ti(O_2SCH_3)Cl$. Excess SO_2 was condensed into a solution of $(\pi\text{-}C_5H_5)_2Ti(CH_3)Cl$ (2 g, prepared by the method of Clauss and Bestian[8]) in CH_2Cl_2 (30 ml) cooled to $-78°$. The reaction mixture was allowed to warm to room temperature and the solvent was removed under reduced pressure to give an orange-red solid. (Found: C, 45.0; H, 4.6; S, 10.8; Ti, 16.3; mol.wt. ebulliometric in $CHCl_3$, 296. $C_{11}H_{13}ClO_2STi$ calcd.: C, 45.14; H, 4.48; S, 10.96; Ti, 16.37%; mol. wt., 292.6)

$(\pi\text{-}C_5H_5)_2Ti(O_2SC_6H_5)_2$. Liquid SO_2 was condensed on to $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ [prepared by the method of Summers, Uloth and Holmes[9], NMR (C_6D_6), δ 5.68 (singlet, C_5H_5) and 6.92 ppm (multiplet, C_6H_6)] cooled in solid CO_2/EtOH, and the SO_2 was then allowed to distil off leaving the bis(benzenesulphinate) as a dark red oil which slowly solidified. (Found: C, 56.8; H, 4.4; S, 13.7; Ti, 10.7; mol.wt. ebulliometric in $CHCl_3$, 498. $C_{22}H_{20}O_4S_2Ti$ calcd.: C, 57.37; H, 4.38; S, 13.93; T, 10.40%; mol.wt., 460.4.)

In CH_2Cl_2 sulphur dioxide will not insert into $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ at $-78°$ but reacts readily at room temperature giving the bis(benzenesulphinate). Care must be taken not to heat the sulphinate above 50°, at which temperature it melts to a red oil.

$(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$. This compound was originally prepared by J. R. Surtees[10] of these laboratories but the following improved method is due to Adcock and Wailes. To a slurry of $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ in CH_2Cl_2 (80 ml) was added $Al_2(CH_3)_6$ (5.5 ml). The oxide rapidly dissolved to give a pale yellow solution which was stirred for a further 30 min before diethyl ether (30 ml) was added. Solvent was pumped off to low bulk and light petroleum (100 ml. b.p. 30–40°) was added with stirring to precipitate $(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$ as pale yellow crystals (8 g, 75% yield) which were collected by filtration in an inert atmosphere, washed several times with light petroleum and dried by pumping under vacuum at 40°. NMR (C_6D_6), δ 5.73 (C_5H_5, intensity 10) and 0.32 ppm (CH_3, intensity 2.99). The compound is very soluble in aromatic solvents and is highly sensitive to moisture forming the bridged oxide again with elimination of methane.

$(\pi\text{-}C_5H_5)(C_5H_5SO_2)Zr(O_2SCH_3)Cl$. $(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$ (2 g) was dissolved in 15 ml of SO_2 in a Schlenk flask cooled in solid CO_2/EtOH. The cooling bath was removed and SO_2 allowed to evaporate over a period of several hours before removing the last traces by pumping. The product was a white solid. (Found: C, 32.7; H, 3.2; Cl. 9.0; S, 15.7; Zr, 23.4. $C_{11}H_{13}ClO_4S_2Zr$ calcd.: C, 33.08; H, 3.26; Cl, 8.87; S, 16.03; Zr, 22.81%.)

$[(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrO]_n$. $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ (8.5 g) was dissolved in CH_2Cl_2 (130 ml) and a steady stream of SO_2 was passed through the solution. After about 1–2 min the solution suddenly became cloudy. Passage of SO_2 was continued for a further 15 min during which the solution became slightly warm and precipitation

continued. The supernatant liquid was decanted from the dense white precipitate, which was then washed with several 50 ml aliquots of CH_2Cl_2. After drying by pumping, 4.0 g of product (83 % yield) was obtained. The compound is air-stable. (Found: C, 39.8; H, 3.4; S, 10.4; Zr, 30.4. $C_{10}H_{10}O_3SZr$ calcd.: C, 39.84; H, 3.34; S, 10.64; Zr, 30.23 %.)

$[(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrSO_3]_n$. $[(\pi\text{-}C_5H_5)(C_5H_5SO_2)ZrO]_n$ (2 g) was sealed in a tube containing 20 ml of liquid SO_2 and the mixture was stirred at room temperature for 4 to 10 days. A gel formed from which the last traces of SO_2 could be removed only by heating to 70° for several hours under vacuum. The sulphite was off-white in colour and hygroscopic. (Found: C, 33.4; H, 2.9; S, 18.2; Zr, 24.9. $C_{10}H_{10}O_5S_2Zr$ calcd.: C, 32.86; H, 2.76; S, 17.54; Zr, 24.96 %.)

The same product was obtained when $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ was treated with SO_2 at room temperature for several days. The SO_2 solution remained clear for 20–30 min and then slowly formed a gel. Continuous extraction with THF in a Soxhet apparatus for several hours left the pure sulphite undissolved.

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INSERTION REACTIONS OF DICYCLOPENTADIENYLDIMETHYLZIRCONIUM AND RELATED CYCLOPENTADIENYL COMPOUNDS WITH SULPHUR DIOXIDE AND NITRIC OXIDE

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SUMMARY

The reactions of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ are characterized by lability of the methyl groups, one or both of which may be displaced by reaction with hydrogen, phenylacetylene, methanol or lead chloride. Sulphur dioxide will insert between both methyl groups and the zirconium atom and also between one of the cyclopentadienyl ligands and the metal atom. Nitric oxide will insert between one of the methyls and the zirconium leading to a novel zirconium complex of methylnitrosohydroxylamine. Insertion reactions of SO_2 and NO were also observed with the monomethyl derivative $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$, and with $(C_5H_5)_4Zr$.

INTRODUCTION

Since the first stable alkylzirconium compounds were prepared in the early 1960's many more have been isolated. However, to date, very little work has been published on the reactions and reactivity of the zirconium–carbon linkage. In this paper the preparation of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ is reported and some of its reactions and the reactions of several related cyclopentadienyl derivatives of both titanium and zirconium are discussed.

RESULTS AND DISCUSSION

Dicyclopentadienyldimethylzirconium, $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (I), was prepared from $(\pi\text{-}C_5H_5)_2ZrCl_2$ and methyllithium. In contrast to the thermal instability of the corresponding titanium derivative[1], the dimethylzirconium compound is stable to heat and is best purified by sublimation under high vacuum at 100–110°. Although stable towards dry oxygen and carbon dioxide, (I) is very sensitive to hydroxylic compounds and so is hydrolysed in air giving methane and oxygen-bridged compounds such as $[(C_5H_5)_2ZrCH_3]_2O$ and $[(C_5H_5)_2ZrO]_n$ which react further, losing cyclopentadiene and giving mixtures of products.

In like manner the methyl group of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ (II) is hydrolytically unstable but in this case the well known oxide $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$[2] is the stable end-product. This behaviour contrasts sharply with the great stability of $(\pi\text{-}C_5H_5)_2$-

TABLE 1

NMR SHIFTS FOR $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (RELATIVE TO TMS)

Solvent	$\delta(C_5H_5)$ (ppm)	$\delta(CH_3)$ (ppm)
C_6D_6	5.80	−0.14
C_6F_6	6.05	−0.57
$CHCl_3$	6.08	−0.39
CH_2Cl_2	6.08	−0.40
Cyclohexane	6.03	−0.33
C_5D_5N	6.12	−0.18

$Ti(CH_3)_2$ towards water and alcohols[1]. Both the zirconium and titanium dimethyl derivatives are quite soluble in petroleum and all common organic solvents. The chemical shifts of the cyclopentadienyl protons in the NMR spectrum of (I) remain almost constant in all solvents except benzene. The large upfield shift observed in this solvent appears to be a general phenomenon occurring with all of the dicyclopentadienyltitanium and -zirconium derivatives studied. The positions of the C_5H_5 and CH_3 protons in the NMR spectra of (I) in a variety of solvents are shown in Table 1. The infrared spectrum of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (KCl disc) is shown in Fig. 1.

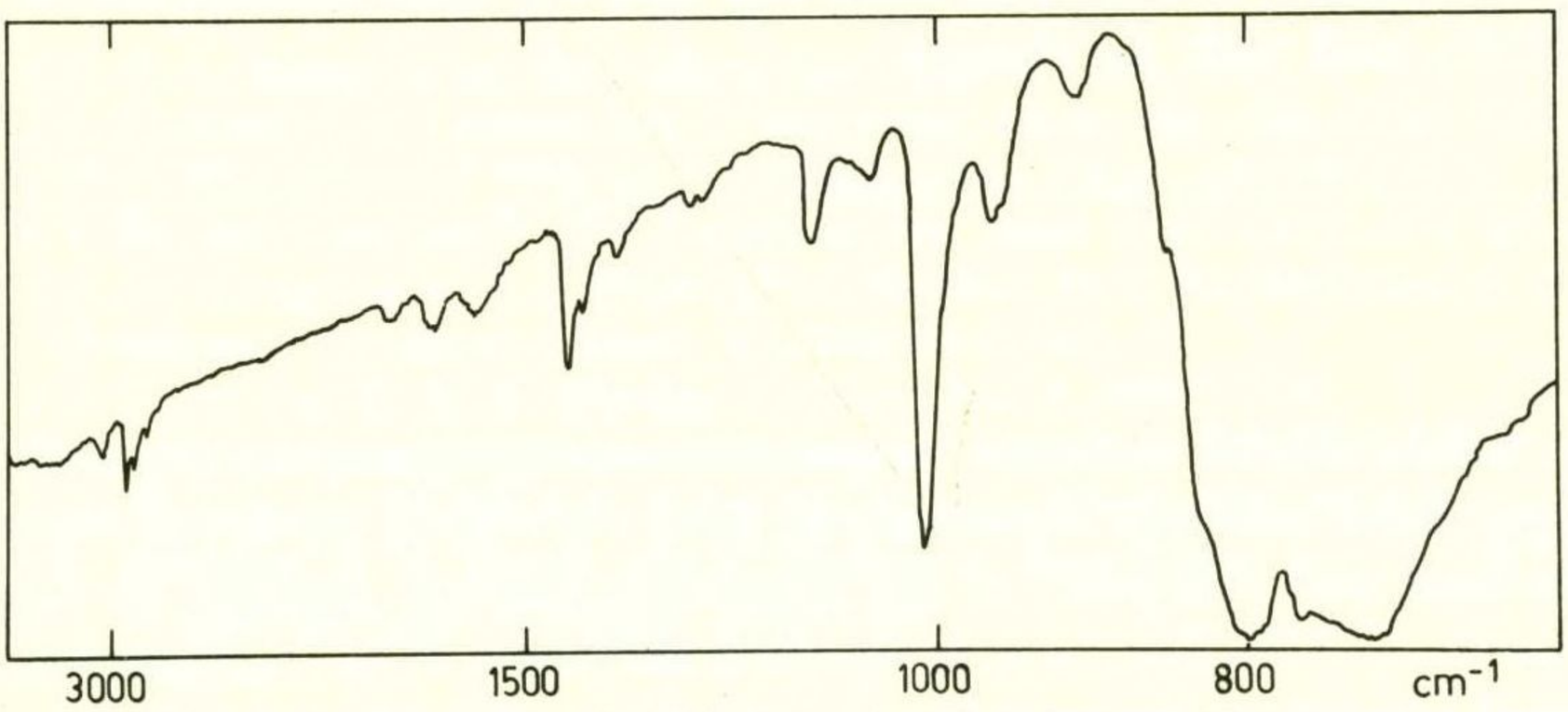


Fig. 1. Infrared spectrum (KCl disc) of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (I).

Reaction with hydrogen

While $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ reacts with hydrogen in solution to give titanocene[1] and in the solid state to give $[(\pi\text{-}C_5H_5)_2TiH]_2$[3], $(\pi\text{-}C_5H_5)_2Ti(Cl)CH_3$ did not react even in petrol at 100–120°. The corresponding monomethylzirconium chloride compound was also inert to hydrogen but the dimethyl derivative was hydrogenated in petrol above 110°. The crimson coloured product contained one methyl group per zirconium and analyzed approximately for $[(\pi\text{-}C_5H_5)_2ZrCH_3]_2$. Since the infrared spectrum showed the normal bands associated with symmetrically bonded cyclopentadienyl groups, the methyl groups are probably bridging.

Reaction with phenylacetylene

With phenylacetylene in boiling toluene over a period of one day $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ reacted slowly to give, besides the starting material, both the mono- and diacetylide, presumably with elimination of methane.

Reaction with methanol

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ with methanol proceeded readily with elimination of methane and the formation of methoxides. If the reaction was carried out stoichiometrically in deuterochloroform using methanol diluted with the same solvent, the initial product was the monomethoxide (III).

$$(\pi\text{-}C_5H_5)_2Zr(CH_3)_2 + CH_3OH \xrightarrow{\text{fast}} (\pi\text{-}C_5H_5)_2Zr(OCH_3)CH_3 + CH_4$$
(III)

The methoxide (III) was identified by its NMR spectrum, in which the C_5H_5 protons showed as a sharp singlet at δ 6.22 ppm (relative intensity 10). Two other bands were present each of relative intensity 3 at δ 3.78 ppm (due to the OCH_3 group) and at δ 0.04 ppm (due to the CH_3 bonded to zirconium).

Addition of a second equivalent of methanol was followed by a slow decrease in the intensity of the bands due to $(\pi\text{-}C_5H_5)_2Zr(OCH_3)CH_3$ and the appearance of two new bands at δ 6.02 and 3.81 ppm due to the dimethoxide. Surprisingly the peak at δ 0.04 ppm due to the $ZrCH_3$ group was still observable even after several hours. In fact a white precipitate identified as the tetramethoxide $Zr(OCH_3)_4$, formed during this period. It is apparent that alcoholysis of the $Zr-C_5H_5$ bonds, presumably in the dimethoxy derivative, occurred at a rate comparable with that of the reaction of the $ZrCH_3$ groups in $(\pi\text{-}C_5H_5)_2Zr(OCH_3)CH_3$ with methanol*.

Reaction with lead dichloride

In chloroform or benzene at room temperature $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ was found to react with $PbCl_2$ to give firstly $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ and then $(\pi\text{-}C_5H_5)_2ZrCl_2$. During the reaction metallic lead was precipitated. By observation of changes in the NMR spectrum of the reaction mixture it was established that formation of the monomethyl product was quite fast, in fact the presence of metallic lead was noted after mixing the solid reactants. Further reaction of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ with $PbCl_2$ was slow and appreciable amounts of the dichloride were present only after reaction periods in excess of 1 day. In fact it was possible to convert the dimethyl derivative almost quantitatively to the monomethylzirconium chloride by vigorous stirring over one hour with a stoichiometric amount of $PbCl_2$. One more peak at δ 0.74 ppm in $CDCl_3$ appears in the NMR spectrum at a growth rate comparable with that of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$. The presence of two satellite peaks approximately 31 Hz either side of the main resonance indicates the presence of a methyllead compound, in particular $Pb(CH_3)_4$. The reaction scheme is shown below:

$$4(\pi\text{-}C_5H_5)_2Zr(CH_3)_2 + 2\,PbCl_2 \xrightarrow{\text{fast}} 4(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3 + Pb + Pb(CH_3)_4$$
(II)

$$4(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3 + 2\,PbCl_2 \xrightarrow{\text{slow}} 4(\pi\text{-}C_5H_5)_2ZrCl_2 + Pb + Pb(CH_3)_4$$

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* Activation of $Zr-C_5H_5$ bonds to hydrolytic type cleavage by the presence of alkoxy groups on zirconium has been established in previous papers[4,5].

The amount of lead required by this scheme could be recovered at the end of each reaction.

Reactions with sulphur dioxide

When $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ was dissolved in SO_2 at solid CO_2/EtOH temperatures and the SO_2 was allowed to evaporate, the yellow product obtained corresponded in analysis to $(C_5H_5)_2Zr(CH_3)_2 \cdot 3SO_2$. The compound was not a sulphite and not an adduct of SO_2. The infrared spectrum of the product in nujol mull or in KCl disc showed a broad strong band between 1100 and 800 cm^{-1} associated with S–O stretches and C_5H_5 vibrations and similar to the spectrum of $\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)Cl$[5]. From this data and by analogy with the reactions of SO_2 with $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ and $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$ reported in a previous paper[5], the product now obtained was considered to be $\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)_2$ (IV). Insertion of SO_2 between the zirconium and the cyclopentadienyl ligand occurred even when reaction and removal of SO_2 were carried out at $-78°$. The insolubility of the compound in non-interacting solvents meant that its NMR spectrum could not be measured and attempts to obtain the spectrum in liquid SO_2 were hampered by further reaction with this solvent. At room temperature in liquid SO_2 a yellow precipitate formed from which sulphur dioxide was liberated on treatment with sulphuric acid. The infrared spectrum showed broad strong absorption between 1100 and 850 cm^{-1}, while the band at 800 cm^{-1} usually very strong in most cyclopentadienyl compounds, was quite weak. From this data the complex was considered to be an *O*-sulphinato-zirconium sulphite (V) formed according to the scheme:

$$(\pi\text{-}C_5H_5)_2Zr(CH_3)_2 + 3\,SO_2 \xrightarrow[<-10°]{\text{liq. } SO_2} \underset{\text{(IV)}}{\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)_2} \xrightarrow[20°]{\text{liq. } SO_2} \rightarrow (C_5H_5SO_2)_2ZrSO_3 + (CH_3)_2SO$$

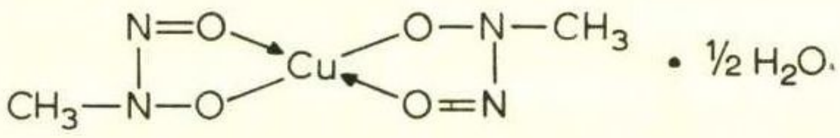
(V)

As added proof that insertion between a metal and a cyclopentadienyl ligand can occur, it is pertinent to mention that SO_2 will insert into $[(\pi\text{-}C_5H_5)_2ZrCl]_2O$, as described in a previous paper[5], and also into tetracyclopentadienylzirconium. In the solid state the latter compound has three cyclopentadienyl ligands π-bonded and one σ-bonded[6]. In liquid SO_2 at room temperature $(C_5H_5)_4Zr$ was converted to the *O*-sulphinato derivative $C_5H_5(C_5H_5SO_2)_3Zr$, the infrared spectrum of which was similar to those of all other $C_5H_5SO_2Zr$ compounds.

Reactions with nitric oxide

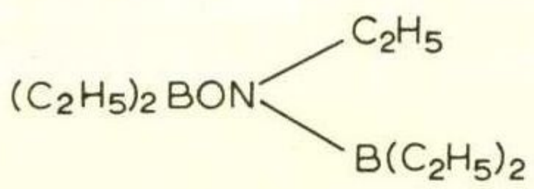
While there are now numerous examples of insertion of SO_2 into a metal–alkyl bond, there are very few corresponding cases of NO insertion. Perhaps one of the first experiments was that of Frankland in 1856 who reacted NO with dimethyl- and diethylzinc[7]. The complexes formed were probably of the type $RZn(NO)_2R$*. Later, in 1903, Sand and Singer[8] isolated the compound $C_6H_5N(NO)OH$ from the reaction of nitric oxide with a phenyl Grignard reagent, while the methyl derivative led to a copper complex to which they assigned the structure (VI).

* Calculated from Frankland's elemental analyses. His assignment of the formula $C_4H_5ZnNO_2$ to the ethyl derivative was based on atomic weights not acceptable now.



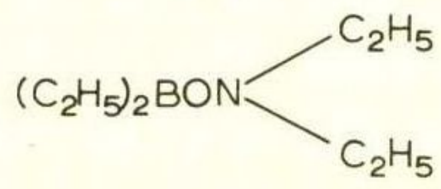
(VI)

More recently Brois[9] (1964) and Inatome and Kuhn[10] (1964) treated trialkylborons with nitric oxide. At $-30°$ the product was the *N*-bonded complex $(C_2H_5)_2BN(NO)OC_2H_5$ (VII). Structural proof came from the NMR chemical shift of the unique ethyl group (CH_2, δ 4.15; CH_3, δ 1.73 ppm, neat) together with the similarities of the infrared spectrum to those of nitrosamines and the fact that N_2O was obtained on treatment with concentrated sulphuric acid. When the reaction was carried out at 70°, a reversal of the mode of insertion was found as the compounds isolated were (VIII) and (IX):



(VIII)

NMR (neat): δ 3.27 (CH_2), 1.10 ppm (CH_3)



(IX)

NMR (neat): δ 2.65 (CH_2), 1.00 ppm (CH_3)

When NO was bubbled through a solution of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ in light petroleum at room temperature a white precipitate was obtained. Analysis suggested that two NO groups were incorporated in the molecule. The NMR spectrum in deuterobenzene consisted of three sharp singlets, one of relative intensity 10 at δ 5.78 ppm due to the C_5H_5 protons, and two of relative intensity 3 at δ 3.03 and 0.55 ppm, which were ascribed to two different methyl groups. The corresponding δ values in deuterochloroform were 5.88, 3.83 and 0.14 ppm. The peak at 0.55 ppm in deuterobenzene was presumably due to a methyl group attached directly to the metal, since in the NMR spectrum of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$ in deuterobenzene the methyl band is found at δ 0.32 ppm, while for the corresponding titanium compound the band is at δ 0.70 ppm. The infrared spectrum (Fig. 2) differed appreciably from that of the

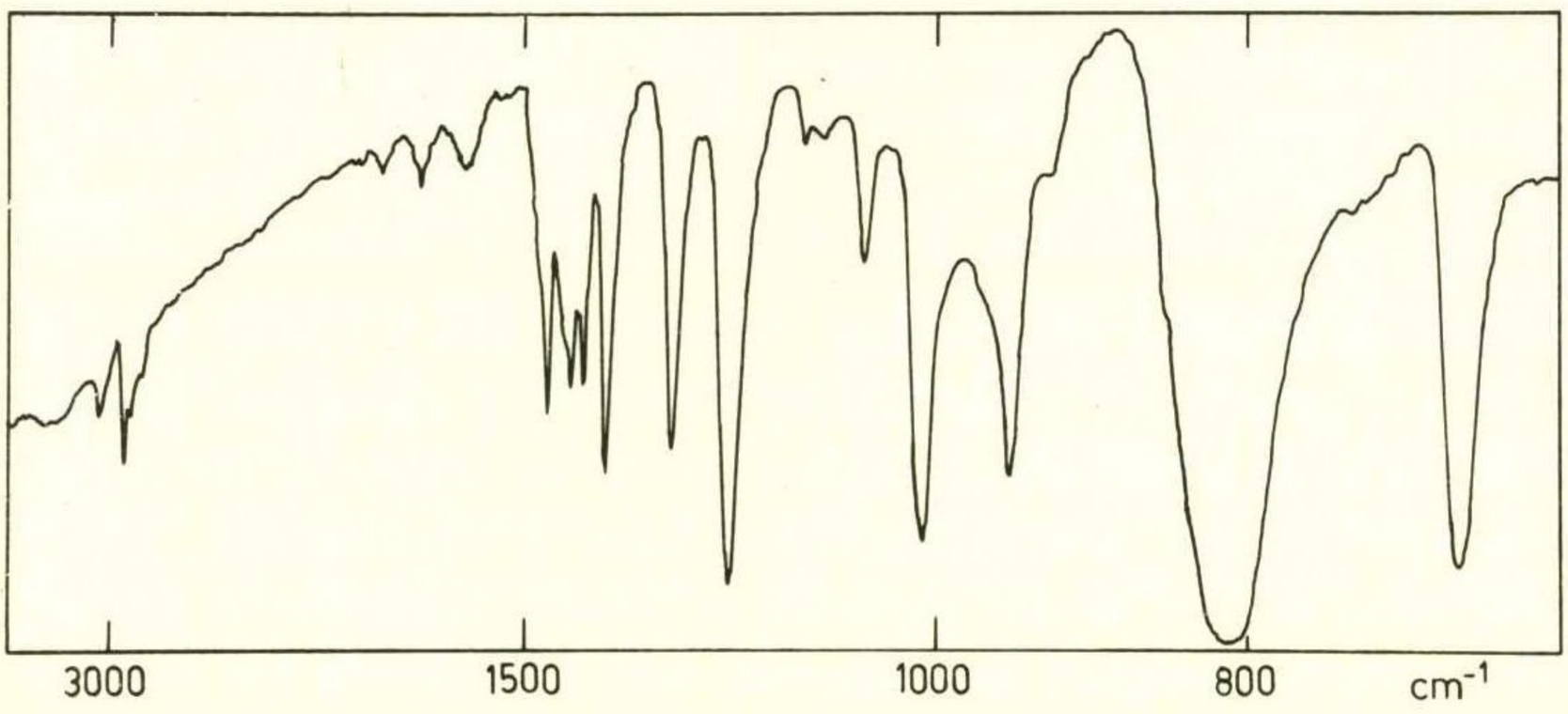
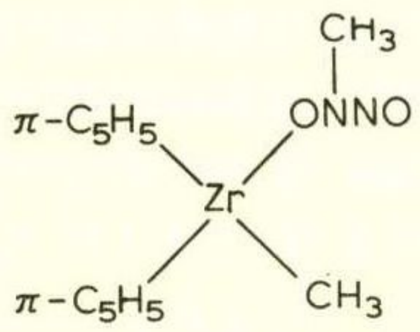
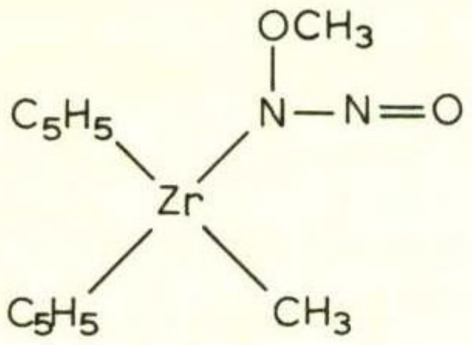


Fig. 2. Infrared spectrum (KCl disc) of

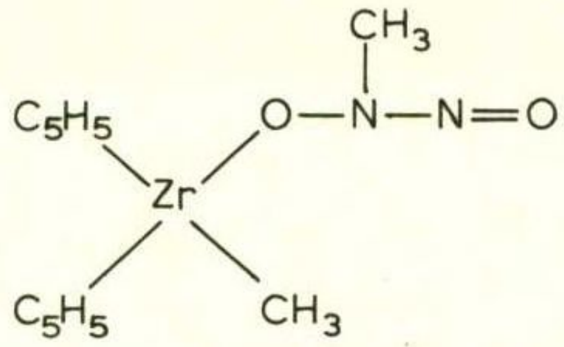


(XI)

dimethyl derivative and indicated that the compound was not a metal nitrosyl. The two possible structures (X) and (XI) were therefore considered for this compound:

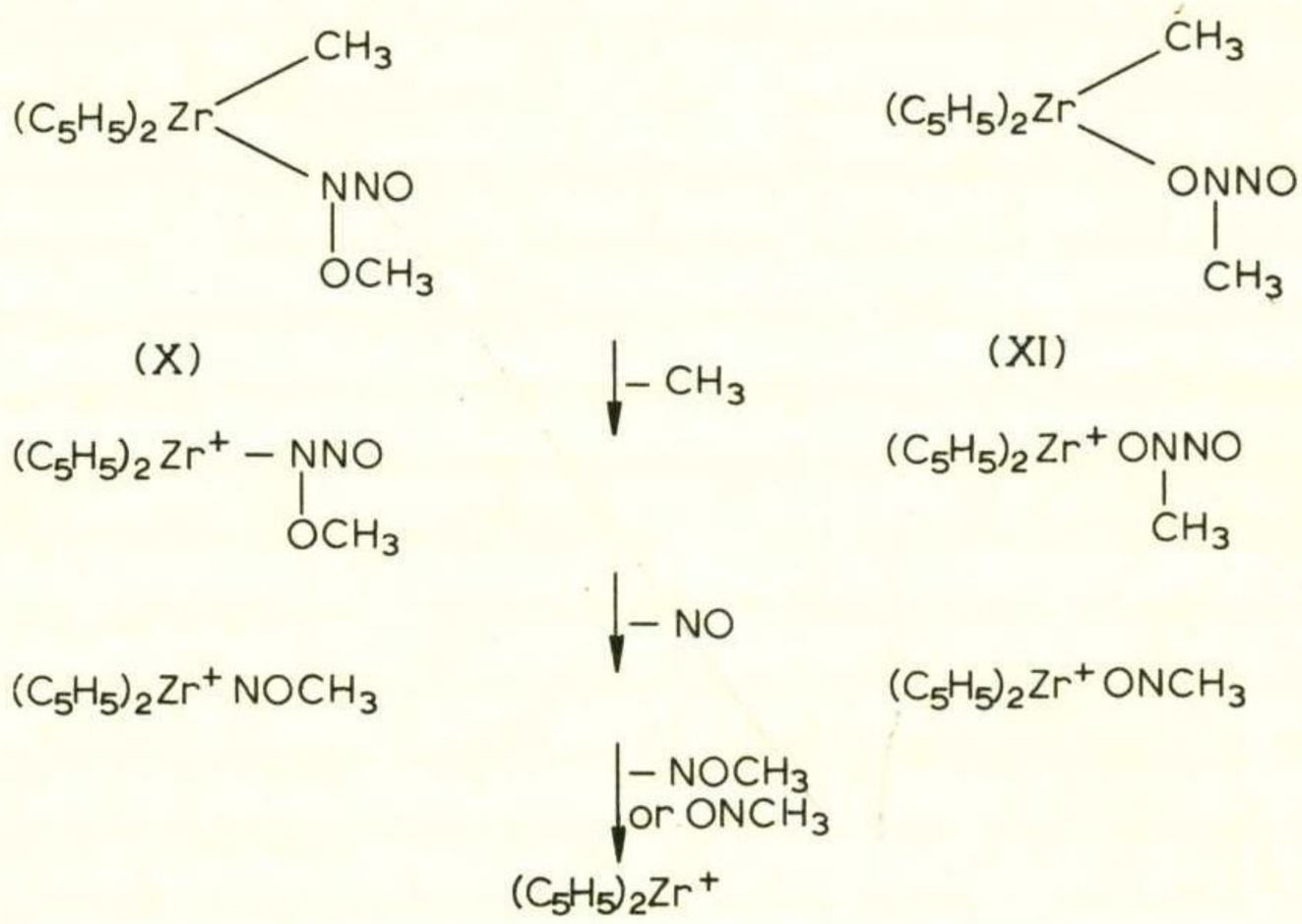


(X)



(XI)

Since the methyl group involved in the reaction had its NMR resonance at δ3.03 ppm it was not possible to assign it with confidence to either an OCH_3 or an NCH_3 group. The mass spectrum, at the mildest inlet temperatures obtainable, showed no strong peaks at mass numbers below 100, so that no peaks could be assigned to species containing OCH_3 or NCH_3 groups. The breakdown pattern of the compound was explicable using either structure (X) or (XI), *viz.*:



The only other zirconium-containing species found were $C_5H_5ZrO^+$ and $C_3H_3ZrO^+$, which may well have been formed by partial hydrolysis of a $ZrCH_3$ group during transfer of the compound into the spectrometer inlet. This is supported by the fact that in the mass spectrum of $(\pi\text{-}C_5H_5)_2ZrCl(N_2O_2CH_3)$, the parent peak together with $C_5H_5ZrCl(N_2O_2CH_3)^+$, $(C_5H_5)_2ZrCl^+$ and $C_5H_5ZrCl(NOCH_3)^+$ were found but not $C_5H_5ZrO^+$ or $C_3H_3ZrO^+$.

As in the case of the alkylboron compounds, treatment with 12 *N* H_2SO_4 at refluxing temperature for 3 h gave N_2O, identified by its infrared spectrum, and no NO. As this could not be taken as a definite indication of one structure or the other, one of the ligands was synthesized. Methylhydroxylamine hydrochloride, CH_3-$NHOH \cdot HCl$, was nitrosylated at $-5°$ in the presence of copper sulphate to protect the hydroxyl group. The copper complex so obtained, which analyzed for the anhydrous form of (VI), showed an infrared spectrum virtually identical with that of the zirconium compound, if the cyclopentadienyl absorption is taken into account (Fig. 3). Furthermore on hydrolysis of the copper complex with 50% H_2SO_4, N_2O was formed and again no NO was detected. On this basis structure (XI) was assigned to the zirconium complex. This is of course what one would intuitively expect as

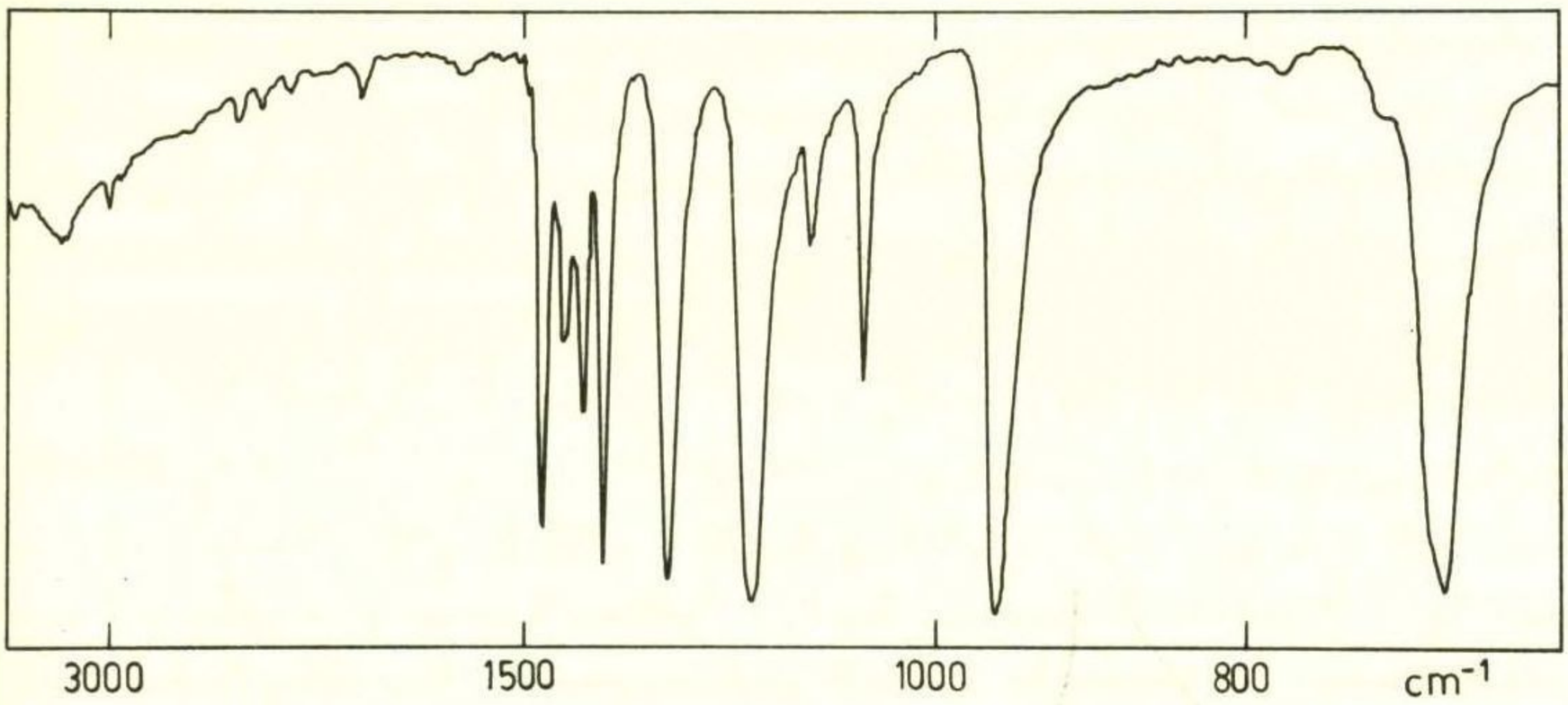
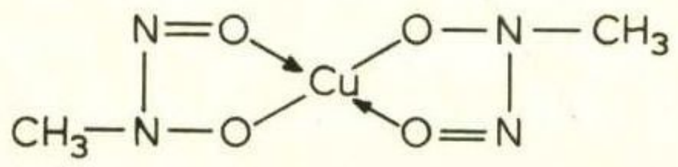


Fig. 3. Infrared spectrum (KCl disc) of



(VI)

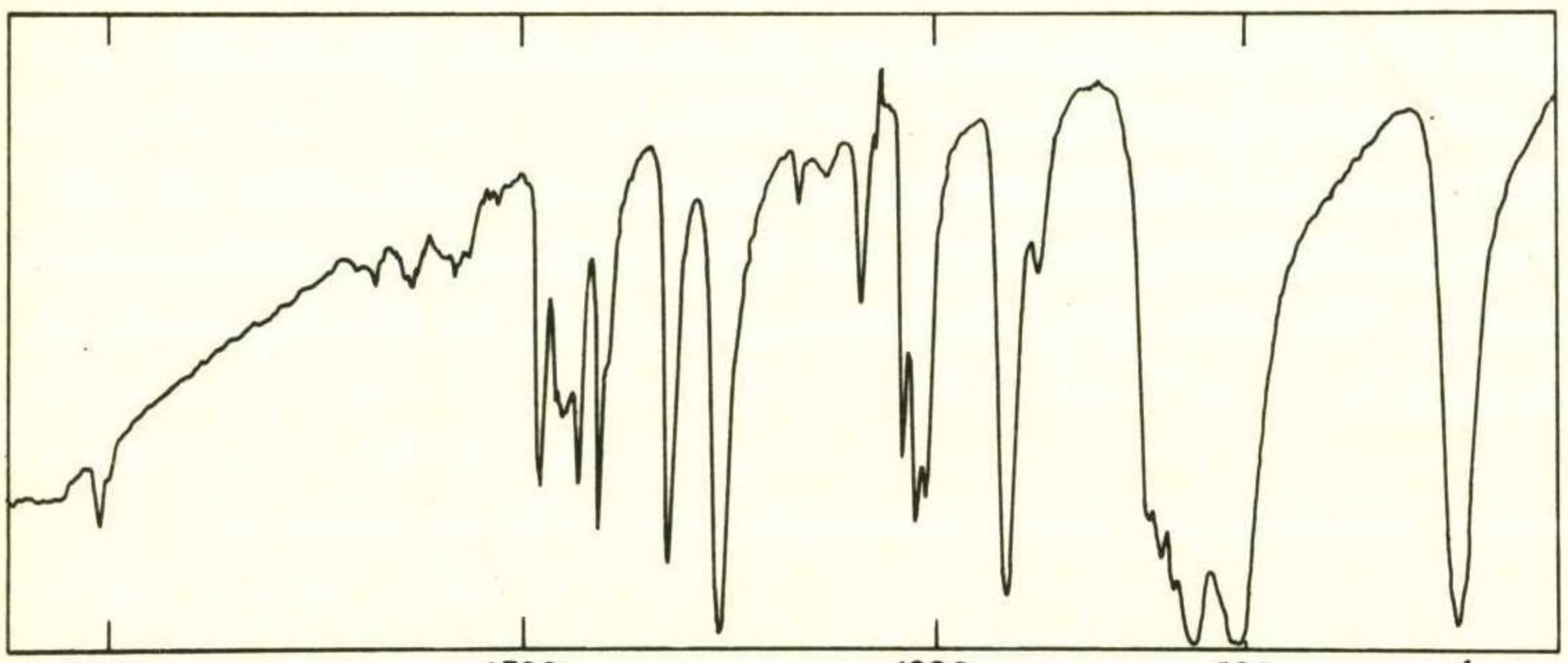
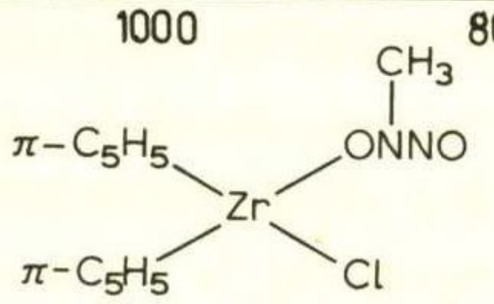


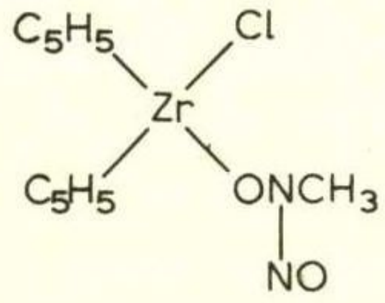
Fig. 4. Infrared spectrum (KCl disc) of



(XII)

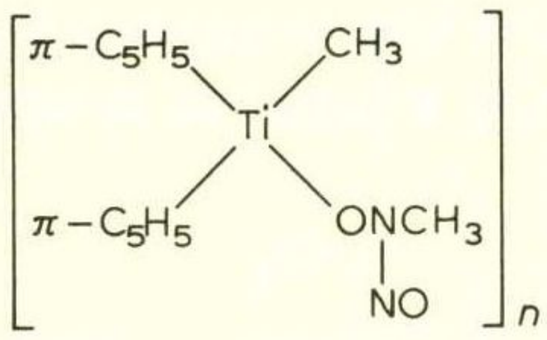
zirconium in general appears to prefer bonding through oxygen rather than through nitrogen.

Attempts to insert NO between the second methyl group and the zirconium by treatment of a solution of $(\pi\text{-}C_5H_5)_2Zr(CH_3)N_2O_2CH_3$ with NO over several hours were not successful, even at reflux temperature in benzene or in higher-boiling solvents. The monomethylzirconium chloride, $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$, on the other hand was readily converted to the corresponding nitrosylated complex (XII) by treatment of a benzene solution with nitric oxide. The infrared spectrum of (XII) was almost identical with that of the dimethylzirconium product (Fig. 4). The lack of reactivity of $(\pi\text{-}C_5H_5)_2Zr(CH_3)N_2O_2CH_3$ with NO is paralleled in the titanium case. Dicyclopentadienyldimethyltitanium reacts with nitric oxide in benzene at room temperature to give (XIII) the infrared spectrum of which was similar to that of the corresponding zirconium compound.



(XII)

NMR ($CDCl_3$): δ 6.14 (C_5H_5), δ 3.84 ppm (CH_3)
(C_6D_6) : δ 6.04 (C_5H_5), δ 2.89 ppm (CH_3)



(XIII)

The molecular weight of (XIII) in boiling tetrahydrofuran was concentration-dependent, varying between an initial value of 740 and increasing to 1050 at concentrations of approximately 16 g/l. This may well be indicative of a trimer (mol.wt. 805) $\rightleftarrows$ tetramer (mol.wt. 1087) equilibrium. The NMR spectrum of the compound was complicated by the polymerization which caused some precipitation in the solvent used (benzene-d_6). The proton chemical shifts were at approximately δ 0.8 ppm ($TiCH_3$), δ 3.05 ppm (NCH_3) with a broad complex band between δ 5.5 and 6.5 ppm (C_5H_5).

Attempts to insert NO into the titanium compound $(\pi\text{-}C_5H_5)_2Ti(Cl)CH_3$ were unsuccessful, even at elevated temperatures.

Tetracyclopentadienylzirconium also reacts with nitric oxide but as yet a product sufficiently pure for identification has not been obtained. Investigation of this and other reactions of NO with alkyl and aryl derivatives of titanium and zirconium is being continued.

EXPERIMENTAL

General

All manipulations of solid materials were carried out in a nitrogen-filled glove box and all reactions were performed in a stream of purified argon. Analyses for carbon and hydrogen were determined by the Australian Microanalytical Service, C.S.I.R.O. and University of Melbourne, on pelleted samples sealed in aluminium capsules. Metal was determined by ashing sulphated pellets of each compound. NMR spectra were measured on Varian T60 or HA 100 instruments. Nitric oxide (Matheson) was passed through a solid CO_2/ethanol trap before use. Sulphur dioxide (B.D.H.) was used without further purification.

Preparation of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$

To a stirred suspension of $(\pi\text{-}C_5H_5)_2ZrCl_2$ (18.0 g, 61.6 mmole) in diethyl ether (100 ml) at room temperature was added methyllithium solution (145 ml of 0.85 *M* solution, 123.2 mmole, in diethyl ether) over 1 h. (The CH_3Li is best prepared from CH_3Cl rather than CH_3I, as the LiCl precipitates from the reaction mixture making subsequent purification easier.) After stirring overnight the mixture was filtered under argon and the filtrate was evaporated to dryness under reduced pressure. After two sublimations at 100–110°/10^{-4} mm, pure $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ was obtained as a colourless solid (11.4 g, 73 % yield) which softened at 150° and melted with decomposition at 190°. (Found: C, 57.7; H, 6.4; Zr, 36.8 %; mol. wt. in boiling benzene, 253. $C_{12}H_{16}Zr$ calcd.: C, 57.31; H, 6.42; Zr, 36.26 %; mol.wt., 251.5.)

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ *with* H_2

The dimethylzirconium compound was heated under reflux in light petroleum

(b.p. 110–120°) while hydrogen was bubbled through the solution. The colour changed to crimson and after $\frac{1}{2}$ h the product was isolated by evaporation of solvent. (Found: C, 56.1; H, 6.1; Zr, 36.4; methane on hydrolysis, 1.0 mole/mole; mol.wt. in boiling benzene, 404. $C_{12}H_{16}Zr$ calcd.: C, 55.89; H, 5.54; Zr, 38.54%; methane on hydrolysis, 1.0 mole/mole; mol.wt., 473.)

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ *with* $PbCl_2$

$(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (1.26 g, 5.0 mmole) was dissolved in benzene (50 ml) and lead chloride (0.70 g, 2.5 mmole) was added with stirring. The colour of the solution darkened immediately due to the formation of metallic lead. After stirring for several hours the mixture was filtered and solvent removed under reduced pressure to give a cream-coloured solid identical in NMR and infrared spectra with $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$[11]. (Found: Zr, 33.3%. $C_{11}H_{13}ClZr$ calcd.: Zr, 33.57%.)

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ *with* SO_2

(*a*). *At low temperature.* Sulphur dioxide (approx. 15 ml) was condensed on to $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (1.5 g) contained in a Schlenk flask cooled in solid CO_2/ethanol. All of the solid dissolved to give a yellow solution. SO_2 was allowed to evaporate and the last traces were removed under reduced pressure giving bright yellow solid $\pi\text{-}C_5H_5(C_5H_5SO_2)Zr(O_2SCH_3)_2$, which was insoluble in all common organic solvents. (Found: C, 31.0; H, 3.6; S, 22.4; Zr, 20.0. $C_{12}H_{16}O_6S_3Zr$ calcd.: C, 32.48; H, 3.63; S, 21.68; Zr, 20.55%.)

The same product was obtained when the reaction and removal of SO_2 were carried out at $-78°$.

(*b*). *At room temperature.* SO_2 (10–15 ml) was condensed on to $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (1.5 g) contained in a tube which was then sealed with a Teflon-stemmed stopcock. After 1–2 h at room temperature an off-white precipitate formed. Excess SO_2 was syphoned off and the product, $(C_5H_5SO_2)_2ZrSO_3$, was dried under reduced pressure. (Found: C, 28.0; H, 3.4; S, 22.4; Zr, 21.6. $C_{10}H_{10}O_7S_3Zr$ calcd.: C, 27.96; H, 2.35; S, 22.39; Zr, 21.23%.)

Reaction of $(C_5H_5)_4Zr$ *with* SO_2

$(C_5H_5)_4Zr$ (0.7 g) was stirred in a sealed tube (as in preceding experiment) with liquid SO_2 (10 ml) at room temperature for 2 days. The clear supernatant liquid was removed and the light brown precipitate was dried under reduced pressure giving $C_5H_5Zr(O_2SC_5H_5)_3$. (Found: C, 43.0; H, 3.7; S, 16.9; Zr, 16.5. $C_{20}H_{20}O_6S_3Zr$ calcd.: C, 44.17; H, 3.71; S, 17.69; Zr, 16.77%.)

Reaction of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ *with NO*

NO was bubbled through a solution of $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ (1.5 g) in light petroleum (40 ml, b.p. 30–40°) at room temperature. After 5–10 min a white precipitate appeared and passage of NO was continued for 30 min. The precipitate was collected by filtration, washed with petrol and dried under vacuum giving $(\pi\text{-}C_5H_5)_2Zr(CH_3)\text{-}N_2O_2CH_3$. (Found: C, 46.2; H, 5.3; N, 8.8; Zr, 29.5; mol.wt. in boiling THF, 329. $C_{12}H_{16}N_2O_2Zr$ calcd.: C, 46.26; H, 5.18; N, 8.99; Zr, 29.27%; mol.wt., 311.5.) Hydrolysis of this compound with boiling 12 *N* H_2SO_4 over 3 h gave a mixture of nitrous oxide, methane and ethane, identified from their infrared spectra. No other nitrogen-containing gases were present.

Preparation of $Cu(O_2N_2CH_3)_2$

Benzophenone oxime was methylated with dimethyl sulphate to give *N*-methylbenzophenone oxime[12]. Hydrolysis of the oxime with concd. HCl after the method of Kjellin[13] yielded *N*-methylhydroxylamine hydrochloride. Nitrosylation of the hydrochloride in the presence of copper sulphate[14] gave the purple copper complex, which was collected by filtration, washed with water and dried under vacuum over P_2O_5. (Found: C, 11.2; H, 2.8; N, 25.7. $C_2H_6CuN_4O_4$ calcd.: C, 11.25; H, 2.83; N, 26.23%.) This complex is paramagnetic with μ_{eff} varying from 1.89 B.M. at room temperature to 1.82 B.M. at 90K and having a θ value of $-8°$★. The g value of the powdered sample was found to be 2.284.

Reaction of $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ *with NO*

Nitric oxide was bubbled through a solution of $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ (2 g) in benzene (40 ml) at room temperature for 2 h. The solution was reduced to dryness giving $(\pi\text{-}C_5H_5)_2Ti(CH_3)N_2O_2CH_3$ as a pale brown powder. (Found: C, 53.6; H, 5.2; N, 9.2; Ti, 17.2. $C_{12}H_{16}N_2O_2Ti$ calcd.: C, 53.74; H, 6.01; N, 10.44; Ti, 17.86%.) The compound can be made also using light petroleum (b.p. 30–40°) as solvent, from which the product precipitates during the course of the reaction.

Reaction of $(\pi\text{-}C_5H_5)_2Zr(Cl)CH_3$[11,5] *with NO*

The reaction was carried out exactly as for the dimethyltitanium compound above giving $(\pi\text{-}C_5H_5)_2Zr(Cl)N_2O_2CH_3$ as a pale brown solid which could be crystallized from benzene/light petroleum. (Found: C, 39.5; H, 4.0; Cl, 10.6; N, 7.9; Zr, 27.4; mol.wt. in boiling THF, 350. $C_{11}H_{15}ClN_2O_2Zr$ calcd.: C, 39.81; H, 3.95; Cl, 10.68; N, 8.44; Zr, 27.48%; mol.wt., 331.9.)

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★ Using the formula $\mu_{eff} = 2.83\sqrt{\chi_A \cdot (T-\theta)}$

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34

Organic Complexes of Lower-Valent Titanium

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I

INTRODUCTION

Early interest in the organic chemistry of titanium was centered mainly on the alkoxides, or titanates, primarily because of their ease of preparation from titanium tetrachloride and alcohols, and also because these derivatives have found use in heat-resistant paints and in the treatment of textiles, wood, and paper.

In more recent years the expansion in the volume of research on organic titanium derivatives corresponds with the increase in research in metal-organic chemistry in general. There seems little doubt, however, that present interest in derivatives of lower-valent titanium is due in no small measure to the ability of this element, generally complexed with another metal, to bring about the polymerization of olefins as well as the formation of complexes of dinitrogen, and its subsequent reduction to ammonia. This interest is expected to continue as the approach to such catalysts becomes less empirical and knowledge of their structures becomes more important.

Titanium is in Group IV of the Periodic Table and is the first of the transition elements. In line with its outer electronic configuration of $3d^2 4s^2$, its maximum and also its most stable valence is 4, but it is the lower oxidation states, namely, 3 and to a lesser extent 2 and below, with which we shall be concerned in this review.

With few exceptions the organic complexes of lower-valent titanium are extremely sensitive to oxygen. In many cases oxidation is so rapid that the compounds are pyrophoric in air. The efficient use of vacuum line and glove-box techniques then becomes extremely important. In addition, the reactivity towards nitrogen of many compounds of titanium in a highly reduced form means that argon remains the only readily available blanketing gas.

The isolation of titanium metal and the preparation of its halides, from which most of its organic derivatives are prepared, have been well documented by Brauer (*12*). Titanium is the ninth most abundant element on earth and is the most persistent constituent of all rocks and sediments. It occupies a larger proportion of the known terrestrial matter than zinc, copper, and lead combined and is five to ten times more abundant than sulfur or phosphorus. With difficulties in the refinement of the metal largely overcome, the future for titanium and its derivatives seems assured.

In the review which follows, the term "organic complexes of titanium" is taken to include not only true organotitanium compounds with carbon-to-titanium bonds, but also compounds containing organic groups bonded to titanium by almost any other element.

In the tables accompanying each chapter the room temperature magnetic moment for each complex is listed. Those cases for which moments at more than one temperature have been measured are indicated by superscript ^{T}. Electronic transition bands due to *d–d* transitions are also listed, but in any titanium complex containing different ligands the distortions are so great and the symmetry is so low that any conclusions based on spectral data must be tentative. For a theoretical treatment of the spectra and magnetics of titanium compounds the reader is referred to Clark (*23*) and references therein.

II

ADDITION COMPLEXES OF TITANIUM TRIHALIDES

A. Preparation

The simplest organic derivatives of lower-valent titanium are addition compounds of the di- and trihalides. All of the lower-valent halides are polymeric with bridging halogens but these bridges are broken by polar solvents and other donor ligands to give a great variety of addition compounds of ever-increasing number.

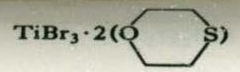
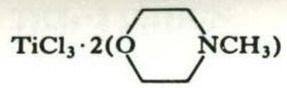
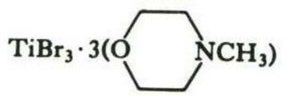
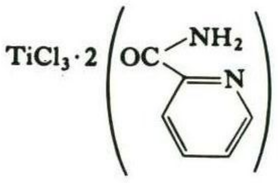
When the ligand is a liquid the complexes may be prepared directly from the reactants by dissolving the halide in the ligand. In many cases the conditions under which this is carried out determine the number of ligands which coordinate to each titanium atom. Compare, for example, the dioxane complexes, in which either one, two, or three dioxane molecules are attached to titanium trichloride according to the reaction conditions (*65*). Displacement of one coordinated ligand by another is also a useful method of preparation, employed successfully by Fowles and co-workers, who found that trimethylamine could be displaced from $TiX_3 \cdot 2\ N(CH_3)_3$ by a variety of ligands including pyridine, bipyridyl, dioxane, and others, to give complexes of the type $TiX_3 \cdot 3L$ or $TiX_3 \cdot 2\ L$ (*73*).

In Table I known complexes are listed according to donor atom. Most are complexes containing ligands coordinated through oxygen or nitrogen, but

TABLE I

ADDITION COMPLEXES OF TITANIUM TRIHALIDES[a,b]

Compound	Probable structure	Color	Visible spectra (kK) Solid	Visible spectra (kK) Solution (ε)	μ_{eff} (BM, 20° C)	References
		O-Coordinated				
Ethers						
$TiCl_3 \cdot 3$ THF	Octahedral	Sky blue	14.7	—	1.72	*21, 24, 99, 106, 159, 160*
$TiBr_3 \cdot 3$ THF	Octahedral	Green	12.4 14.0	13.25 (4)	1.75	*63*
$TiI_3 \cdot 3$ THF	Octahedral	Red-brown	10.9 14.2	10.8 14.1	1.64	*69*
$TiCl_3 \cdot 2$ THF	—	Green	—	—	—	*145*
2 $TiCl_3 \cdot 3$ $(CH_2OCH_3)_2$	ψ-Oct., bridging ether or $[TiCl_2 \cdot 2\ (CH_2OCH_3)_2][TiCl_4(CH_2OCH_3)_2]$	Blue	12.4 13.8	—	1.74^T	*49, 65, 115*
2 $TiBr_3 \cdot 3$ $(CH_2OCH_3)_2$	Oct., as for chloride	Green	13.0	14.2 (12)	1.67	*49, 63*
$TiI_3 \cdot 2$ $(CH_2OCH_3)_2$	$[TiI_2 \cdot 2\ (CH_2OCH_3)_2]^+I^-$	Yellow	11.25 14.7	—	1.73	*69*
$TiCl_3 \cdot 3$(O O)	Oct., only one O coord.	Blue-green	13.4 15.2	—	1.69	*65*
$TiCl_3 \cdot 2$(O O)	ψ-Oct., dimer, Cl bridge	Blue-green	12.5 14.8	—	1.72	*24, 49, 65, 160*
$TiCl_3 \cdot$(O O)	Oct., polymer, Cl and diox. bridge, both O's coord.	Blue-green	13.5	—	1.77^T	*65, 115*
$TiBr_3 \cdot 3$(O O)	Oct., one O coord.	Green	12.5 14.1	13.6	1.75	*63, 72*
$TiI_3 \cdot 3$(O O)	Oct., only one O coord.	Red-brown	11.4 14.1	14.4 (15)	1.64	*69*
$TiCl_3 \cdot 2$(O S)	—	Green	—	15.0	1.58	*4, 72*
$TiCl_3 \cdot$(O S)	Likely to involve S	Brown	13.5	—	1.71	*49, 65, 72, 115*

	—	Yellow-brown	—	14.2	1.60	*4, 72*
	Coord. through O	Green	—	15.0	1.62	*72*
	As for chloride	Yellow-brown	—	14.25	1.49	*72*
$H[TiCl_4 \cdot O(C_2H_5)_2]$	—	Yellow-brown	16.6	—	0.78^T	*78*
Ketones						
$TiCl_3 \cdot 3\ OC(CH_3)_2$	Oct.	Brown	—	15.4 (37)	1.61	*24, 65*
$TiCl_3 \cdot 2\ OC(C_2H_5)_2$	Oct., probably Cl bridge	Green	—	15.6 (140)	1.61	*65*
$TiCl_3 \cdot 2\ OCPh_2$	Oct., probably Cl bridge	Steel blue	15.6	—	—	*65*
Alcohols						
$TiCl_3 \cdot 3\ CH_3OH$	Oct.	Pale blue	13.8 16.9	13.4 15.1	1.79^T	*78*
$TiCl_3 \cdot 4\ CH_3OH$	$[TiCl_2(CH_3OH)_4]Cl$, probably *cis*	Blue	15.4 18.2	—	1.79^T	*77*
$TiCl_3 \cdot 4\ (iso\text{-}C_3H_7OH)$	$[TiCl_2(ROH)_4]Cl$	Blue	—	16.7 (9)	1.74^T	*159, 160*
$TiCl_3 \cdot 4\ (sec\text{-}C_4H_9OH)$	$[TiCl_2(ROH)_4]Cl$	Blue	—	16.1 (9)	1.77^T	*159, 160*
$TiCl_3 \cdot 4\ (cyclo\text{-}C_6H_{11}OH)$	$[TiCl_2(ROH)_4]Cl$	Blue	—	16.1 (8)	1.81^T	*159, 160*
$TiBr_3 \cdot 4\ (iso\text{-}C_3H_7OH)$	$[TiBr_2(C_3H_7OH)_4]Br$	Green	—	—	1.75^T	*159, 160*
$TiCl_3 \cdot 5\ CH_3OH$	$[TiCl(CH_3OH)_5]Cl_2$	Pale blue	15.2 18.6	15.1 16.8 (5)	1.79^T	*77*
$(C_5H_6N)_2[TiCl_5(CH_3OH)_2]$	Unknown	Green	12.9 15.6	14.0 14.8	1.76^T	*77*
$C_5H_6N \cdot [TiCl_4(CH_3OH)_2]$	Oct., probably *cis*	Turquoise	12.9 15.7	12.7 14.6	1.79^T	*78*
$(C_5H_6N)_2[TiCl_5 \cdot CH_3OH]$	Oct.	Yellow	11.4 13.6	—	1.79^T	*78*
$TiCl_3 \cdot 6\ (CH_3OH)$	$[Ti(CH_3OH)_6]Cl_3$, oct.	Blue	—	15.1 16.8	—	*78, 80*
$TiCl_3 \cdot 6\ (C_2H_5OH)$	$[Ti(C_2H_5OH)_6]Cl_3$, oct.	Blue	—	—	—	*80*
$TiCl_3 \cdot 6\ (iso\text{-}C_3H_7OH)$	$[Ti(C_3H_7OH)_6]Cl_3$, oct.	Blue	—	—	—	*80*
Acids, amides, etc.						
$CsTiCl_5 \cdot CH_3CO_2H$	Oct.	Green	—	—	1.84^T	*116*
	Bonded through amide and ring N	Red-brown	—	—	2.08^T	*116*

(*Continued*)

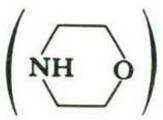
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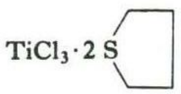
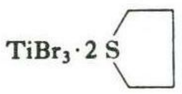
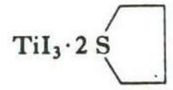
Compound	Probable structure	Color	Visible spectra (kK) Solid	Solution (ϵ)	μ_{eff} (BM, 20° C)	References
$TiI_3 \cdot 6$ urea	$(Ti[OC(NH_2)_2]_6)I_3$, oct.	Blue	16.4 18.2	—	1.69^T	*81, 112, 115, 160*
$TiI_3 \cdot 6$ acetamide	$(Ti[NH_2COCH_3]_6)I_3$, oct.	Blue	—	—	—	*81*
$TiCl_3 \cdot 3$ DMF	Oct.	Blue	—	—	1.63–1.65	*47*
$TiCl_3 \cdot 3$ MF	Oct.	Blue	—	—		
$TiCl_3 \cdot 3$ F	Oct.	Blue	—	—		
$\left[Ti\left(OC\begin{smallmatrix}NH—CH_2\\NH—CH_2\end{smallmatrix}\right)_6\right]Cl_3 \cdot 2C_2H_5OH$	Oct.	Blue	15.6 17.0	—	1.79	*10*
$\left[Ti\left(OC\begin{smallmatrix}NH—CH_2\\NH—CH_2\end{smallmatrix}\right)_6\right]I_3$	Oct.	Blue	15.4 17.0	—	1.81	*10*
$\left[Ti\left(OC\begin{smallmatrix}C_6H_5\\N—NCH_3\\CH=CCH_3\end{smallmatrix}\right)_6\right]Br_3 \cdot 2C_2H_5OH$	Oct.	Green	15.0 16.5	—	1.88	*10*
$\left[Ti\left(OC\begin{smallmatrix}C_6H_5\\N—NCH_3\\CH=CCH_3\end{smallmatrix}\right)_6\right]I_3$	Oct.	Green	15.4 17.0	—	1.81	*10*
	N-Coordinated					
Nitriles						
$TiCl_3 \cdot 3\ CH_3CN$	ψ-Oct., monomeric	Light blue	—	14.7 (15) 17.2 (31)	1.71^T	*22, 25, 53, 65, 107, 116*

$TiCl_3 \cdot 3\ C_2H_5CN$	ψ-Oct., monomeric	Blue	—	14.7 17.2	1.53	*53, 65*
$TiCl_3 \cdot 3\ C_3H_7CN$	ψ-Oct., monomeric	Blue	—	14.7 17.2	1.61	*53, 107*
$(C_2H_5)_4N[TiCl_4 \cdot 2\ CH_3CN)$	Oct., not known if *cis* or *trans*	Green	14.3 15.0	—	1.76^T	*115, 152*
$TiBr_3 \cdot 3\ CH_3CN$	ψ-Oct.	Green	—	16.3 (500)	1.51	*53, 72*
$(C_2H_5)_4N[TiBr_4 \cdot 2\ CH_3CN]$	Oct.	—	12.7 14.8	—	—	*152*
$(C_5H_6N)_2[TiCl_5 \cdot CH_3CN]$	Oct.	Yellow-green	—	13.6 15.2	1.76^T	*77, 78*
$TiI_3 \cdot 4\ CH_3CN$	$[TiI_2 \cdot (CH_3CN)_4]I$, Oct.	Red-brown	16.0	15.9	1.62	*69*
$Ti(CH_3CN)_6I_9$	$[Ti(CH_3CN)_6][I_3]_3$, oct.	Black	—	—	1.80	*82*
Pyridine, bipyridyl, etc.						
$TiCl_3 \cdot 3$ py	Oct.	Green	16.5	—	1.63	*64, 125, 167*
$TiCl_3\ 2$ py $\cdot CH_3CO_2C_2H_5$	—	Light brown	—	—	—	*144*
$TiCl_3 \cdot$ py	—	Gray	—	—	—	*75*
$TiBr_3 \cdot 3$ py	ψ-Oct., monomeric	Green	14.5 16.0	14.5 16.5	1.71	*64, 73*
$TiI_3 \cdot 3$ py	Oct.	Tan	11.9 14.8	11.8 14.2	1.69	*69*
$TiCl_3 \cdot 2\ \alpha$-pic	*trans*-Trigonal bipyramidal	Green-blue	7.3 16.4	7.5 15.9	1.62	*49, 64*
$TiBr_3 \cdot 2\ \alpha$-pic	As for chloride above	Green	6.5 15.8	—	1.69	*49, 73*
$TiI_3 \cdot 2\ \alpha$-pic	As for chloride above	Tan	5.7 14.7	— 14.8	1.65	*49, 69*
$TiCl_3 \cdot 3\ \gamma$-pic	ψ-Oct., monomer	Green	16.8	16.7	1.75^T	*64, 115*
$TiBr_3 \cdot 3\ \gamma$-pic	ψ-Oct., monomer	Green	16.0	15.8 (58)	1.70	*73*
$TiI_3 \cdot 3\ \gamma$-pic	ψ-Oct.	Tan	12.9 20.9	15.0 (250) 20.0	1.89	*69*
$TiCl_3 \cdot 2$ bipy	$[TiCl_2(bipy)_2]Cl$	Colorless	—	—	—	*163*
$TiBr_3 \cdot 2$ bipy	$[TiBr_2(bipy)_2]Br$	Purple	16.0 19.3	15.9 19.1	—	*68*
$2\ TiCl_3 \cdot 3$ bipy	$[TiCl_2(bipy)_2]^+[TiCl_4(bipy)]^-$	Dark blue	13.5 15.8	17.8	1.68	*68*
$2\ TiBr_3 \cdot 3$ bipy	As for chloride	—	15.9 18.7	15.4 18.5	1.72	*68, 73*
$2\ TiI_3 \cdot 3$ bipy	As for chloride	Brown	10.8 15.5 20.0	18.9	1.39	*69*
$TiBr_3 \cdot 2$ bipy $\cdot CH_3CN$	$[TiBr_2(bipy)_2]^+Br^-$, CH_3CN; CH_3CN not coord.	Purple	16.4 19.1	15.2 15.9 19.1	2.06	*68*
$TiBr_3 \cdot 2$ bipy $\cdot CHCl_3$	$[TiBr_2(bipy)_2]^+Br^-$, $CHCl_3$	Purple	16.3 18.9	15.2 15.9 19.1	1.85	*68*

(*Continued*)

TABLE I (*Continued*)

Compound	Probable structure	Color	Visible spectra (kK) Solid	Solution (ϵ)	μ_{eff} (BM, 20° C)	References
$TiCl_3 \cdot$ bipy	ψ-Oct., dimer, Cl bridge	Dark blue	13.5 15.8	—	1.72	*66*
$TiBr_3 \cdot$ bipy	ψ-Oct., dimer, Br bridge	Purple	12.9 15.9 18.7	15.2 18.0	1.88	*68*
$TiCl_3 \cdot$ bipy $\cdot CH_3CN$	Oct.	Purple-violet	—	15.2 17.4	1.74	*66*
$TiCl_3 \cdot$ bipy $\cdot C_2H_5CN$	Oct.	Violet	17.0	14.9 17.2	1.67	*66*
$TiCl_3 \cdot 2$ phen	—	Yellow	—	—	0.37 ?	*108*
$TiI_3 \cdot 2$ phen	$[TiI_2(phen)_2]I$	Brown	14.3 19.6	18.7	1.39	*69*
$TiCl_3 \cdot 2\ N(CH_3)_3$	*trans*-Trigonal bipyramidal	Blue	6.1 15.1	6.6 (88) 15.1 (17)	1.73	*3, 49, 64, 153*
$TiBr_3 \cdot 2\ N(CH_3)_3$	*trans*-Trigonal bipyramidal	Green	5.1 14.1	—	1.71^T	*49, 64, 115, 153*
$TiI_3 \cdot 2\ N(CH_3)_3$	*trans*-Trigonal bipyramidal	Red-brown	13.4 19.0	13.0	—	*69*
$TiCl_3 \cdot$ terpy	Oct., monomer	Dark green	—	—	—	*19, 47*
$TiCl_3 \cdot 2$ piperidine $CH_3CO_2C_2H_5$	—	Light brown	—	—	—	*144*
Amines						
$TiCl_3 \cdot 4$ en	Oct., bridging en	Pale blue	13.9	—	1.66^T	*54, 115*
$TiBr_3 \cdot 4$ en	Oct., bridging en	Pale blue	14.1	—	1.58^T	*54, 115*
$TiCl_3 \cdot 3$ en	$[Ti(en)_3]^{3+}3\ Cl^-$	Blue	13.5	—	1.67^T	*24, 116*
$TiCl_3 \cdot 3$ pen	$[Ti(pen)_3]^{3+}3\ Cl^-$	Blue	14.0	—	1.66	*24*
$TiCl_3 \cdot 2$ dien	$[Ti(dien)_2]^{3+}3\ Cl^-$	Blue	—	—	1.42^T	*116*
$TiCl_3 \cdot 3$ 	*N*-Coordinated	Blue	13.3 15.4	—	1.60	*65*

$TiCl_3 \cdot 2\ L \cdot CH_3CO_2C_2H_5$ L = *o*-, *m*-, and *p*-aminophenol, *o*-, *m*-, and *p*-aminobenzoic acid, *o*-, *m*-, and *p*-nitroaniline, *p*-aminoacetanilide	—	Brown Brown Yellow to brown Yellow	— — — —	— — — —	— — — —	*144* *144* *144* *144*
	S-Coordinated					
$TiCl_3 \cdot 2\ S(CH_3)_2$	Polymeric, bridging mechanism unknown	Brown	12.1 17.3	12.1 15.6 (25)	1.03^T	*70*
$TiBr_3 \cdot 2\ S(CH_3)_2$	Polymeric, bridging mechanism unknown	Brown	12.5	11.8 14.3 (12)	1.67	*70*
$TiI_3 \cdot 2\ S(CH_3)_2$	Polymeric, bridging mechanism unknown	Black	—	—	1.67	*70*
$TiCl_3 \cdot 2$ 	Polymeric, bridging mechanism unknown	Gray	12.2 17.3	11.8 15.3	1.12^T	*70*
$TiBr_3 \cdot 2$ 	Polymeric, bridging mechanism unknown	Brown	12.9	11.9 13.8 (13)	1.72	*70*
$TiI_3 \cdot 2$ 	Polymeric, bridging mechanism unknown	Brown	10.8	10.8 12.6 (13)	—	*70*
	P-Coordinated					
$TiCl_3(C_2H_4[P(C_2H_5)_2]_2)$	—	Dark brown	—	—	—	*21*
	As-Coordinated					
$TiCl_3 \cdot H_2O \cdot D$	Oct., monomeric	Red	—	—	0.91	*166*
$TiBr_3 \cdot H_2O \cdot D$	Oct., monomeric	Red	—	—	0.88	*166*

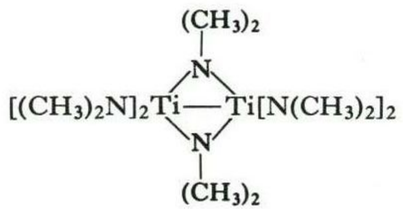
[a] bipy = 1,1′-bipyridyl; D = *o*-phenylenebis(dimethylarsine); dien = diethylenetriamine; DMF = dimethylformamide; en = ethylenediamine; F = formamide; MF = methylformamide; pen = propylenediamine; phen = 1,10-phenanthroline; α- and γ-pic = α- and γ-picoline; py = pyridine; terpy = 1,1′,1″-terpyridyl; THF = tetrahydrofuran.

[b] ^{T} indicates cases for which moments have been measured at more than one temperature.

TABLE II

COMPLEXES OF TYPE $TiX_n \cdot (3-n)L$[a]

Compound	Probable structure	Color	Visible spectra (kK) Solid	Visible spectra (kK) Solution (ϵ)	μ_{eff} (BM, 20° C)	References
Alkoxides						
$Ti(OCH_3)_3$	Polymeric, O bridge, oct.	Yellow-green	10.0	—	Diamag.	*1, 2, 77*
$Ti(OC_2H_5)_3$	Polymeric	Blue	—	—	—	*2, 114*
$Ti(OC_3H_7\text{-}n)_3$	Polymeric	Pink-lilac	—	—	—	*137*
$Ti(OC_4H_9\text{-}n)_3$	Polymeric	Pink-lilac	—	—	—	*137*
$TiCl_2(OCH_3) \cdot 2\ CH_3OH$	Trinuclear cluster, OCH_3 bridges	Red	10.0	—	1.0^T	*189*
$TiCl(OCH_3)_2 \cdot CH_3OH$	Trinuclear	Dark brown	10.0	—	—	*189*
Carboxylates and Phosphate						
$Ti_2(C_2O_4)_3 \cdot 10\ H_2O$	Pentagonal bipyramid, 7 coord. Ti	Yellow-brown	9.4 12.3	—	1.65^T	*52, 56, 160, 165*
$NH_4[Ti(C_2O_4)_2 \cdot 2\ H_2O]$ also K, Rb	Oct., bridging oxalate	Orange	12.8	—	1.76^T	*56, 154, 160*
$Ti(OCOCH_3)Cl_2$	Oct., bridging acetate	Dark brown	—	13.0 18.4	2.38^T	*116*
$Ti(OCOCH_3)Cl_2 \cdot CH_3CO_2H$	Oct.	—	—		1.70^T	*116*
$Ti(OCOCH_3)_2Cl$	Oct., 2 acetate bridges	Yellow-brown	—		1.61^T	*116*
$MTi(EDTA) \cdot n\ H_2O$ M = H, Li, Na, K, Rb, Cs, NH_4, Ba/2	Oct.	Blue to purple	—	12.8 18.0	1.63– 1.82	*143*
$Ti[O_2P(OCH_3)_2]_3$	Oct.	Pink	20.0	—	—	*79*
β-Diketonates						
$Ti(acac)_3$	Monomeric, strongly distorted oct.	Blue	—	15.2 (870) 16.5 (1120) 17.9 (930)	1.68^T	*2, 5, 20, 48, 58, 142, 156*
$Ti(F_6\text{-acac})_3$	Monomeric, distort. oct.	Blue	—	—	—	*74*
$Ti(benzoylac)_3$	Monomeric, distort, oct.	Green	—	12.8 (800) 14.1 (880) 15.9 (670)	1.67^T	*48, 58*

$Ti(3\text{-}CNacac)_3$	Monomeric, distort. oct.	Purple	—	16.1 (810) 17.3 (1000) 18.5 (910)	—	*48*
$Ti(dibenzoylCH_2)_3$	Monomeric, distort. oct.	Green	—	—	1.66	*48*
$Ti(F_3thenoylac)_3$	Monomeric, distort. oct.	Green	—	12.1 (2600) 13.5 (2380) 15.3 (1320)	1.66	*48*
$Ti(acac)_2Cl$	Dimeric, bridging Cl	Red-violet	16.6 18.5	17.4 (430) 18.8 (417)	1.39^T	*141, 156*
$Ti(acac)Cl_2$	Insol., probably polymeric	Red	16.9 17.6	18.7 (519)	1.70^T	*156*
Amido Complexes						
$Ti[N(CH_3)_2]_3$		Red-brown oil	—	—	Diamag.	*2*
$Ti[N(C_2H_5)_2]_3$	As for CH_3 above?	—	—	—	—	*2*
$Ti[N(CH_3)_2]_3 \cdot O(C_2H_5)_2$	—	Red-brown oil	—	—	Diamag.	*2*
$Ti[N(CH_3)_2]_2 \cdot N(C_2H_5)_2$	—	—	—	—	—	*2*
$Ti[N(CH_3)_2]_2 \cdot N(iso\text{-}C_3H_7)_2$	—	—	—	—	—	*2*
$Ti[N(CH_3)_2]_2 \cdot N[Si(CH_3)_3]_2$	—	—	—	—	—	*2*
Borohydride						
$Ti(BH_4)_3$	—	Green	—	—	—	*96*

[a] ^{T} indicates cases for which moments have been measured at more than one temperature.

sulfur-, phosphorus-, and arsenic-bonded compounds are included. Space does not permit a detailed discussion of each type, but despite their great variety it would appear that the titanium(III) ion is mostly hexacoordinate. For this reason, the most common complex is of stoichiometry $TiX_3 \cdot 3$ L.

When the number of coordinating ligands is other than 3, hexacoordination of titanium is achieved by bridging through halogen or through bidentate ligands, or by forming ionic species. Examples of all of these types are shown in Table I.

Notable exceptions to the pseudo-octahedral symmetry of most of these compounds are those of type $TiX_3 \cdot 2$ L, where X = Cl, Br, or I and L = $N(CH_3)_3$ or α-picoline. Although originally thought to be octahedral (*64*), these have recently been assigned a five-coordinate, trans trigonal bipyramidal structure on the basis of X-ray crystallographic data from the bromide complex (*153*). Bands in the near-infrared around 4.5–7.0 kK are believed to be characteristic of this configuration (*49*).

In addition to the compounds formed with amines, nitriles, and ethers, two series of alcohol complexes are known. From $TiCl_3$ or $TiBr_3$ and isopropanol, *sec*-butanol or cyclohexanol, complexes of formula $TiX_3 \cdot 4$ ROH have been isolated (*159*). These are probably ionic with hexacoordinate titanium, viz., $[Ti(ROH)_4X_2]^+X^-$. From $TiCl_3$ in methanol all of the monomeric complexes $[TiCl_n(CH_3OH)_{6-n}]^{(3-n)+}$, where $n = 1$–6, have now been prepared and characterized (*77*, *78*). The existence of the species $[Ti(ROH)_6]^{3+}$, where R = CH_3, C_2H_5, C_3H_7, in solution has been demonstrated but the compounds were not isolated (*80*).

Several sulfur-bonded complexes of type $TiX_3 \cdot 2$ L have been prepared by Fowles, Lester, and Walton (*70*). All show magnetic exchange between neighboring titanium atoms so that their structure is probably polymeric with bridging ligands and not trigonal bipyramidal like the trimethylamine and α-picoline adducts.

The only phosphine complex known is $TiCl_3 \cdot (C_2H_4[P(C_2H_5)_2]_2)$, prepared by Chatt and Hayter (*21*) as a dark brown solid from the two reactants in boiling benzene.

Hexacoordination of titanium in the two adducts of σ-phenylenebis(dimethylarsine) with titanium trichloride and titanium tribromide has been achieved by the formation of monohydrates, viz., $TiX_3 \cdot D \cdot H_2O$, where $D = C_6H_4(As[CH_3]_2)_2$ (*166*).

From a practical point of view the importance of many of these complexes lies in their usefulness in preparing titanium compounds which may not be

accessible otherwise. The use of $TiX_3 \cdot 2\ N(CH_3)_3$ in this regard has already been mentioned, and complexes such as $HTiCl_4 \cdot O(C_2H_5)_2$ may often be substituted for titanium trichloride in the preparation of neutral $TiX_3 \cdot 3$ L complexes (*78*).

It has been claimed (*106*) that the tetrahydrofuran adduct of titanium trichloride disproportionates several hundred degrees below $TiCl_3$ itself, according to Eq. (1). Since $TiCl_4 \cdot 2$ THF is volatile such a process should constitute a useful synthesis of titanium dichloride, but in fact the residue is low in chlorine and contains, in addition to $TiCl_3$, carbonaceous matter (*183*).

$$2\ TiCl_3 \cdot 3\ THF \rightarrow TiCl_4 \cdot 2\ THF + TiCl_2 + 4\ THF \quad (1)$$

B. Visible Spectra

As stated above, in many of the complexes of titanium trihalides there is little doubt that the central metal ion is in a pseudo-octahedral environment. In most cases the visible spectrum of the compounds shows an asymmetric absorption band in the 14–16 kK region, which is typical of octahedrally coordinated titanium(III). With some complexes, distortions occur which result in a lowering of symmetry. As a result the ^2E_g and $^2T_{2g}$ terms are split and distinct shoulders or multiplet structures appear in the spectrum. The solid state reflectance spectrum is sometimes shifted relative to the solution spectrum, possibly because of site distortions.

C. Magnetics

In most cases the magnetic moment at room temperature only is available. Those cases for which moments at more than one temperature have been measured are marked in Table I with superscript ^{T}. At room temperature most are close to the spin-only value for a d^1 system (1.73 BM), but lowering of the moment with temperature by exchange through bridging ligands would be expected and in some case has been demonstrated.

Many of the structural proposals in Table I are based on visible spectra, magnetic data, molar conductance, and molecular weight determinations. In those cases where the complexes are so insoluble that solution data is excluded, then structural predictions must of necessity be based on magnetics and solid state spectra alone. It should be pointed out that

interpretations based on these two properties can lead to erroneous conclusions and care should be taken in the interpretation of such data. It is to be expected, therefore, that as further X-ray crystal structures are determined, some of the probable structures in Table I may need some adjustment.

III

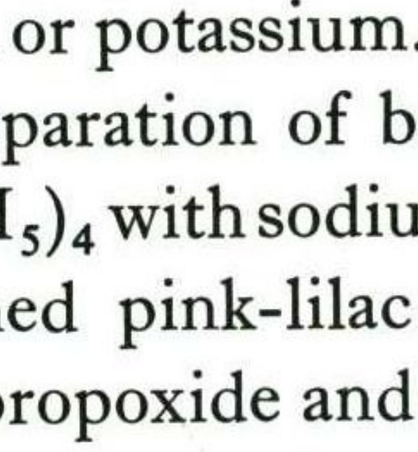
COMPLEXES OF TYPE $TiX_n \cdot (3-n)L$

A. Alkoxides of Titanium(III) (Titanites)

The structural chemistry of titanium alkoxides is dominated by the formation of polynuclear molecular clusters with bridging alkoxide groups. The mode and degree of association in alkyl titanates is reasonably well understood and has been adequately covered by Feld and Cowe (*57*). Similar alkoxy bridges exist in the few titanium(III) compounds known, and these offer efficient pathways for magnetic interaction between neighboring titanium atoms. As a result all of these derivatives have low magnetic moments.

From titanium trichloride and lithium methoxide in anhydrous methanol, the trimethoxide, $[Ti(OCH_3)_3]_n$, was obtained by Martin, Winter, and co-workers (*1*), as a yellow-green polymeric solid. Magnetic interaction between metal atoms is so strong that the complex is diamagnetic. Higher homologs have been obtained by reduction of the corresponding tetraalkoxides (titanates) by sodium or potassium. In 1928, MacCorquodale and Adkins reported (*114*) the preparation of blue triethoxytitanium in 87% purity by reduction of $Ti(OC_2H_5)_4$ with sodium in ethanol, and Nesmeyanov and collaborators have obtained pink-lilac alkoxides by potassium and alcohol reductions of the tetrapropoxide and tetrabutoxide (*137*).

From one equivalent of titanium trimethoxide and two of titanium trichloride, Winter has isolated (*189*) a red complex, $[TiCl_2(OCH_3) \cdot 2\ CH_3OH]_3$, the magnetic moment of which (1.0 BM per titanium atom) is virtually independent of temperature and indicative of the trinuclear cluster (I).



(I)

On reversing the proportions of the reactants, a dark brown complex was obtained, $TiCl(OCH_3)_2 \cdot CH_3OH$, which is also believed to contain a trinuclear cation $[Ti(OCH_3)_2 \cdot CH_3OH]^{3+}$ (*189*, *190*). Both of these compounds absorb in the visible region around 10 kK, giving spectra very similar to that of $Ti(OCH_3)_3$.

The most recent work is described in a communication from Bradley, Lappert, and co-workers (*2*), in which titanium trimethoxide and triethoxide are formed by the action of methanol or ethanol on the tris(dimethylamido) compound $Ti[(NCH_3)_2]_3$, but as yet no details are available.

It should be mentioned that alkoxides of lower-valent titanium are formed from sodium naphthalide reductions of titanium tetraalkoxides in nitrogen fixation experiments, but none of the reduced species were isolated (see Section IX,B).

B. Carboxylates of Titanium(III) (Acylates)

Much of the early work in this field was carried out by Stähler, Grossman, and others during the early part of this century by treatment of titanous chloride with various carboxylic acids and derivatives. This early work has been reviewed by Feld and Cowe (*57*) and although some of the products were not isolated and many were not characterized, several interesting carboxylates resulted.

The oxalato compounds $Ti_2(ox)_3 \cdot 10\ H_2O$, and $MTi(ox)_2 \cdot 2\ H_2O$, where $M = K$, Rb, or NH_4, were prepared by Stähler in 1905 (*165*) and have been reinvestigated by Eve and Fowles recently (*56*). The potassium, ammonium, and rubidium compounds are polymeric and spectral evidence suggests that the titanium is in an octahedral environment provided by bridging oxalato groups. The water molecules are not coordinated to the titanium atoms and can be removed from the ammonium and potassium salts by heating.

Although the decahydrate $Ti_2(ox)_3 \cdot 10\ H_2O$ was originally given an octahedral configuration (*56*), X-ray data has shown the titanium to be seven-coordinate in a pentagonal bipyramid with one oxalato group bridging the two titanium atoms (*52*).

From titanium trichloride in acetic anhydride and acetic acid McDonald, Thompson, and Larsen (*116*) have prepared acetate complexes in which one or two acetato ligands have replaced chloride, i.e., $Ti(OCOCH_3)_{1\text{ or }2}$ $Cl_{2\text{ or }1}$. Despite good analytical results, there is a possibility that with excess

acetic anhydride replacement of chloride is a continuous process without the production of unique compounds.

Many complexes of titanium(III) with ethylenediaminetetraacetic acid (EDTA) were prepared by Podlahová and Podlaha (*143*). All of these highly colored compounds, of general formula $MTi(EDTA)\cdot n\,H_2O$, where M = Ba/2 or an alkali metal, have magnetic moments around the spin-only value and their visible spectra are indicative of octahedral titanium.

An isolated phosphato complex was prepared by Gutmann and Beer (*79*) from $TiCl_3\cdot 3\,CH_3CN$ and trimethylphosphate. Methyl chloride was eliminated, giving the pink octahedral complex $Ti(O_2P[OCH_3]_2)_3$ in which the phosphato ligands are bidentate.

C. β-Diketonates of Titanium(III)

The tris(acetylacetonate) of titanium(III) was prepared by Chakravarti in 1958 from titanium trichloride and acetylacetone in benzene using gaseous ammonia as a base (*20*). The same compound has since been prepared by others (*5*, *48*, *156*), using similar methods, and by displacement of dimethylamine from $Ti(NMe_2)_3$ with acetylacetone (*2*). From benzoylacetone, dibenzoylmethane, trifluorothenoylacetone, and 3-cyanoacetylacetone, Cox, Lewis, and Nyholm (*48*) have prepared similar tris(β-diketonates). All of these complexes are intensely colored and monomeric, with magnetic moments in the range 1.66–1.68 BM at room temperature.

The extinction coefficients of their bands in the visible spectra are around 1000 liters $mole^{-1}$ cm^{-1}, which is high for *d–d* transitions. Nevertheless in the case of the tris(acetylacetonate) the major component of the band system has been assigned to a *d–d* transition, modified by mixing of the metal and ligand systems through low-lying π-orbitals (*48*, *142*). The shoulders on this main band have been attributed to vibrational fine structure (*5*, *142*).

It would be expected that distortion from octahedral symmetry in a complex with three symmetrical chelate rings would be small. In fact, from electron spin resonance (*101*), visible spectra (*5*, *142*), and magnetic measurements (*58*), the tris(acetylacetonate) has been shown to contain strong trigonal distortion.

In 1958 Pflugmacher, Carduck, and Zucketto (*141*) isolated a red complex from titanium trichloride and neat acetylacetone, to which was assigned a dimeric chlorine-bridged structure $[Ti(acac)_2Cl]_2$. The identity

of this compound as a titanium(III) derivative has been disputed (*47*), but more recently Salzmann (*156*) has prepared all three acetylacetonates of general formula $Ti(acac)_nCl_{3-n}$, where $n = 1$–3, and has investigated their magnetics. $Ti(acac)_2Cl$ shows magnetic interaction between titanium atoms with a Néel point at 120°K, behavior which would be expected of the chlorine-bridged dimer proposed by Pflugmacher and co-workers (*141*).

In physical and chemical properties the compounds $Ti(acac)_nCl_{3-n}$ bear a striking resemblance to the corresponding cyclopentadienyl derivatives $(C_5H_5)_nTiCl_{3-n}$, in Section IV.

D. Amido Compounds of Titanium(III)

Dialkylamido compounds of titanium(III) are finding use as intermediates in the preparation of other complexes. Bradley, Lappert, and co-workers have recently reported the synthesis of $Ti(NR_2)_3$, where $R = CH_3$ and C_2H_5, from titanium trichloride and the lithium dialkylamide (*2*). The isopropyl and *sec*-butyl derivatives could not be made by this method. With protic reagents such as C_5H_6, $(C_2H_5)_2NH$, $(iso\text{-}C_3H_7)_2NH$, and $[(CH_3)_3Si]_2NH$ one of the dimethylamido groups of $Ti[N(CH_3)_2]_3$ was displaced by the new ligand.

Methanol and ethanol displaced all three amido ligands to give alkoxides, and acetylacetone gave the tris(β-diketonate), $Ti(acac)_3$. Insertion of carbon disulfide into $Ti[N(C_2H_5)_3]_3$ failed to give the titanium(III) diethyldithiocarbamate; instead disproportionation occurred to the titanium(IV) and titanium(II) dithiocarbamates. Disproportionation was also observed on attempted distillation of $XTi[N(CH_3)_2]_2$, where $X = N(CH_3)_2$, $N(C_2H_5)_2$, $N(iso\text{-}C_3H_7)_2$, giving $Ti[N(CH_3)_2]_4$ and TiX_2.

E. Phosphido Compounds of Titanium(III)

The only phosphido compounds of titanium(III) are the cyclopentadienyl derivatives, $[(\pi\text{-}C_5H_5)_2Ti \cdot PR_2]_2$, where $R = C_2H_5$ or C_4H_9, which will be dealt with in Section IV,B,4.

With titanium trichloride and lithium di(cyclohexyl)phosphide, Issleib and co-workers found that reduction occurred and only the titanium(II) compound, $Ti[P(C_6H_{11})_2]_2$, could be isolated (*99*).

F. Borohydride

A green borohydride of titanium(III), $Ti(BH_4)_3$, was described by Hoekstra and Katz (*96*). It was prepared from titanium tetrachloride by reaction with lithium borohydride and is much more unstable than the cyclopentadienyl derivative described in Section IV,B,4.

IV

ORGANOMETALLIC COMPOUNDS OF TITANIUM(III)

By far the major part of the work carried out in organotitanium chemistry has been concerned with cyclopentadienyl compounds in all valence states. The reasons for this are connected with the unique stabilizing influence exerted by the π-cyclopentadienyl ligands, which allows the isolation of compounds that would undoubtedly not survive in the presence of ligands other than cyclopentadienyl. Although advantageous where the isolation of new compounds is concerned, this stability can be a disadvantage in some types of catalytic processes.

A. Tris(cyclopentadienyl)titanium(III)

$(C_5H_5)_3Ti$ was first prepared in 1960 by Fischer and Löchner (*61*) in "low yield" from sodium cyclopentadienide and $(\pi\text{-}C_5H_5)_2TiCl_2$. A much better yield (70%) was obtained by Canty, Coutts, and Wailes (*18*) from $(\pi\text{-}C_5H_5)_2TiCl$. Over the range 100–300°K the magnetic moment was found to be independent of temperature and close to the spin-only value for a d^1 system. The solubility and volatility of $(C_5H_5)_3Ti$ are strong indications of its monomeric nature.

Under 150 atmospheres pressure of carbon monoxide at 80°C the tris(cyclopentadienyl) derivative is converted to the dicarbonyl, $(C_5H_5)_2Ti(CO)_2$ (*61*). It will also react immediately with dialkyl- and diaryl disulfides, RSSR, the color changing from green to red, giving an equilibrium mixture of thiolatotitanium(IV) compounds of type $(C_5H_5)_nTi(SR)_{4-n}$ (*36*).

B. Bis(cyclopentadienyl)titanium(III) Compounds

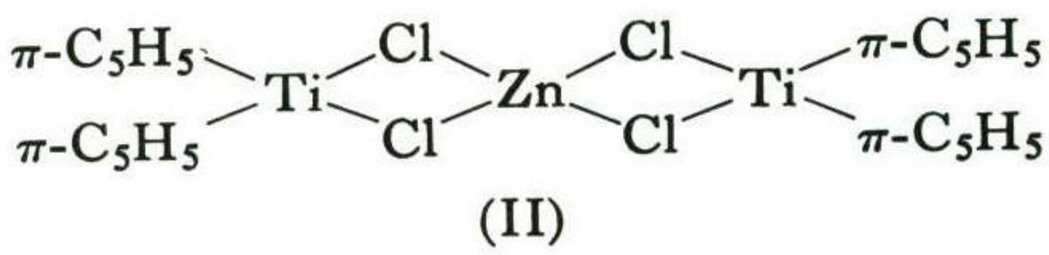
The ready availability of $(\pi\text{-}C_5H_5)_2TiCl$, both from reduction of $(\pi\text{-}C_5H_5)_2TiCl_2$ and from $TiCl_3$ with metal cyclopentadienides, has led to the widespread use of this compound as a starting material. Consequently this

group is the largest of the organotitanium(III) compounds. A characteristic of many of the bis(cyclopentadienyl)titanium(III) complexes is the distorted tetrahedral environment around the titanium atom. To achieve this configuration the compounds will polymerize, solvate, or in some way coordinate a ligand into the fourth position. Polymerization generally leads to magnetic exchange between neighboring titanium atoms, resulting in low magnetic moments.

The visible spectral bands listed in Table III are believed to be due to *d–d* transitions but in some cases it is difficult to distinguish these from charge-transfer bands. In addition the shift in band maxima with changes in the ligands means that interpretation of the spectra is a difficult process which can give misleading results.

1. *Reduction of* $(\pi\text{-}C_5H_5)_2TiCl_2$

In polar organic solvents such as methanol, tetrahydrofuran, or acetone, bis(cyclopentadienyl)titanium dichloride will react rapidly with finely divided zinc, giving the green complex (II).



(II)

Similar but slower reductions occur in the presence of magnesium and aluminum (*187*). The zinc chloride complex, which gives only small amounts of $(\pi\text{-}C_5H_5)_2TiCl$ on attempted sublimation, is probably the same compound obtained by Birmingham, Fischer, and Wilkinson in 1955 (*9*), although its composition was not recognized at the time.

In the presence of thiocyanate, cyanate, cyanide, nitrate, etc., during the reduction, the chloride bridges are replaced by the more abundant anion (*187*). Contrary to a previous claim (*9*), as yet no satisfactory method has been found for removal of the zinc salt from these complexes in organic solvents to give $(\pi\text{-}C_5H_5)_2TiCl$, and in the use of the zinc complex for the preparation of other titanium(III) derivatives the presence of the zinc should not be overlooked. The lack of spin-pairing in the ESR spectrum of the zinc-reduced $(\pi\text{-}C_5H_5)_2TiCl_2$, for example, which has been attributed to the presence of a solvated monomer of $(\pi\text{-}C_5H_5)_2TiCl$ (*16*), is due to the fact that the magnetic moment of the zinc complex shows the spin-only value, independent of temperature, with no magnetic interaction between

TABLE III

ORGANOMETALLIC COMPOUNDS OF TITANIUM(III)[a]

Compound	Color	Visible spectra (kK)		μ_{eff} (BM, 20°C)	References
		Solid	Solution (ϵ)		
	Tris(cyclopentadienyl)titanium(III)				
$(C_5H_5)_3Ti$	Dark green	14.3 16.8	—	1.69[T]	*18, 61*
	Bis(cyclopentadienyl)titanium(III) compounds				
Prepared in Air-Free Water					
$[(C_5H_5)_2TiCl]_2$	Green	8.85 13.3	10.0 13.9	1.6[T]	*151*
$(C_5H_5)_2Ti$ picrate	Brown	—	—	2.3	*188*
$[(C_5H_5)_2Ti]_2SO_4$	Pale green	9.35 13.9	—	1.64[T]	*39*
$[(C_5H_5)_2Ti]_2CO_3$	Pale blue	10.8 12.2 13.7	—	0.8[T]	*39*
$(C_5H_5)_2Ti(acac)$	Deep blue	—	10.3 13.0 14.6 (61) 17.2 (43)	1.74[T]	*42*

$(C_5H_5)_2Ti(O_2C{-}R)$					
R = H	Green	11.8 14.5	—	1.69^{τ}	*35*
R = CH_3	Royal blue	10.6 13.9 16.7	—	1.71^{τ}	*35*
R = C_9H_{19}	Royal blue	10.5 13.9 16.9	—	1.72^{τ}	*35*
R = $C_{17}H_{35}$	Royal blue	10.9 13.9 16.7	—	1.55^{τ}	*35*
R = C_6H_5	Dark green	10.4 13.3 17.2	—	1.62^{τ}	*35*
$[(C_5H_5)_2Ti(O_2C)]_2R'$					
R′ = —CH_2CH_2—	Gray-blue	10.8 14.1 16.7	—	1.66^{τ}	*35*
R = —CH=CH— (*cis*)	Pale green	10.2 13.9 16.7	—	1.61^{τ}	*35*
R = —CH=CH— (*trans*)	Mauve	10.5 13.5 17.5	—	1.68^{τ}	*35*
$(C_5H_5)_2Ti(SO{-}C{-}R)$					
R = H	Dark green	10.0 13.8 16.4	—	1.64^{τ}	*38*

(*Continued*)

TABLE III (*Continued*)

Compound	Color	Visible spectra (kK) Solid	Visible spectra (kK) Solution (ϵ)	μ_{eff} (BM, 20°C)	References
$R=CH_3$	Dark green	10.6 13.7 15.8	—	1.74^T	*38*
$R=C_2H_5$	Dark green	10.4 13.2 15.9	—	1.64^T	*38*
$R=C_{17}H_{35}$	Dark green	10.5 13.3 15.9	—	1.55^T	*38*
$R=C_6H_5$	Teal blue	13.1 16.95	—	1.71^T	*38*
$(C_5H_5)_2Ti$(S,S)$C-NR_2$					
$R=H$	Pale green	—	13.3 (60) 16.0 (110)	1.60^T	*43, 44*
$R=CH_3$	Blue-green	—	13.3 (43) 16.3 (82) 21.7 (140)	1.64^T	*43, 44*
$R=C_2H_5$	Deep green	—	13.3 (43) 16.3 (79) 21.55 (176)	1.68^T	*43, 44*
$R=n\text{-}C_3H_7$	Deep green	—	13.3 (41) 16.45 (76)	1.63^T	*43, 44*

			21.5 (158)		
$R=n\text{-}C_4H_9$	Deep green	—	13.3 (47) 16.4 (87) 21.4 (179)	1.47^T	*43, 44*
$R=n\text{-}C_5H_{11}$	Deep green	—	13.3 (51) 16.5 (94) 21.4 (188)	—	*43, 44*
$R_2=-(CH_2)_5-$	Deep green	—	13.3 (43) 16.4 (78) 21.4 (140)	1.71^T	*43, 44*
$(C_5H_5)_2Ti(S_2C{=}O{-}R)$					
$R=CH_3$	Light blue	—	14.3 (55) 16.4 (82) 18.5 (126)	1.60^T	*45*
$R=C_2H_5$	Bright blue	—	14.3 (47) 16.5 (74) 18.6 (111)	1.54^T	*45*
$R=n\text{-}C_3H_7$	Bright blue	—	14.3 (49) 16.5 (77) 18.5 (115)	1.60^T	*45*
$R=n\text{-}C_4H_9$	Dark blue	—	14.3 (53) 16.5 (86) 18.5 (132)	1.63^T	*45*
$R=n\text{-}C_5H_{11}$	Dark blue	—	14.3 (52) 16.6 (85) 18.6 (128)	1.62^T	*45*
$[(C_5H_5)_2TiCN]_3$	Purple	—	12.9	1.03^T	*34*
$[(C_5H_5)_2TiNCS]_3$	Red-brown	—	12.0	1.00^T	*34*
$[(C_5H_5)_2TiNCSe]_3$	Chocolate brown	—	9.8 15.9 20.4	0.88^T	*36*

(Continued)

TABLE III (*Continued*)

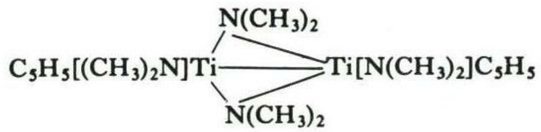
Compound	Color	Visible spectra (kK) Solid	Visible spectra (kK) Solution (ϵ)	μ_{eff} (BM, 20°C)	References
$(C_5H_5)_2TiNCO$	Green		9.7 12.8 15.4	1.64^T	*34*
$[(C_5H_5)_2Ti(H_2O)_3]_2[BPh_4]_2$	Pale blue	9.1 14.8	—	1.4^T	*31*
$[(C_5H_5)_2Ti(py)_2][BPh_4]$	Dark green	11.0 13.9	—	1.72^T	*31*
$[(C_5H_5)_2Ti(N{\equiv}CCH_3)_2][BPh_4]$	Bright blue	13.0 17.8	—	1.74^T	*31*
$([(\pi\text{-}C_5H_5)_2Ti]_2O)_n$	Deep blue	11.0 13.7 17.7	—	0.97^T	*31*
Prepared in Organic Media					
$[(C_5H_5)_2TiCl]_2$	Green	8.85 13.3	10.0 13.9	1.6^T	*151*
$[(C_5H_5)_2TiBr]_2$	Red-brown	—	—	—	*138*
$[(C_5H_5)_2TiI]_2$	Black-brown	—	—	—	*138*
$(C_5H_5)_2TiCl.py$	Red	—	9.5 (32) 12.3 (46) 13.9 (50) 19.3 (100)	1.72^T	*184*

$(C_5H_5)_2TiCl \cdot 4,4'$-bipy	Green	—	9.65 (40) 12.1 (60) 16.2 (90)	1.62^T	*184*
$[(C_5H_5)_2TiCl \cdot dipy]_2 \cdot dipy$	Blue	—	11.3 (72) 13.3 (65) 17.6 (180)	1.82^T	*40*
$[(C_5H_5)_2TiCl \cdot phen]_2 \cdot phen$	Mauve	—	11.6 (54) 13.0 (47) 17.85 (134)	1.85^T	*40*
$[(C_5H_5)_2TiCl \cdot phm]_2 \cdot phm$	Pale green	—	9.1 (26) 13.5 (54) 14.3 (57)	1.94^T	*40*
(phm = *o*-phenylenediamine) $[(C_5H_5)_2TiCl \cdot picam]_2 \cdot picam$	Fawn	—	13.4 (85) 17.2 (120)	1.78^T	*40*
(picam = α-picolylamine) $(C_5H_5)_2TiCl \cdot terpy$	Dark green	—	17.0	—	*36*
$[(C_5H_5)_2TiP(C_2H_5)_2]_2$	Violet	—	—	Diam.	*98, 105*
$[(C_5H_5)_2TiP(C_4H_9)_2]_2$	Violet	—	—	Diam.	*98, 105*
$(C_5H_5)_2Ti \cdot BH_4$	Violet	—	—	—	*138, 100*
$(C_5H_5)_2Ti \cdot BF_4$	Blue	—	—	—	*138*
$(C_5H_5)_2TiSn(C_6H_5)_3 \cdot THF$	Green	—	—	1.6	*37*
$(C_5H_5)_2TiGe(C_6H_5)_3 \cdot THF$	Green	—	—	1.6	*37*
$[(C_5H_5)_2TiC_6H_5]_2$	Olive green	12.3 14.9	—	Diam.	*46*
$[(C_5H_5)_2TiC{\equiv}CC_6H_5]_n$	Dark green	—	13.4 15.3	Diam.	*46, 169*
$[(C_5H_5)_2TiC{\equiv}CH]_n$	Black	—	—	—	*104*
$[(C_5H_5)_2TiC{\equiv}CTi(C_5H_5)_2]_n$	Blue	—	—	—	*104*
$(C_5H_5)_2Ti$-allyl	Violet	—	19.5 (364)	1.65	*120*
$(C_5H_5)_2Ti$-1-methylallyl	Blue-violet	—	18.55 (364)	1.67	*120*
$(C_5H_5)_2Ti$-2-methylallyl	Purple	—	16.8 (62) 20.1 (283)	1.72	*120*

(*Continued*)

TABLE III (*Continued*)

Compound	Color	Visible spectra (kK) Solid	Visible spectra (kK) Solution (ϵ)	μ_{eff} (BM, 20°C)	References
$(C_5H_5)_2Ti$-1,3-dimethylallyl	Blue	—	17.3 (445)	1.72	*120*
$(C_5H_5)_2Ti$-1,1-dimethylallyl	Brown-red	—	—	1.48	*120*
$(C_5H_5)_2Ti$-1,2-dimethylallyl	Violet	—	19.15	—	*120*
$(C_5H_5)_2Ti$-1-methyl-3-ethylallyl	Blue	—	17.2	—	*121*
$(C_5H_5)_2Ti$-1,2,3-trimethylallyl	Violet	—	17.7	—	*121*
$[(C_5H_5)_2TiN(CH_3)_2]_2$	Red-brown	—	—	—	*2*
$[(C_5H_5)_2TiOCH_3]_n$	Dark brown	—	12.3 18.5	1.38^T	*36*
$[(C_5H_5)_2TiOC_2H_5]_n$	Dark brown	—	12.0 17.5	—	*36*
$[(C_5H_5)_2TiOC_4H_9$-*tert*$]_n$	Dark brown	—	12.5 16.9	—	*36*
$(C_9H_7)_2TiCl$	Yellow-red	—	—	—	*118*
$(C_9H_7)_2TiBr$	Brick red	—	—	—	*118*
$(C_9H_7)_2TiI$	—	—	—	—	*118*
[(C_9H_7 = indenyl)]					
	Mono(cyclopentadienyl)titanium(III) compounds				
$C_5H_5TiCl_2$	Purple	9.6 14.1 19.6	—	1.69^T	*7, 18, 36*

$C_5H_5TiCl_2 \cdot 2$ py	Green	—	15.3 22.5	—	*36*
$C_5H_5TiCl_2 \cdot$ bipy	Blue-gray	—	14.3 19.6	—	*36*
	Red-brown	—	—	Diamag.	*2*
$C_5H_5TiC_8H_8$	Green	—	—	1.60	*170*
Alkyl and aryl titanium(III) compounds					
CH_3TiCl_2		—	—	—	*110*
$CH_3TiCl_2 \cdot 3$ py	Blue	—	—	—	*127*
$C_6H_5TiCl_2 \cdot 3$ py	Blue	—	15.15	—	*127*
$(CH_3)_3Ti$	Green	—	—	—	*26*
$C_2H_5TiCl_2$	—	—	—	—	*139*
$C_8H_{17}TiCl_2$	—	—	—	—	*139*
$[Ti_3[C_6(CH_3)_6]_3Cl_6]Cl$	Violet	—	—	1.84 per trimer	*62*

[a] T indicates cases for which moments have been measured at more than one temperature.

titanium atoms (*155*, *184*). Its subsequent reactions with Grignard reagents and lithium alkyls cannot necessarily be equated with the reactions of $(\pi\text{-}C_5H_5)_2TiCl$ with these reagents.

If the reduction with zinc is carried out in air-free water, however, a bright blue solution containing the $(\pi\text{-}C_5H_5)_2Ti^+$ cation is obtained. Bis(cyclopentadienyl)titanium(III) compounds can then be precipitated from this solution by those anions which do not have insoluble zinc derivatives. The aqueous chemistry of $(\pi\text{-}C_5H_5)_2Ti^+$ will be covered below in Section IV,B,3.

The zinc complex (II) is in the same class as the halogen-bridged bimetallic species $(\pi\text{-}C_5H_5)_2TiX_2MR_2$. where M = boron, aluminum, gallium, or indium and R = alkyl or halogen, which are formed from reduced $(\pi\text{-}C_5H_5)_2TiCl_2$ and the trihalides or mixed alkyl halides of Group III elements. These are being extensively studied in connection with their Ziegler-Natta-type polymerization properties, and will be dealt with more fully later in Section IX,A.

For the preparation of $(\pi\text{-}C_5H_5)_2Ti^{III}$ compounds in organic media, $(\pi\text{-}C_5H_5)_2TiCl$ is the starting material of choice. It may be prepared from the bimetallic complexes mentioned above, e.g., $(\pi\text{-}C_5H_5)_2TiCl_2AlR_2$, by complexing the aluminum with trimethylamine or ether (*14*, *27*) according to Eq. (2),

$$(\pi\text{-}C_5H_5)_2Ti\begin{matrix}Cl\\Cl\end{matrix}Al\begin{matrix}R\\R\end{matrix} + (C_2H_5)_2O \longrightarrow (\pi\text{-}C_5H_5)_2TiCl + R_2AlCl,O(C_2H_5)_2 \quad (2)$$

From 0.25 mole of lithium aluminum hydride and $(\pi\text{-}C_5H_5)_2TiCl_2$ in tetrahydrofuran, $(\pi\text{-}C_5H_5)_2TiCl$ can be obtained in 70% yield by sublimation directly from the reaction mixture (*104*). Alternative preparations are from titanium trichloride and sodium cyclopentadienide (*130*), or best, magnesium cyclopentadienide (*151*). The latter reagent will not place any more than two cyclopentadienyl rings on titanium(III) halides.

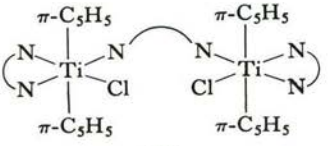
2. *Properties of* $(\pi\text{-}C_5H_5)_2TiCl$

$(\pi\text{-}C_5H_5)_2TiCl$ is a green-brown, air-sensitive dimer (*130*) which oxidizes in air to give yellow oxygen-bridged polymers (*76*). The magnetic moment is low due to magnetic interaction, either through the bridging chlorines or by titanium–titanium bonding (*18*, *123*). In organic solvents the compound will split disulfides, giving thiolatotitanium(IV) derivatives (*33*), Eq. (3).

$$2\,(\pi\text{-}C_5H_5)_2TiCl + RSSR \longrightarrow 2\,(\pi\text{-}C_5H_5)_2Ti\begin{matrix}SR\\Cl\end{matrix} \qquad (3)$$

With organic azides, RN_3, nitrogen is liberated and the nitrogen-bridged compounds $[\pi\text{-}(C_5H_5)_2TiCl]_2NR$, where $R = C_6H_5$ or $p\text{-}ClC_6H_4$, are obtained (*32*). In halogenated solvents the monochloride will also abstract halogen rapidly giving red $(\pi\text{-}C_5H_5)_2TiCl_2$.

Several complexes of $(\pi\text{-}C_5H_5)_2TiCl$ with various nitrogen-containing ligands are known. Thus with bipyridyl, phenanthroline, α-picolylamine, and σ-phenylenediamine, the dimeric complexes (III) with bridging



(III)

bidentate ligands are precipitated (*40*), whereas by reduction of $(\pi\text{-}C_5H_5)_2TiCl_2$ with sodium pyridyl two more complexes were obtained (*184*). That in higher yield was $(\pi\text{-}C_5H_5)_2TiCl\cdot py$, a red air-sensitive monomer very soluble in organic solvents. A by-product was the green, less-soluble 4,4′-bipyridyl complex, $(\pi\text{-}C_5H_5)_2TiCl\cdot bipy$, the ligand of which was undoubtedly formed from sodium pyridyl. Magnetic measurements on both compounds show that the moments are around 1.6–1.7 BM and are independent of temperature.

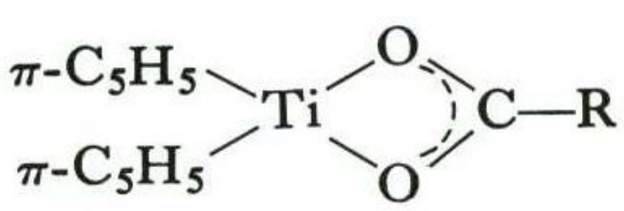
A deep green terpyridyl adduct, $(C_5H_5)_2TiCl\cdot terpy$, can be formed from the two reactants in tetrahydrofuran over several days. Since the complex is sparingly soluble in organic solvents but dissolves readily in water, it is probably ionic in nature (*36*).

The diamagnetic, halogen-free titanium-aluminum derivative, $[(\pi\text{-}C_5H_5)_2TiAl(C_2H_5)_2]_2$, has been obtained by Natta and co-workers from $(\pi\text{-}C_5H_5)_2TiCl$ and triethylaluminum (*29*, *132*). The same compound was prepared by Wailes and Weigold (*184*) from titanocene and triethylaluminum and will be discussed in Sections VII,A,2 and IX,A.

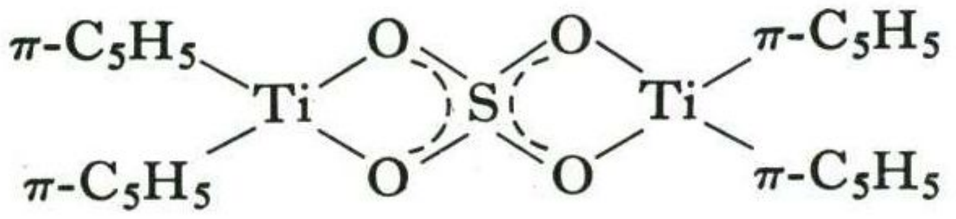
3. *Aqueous Chemistry of* $(\pi\text{-}C_5H_5)_2TiCl$

In air-free water $(\pi\text{-}C_5H_5)_2TiCl$ dissolves to give a bright blue solution which shows the molar conductance of a 1:1 electrolyte. Wilkinson and Birmingham (*188*) showed in 1954 that picrate and silicotungstate derivatives could be precipitated from solutions containing the $(\pi\text{-}C_5H_5)_2Ti^+$

ion, and more recently Coutts and Wailes have prepared a great range of new titanium(III) compounds using water as solvent. Of those compounds listed in Table III the carboxylates (*35*), thiocarboxylates (*38*), dithiocarbamates (*43*), xanthates (*45*), and sulfate (*39*) are all monomeric and volatile with magnetic moments which are virtually independent of temperature and close to the spin-only value for titanium(III) (1.73 BM). All of these derivatives are unusual in that the bidentate chelating ligands do not bridge but form four-membered rings with the titanium atom giving monomeric structures, e.g., carboxylates (IV) and sulfate (V).



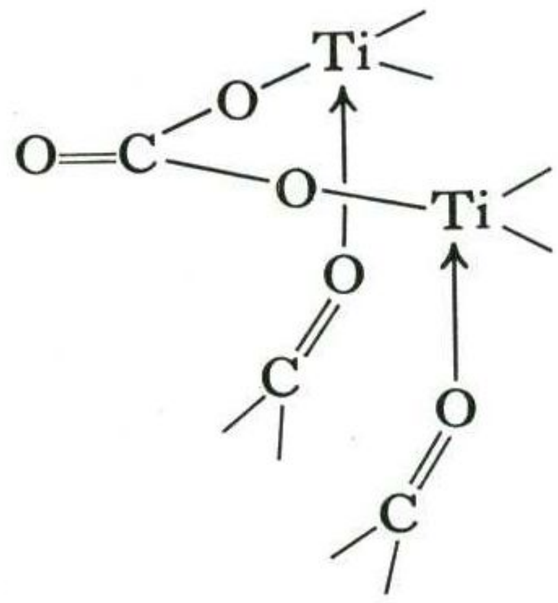
(IV)



(V)

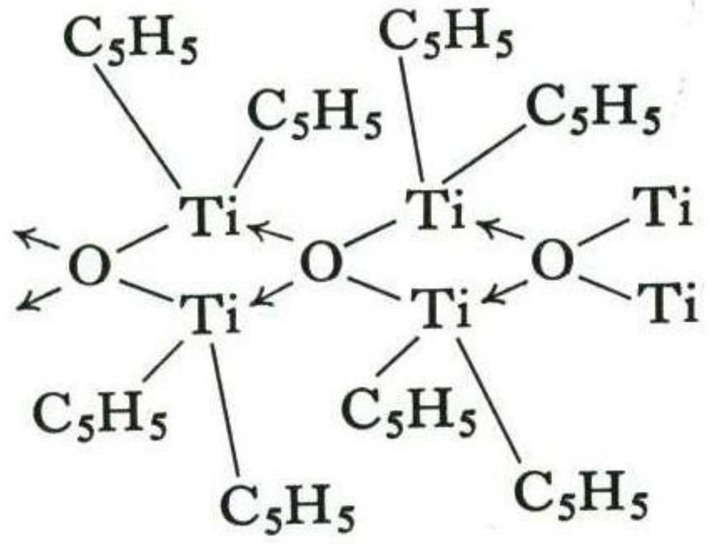
Although it has been claimed (*51*) that an acetylacetonate of π-$C_5H_5Ti^{III}$ does not form, the deep blue $(\pi\text{-}C_5H_5)_2Ti\cdot acac$ was obtained (*42*) by vigorously stirring acetylacetone in excess with an aqueous solution of $(\pi\text{-}C_5H_5)_2TiCl$. This monomeric derivative is extremely volatile and can be sublimed below 100° C under high vacuum.

The carbonato complex, $[(C_5H_5)_2Ti]_2CO_3$, can be prepared from either sodium carbonate or bicarbonate, as a pale blue solid which has low magnetic moments due to interaction between neighboring titanium atoms (*39*). This magnetic exchange may proceed via the π-electrons of the symmetric O—C—O group, by a mechanism similar to that proposed for copper formate (*140*), although metal–metal bonding is also possible. The third oxygen atom of the carbonato ligand may be involved in satisfying the coordination requirements of the titanium atom, as in (VI) for example. The insolubility in organic solvents of the carbonato relative to the sulfato derivative could be indication of this.



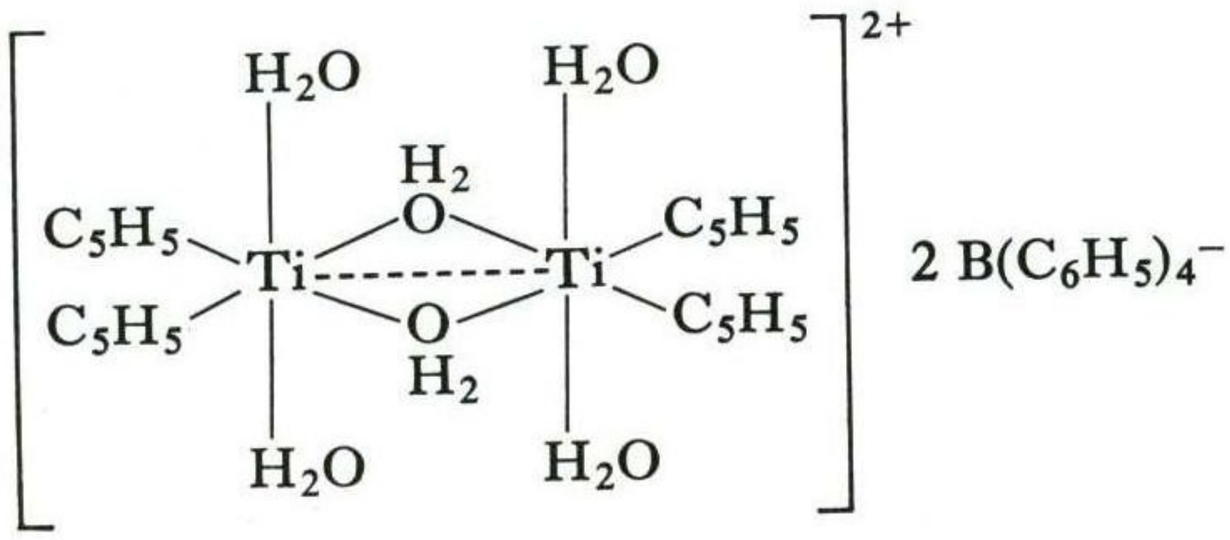
(VI)

The magnetic susceptibility of the carbonato compound could not be measured above 100° C due to decomposition. Carbon dioxide was liberated leaving a deep blue insoluble residue which is apparently a polymer of titanocene oxide, $([(\pi\text{-}C_5H_5)_2Ti]_2O)_n$. Its insolubility, involatility, and low magnetic moment (0.9 BM) suggest a highly polymerized structure, probably bridged through oxygen (*39*), as in (VII).



(VII)

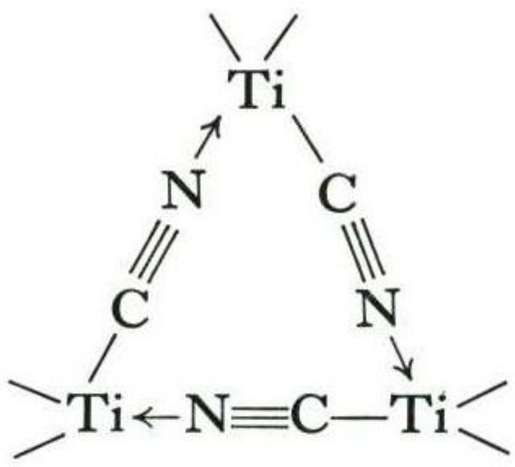
A similar compound was obtained by pyrolysis of the pale blue hydrated tetraphenylborato derivative $[(\pi\text{-}C_5H_5)_2Ti \cdot 3\ H_2O]_2 \cdot 2\ BPh_4$, prepared by addition of $NaBPh_4$ to $(\pi\text{-}C_5H_5)_2TiCl$ in water (*31*). The tetraphenylborato group is noncoordinating and in the aquo complex the coordination number of the titanium ions has been increased by formation of hydrated species. Since water molecules in two different environments can be distinguished in the infrared spectrum, it is believed that bridging water is present, providing a pathway for magnetic exchange between the two titanium atoms.



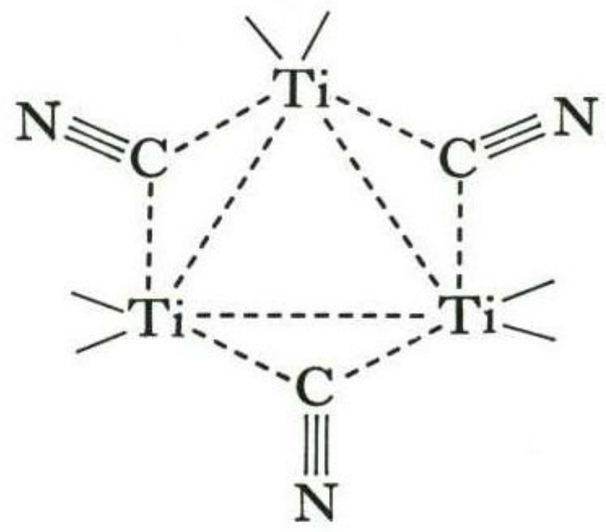
(VIII)

From methanolic solutions of $(\pi\text{-}C_5H_5)_2TiCl$ and $NaBPh_4$ in the presence of methyl cyanide, the bright blue crystalline complex $[(\pi\text{-}C_5H_5)_2Ti \cdot 2\ N{\equiv}CCH_3]BPh_4$ was obtained (*31*), and could be converted to the corresponding pyridine complex $[(\pi\text{-}C_5H_5)_2Ti \cdot 2\ py]BPh_4$ by recrystallization from this solvent (*31*). In both of these compounds the variation of magnetic susceptibility with temperature follows a Curie-Weiss law, the moments being independent of temperature and close to 1.7 BM.

The pseudohalides $(\pi\text{-}C_5H_5)_2TiX$, where X = CN, NCS, NCO (*34*), and NCSe (*36*) have been prepared similarly in water as highly colored, air-sensitive solids. From infrared and mass spectral data the compounds X = NCO, NCS, and NCSe were shown to be iso derivatives bonded through nitrogen. The cyanide, isothiocyanate, and isoselenocyanate have uncorrected magnetic moments around 1 BM per titanium atom, which is independent of temperature over a limited range. This effect is claimed to be indicative of trinuclear metal clusters (*28*). Confirmation of the trimeric nature of the cyanide came from the mass spectrum. Whether the bridging ligands are linear, (IXa), or of the three-center type, (IXb), has not been determined.



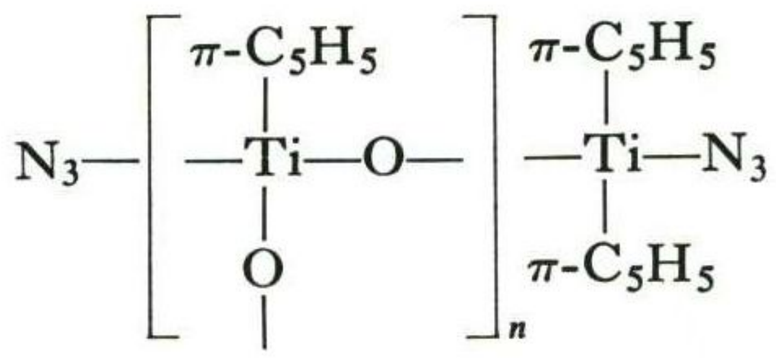
(IXa)



(IXb)

Surprisingly the pale green isocyanate does not show a reduced magnetic moment and thus differs from the other pseudohalides. It is more soluble and more volatile than the others and would appear to be monomeric.

Many attempts have been made to prepare the corresponding azido derivative $[(\pi\text{-}C_5H_5)_2TiN_3]$, but in water the product of the reaction between sodium azide and $(\pi\text{-}C_5H_5)_2TiCl$ liberates nitrogen and cyclopentadiene, giving yellow insoluble products (*41*). From the presence of an azide band in the infrared spectrum it seems likely that the compound is a polymer terminated by azide of type (X) [cf. the chloride polymers (*76*)].

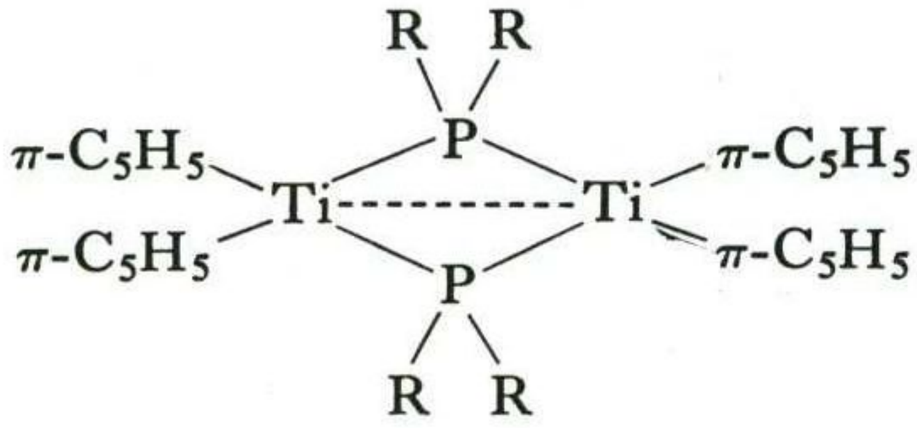


(X)

In dimethylformamide the solvated complex of the azide $(\pi\text{-}C_5H_5)_2TiN_3 \cdot DMF$, was obtained as a green unstable solid which decomposed at room temperature (*41*).

4. *Preparation of* $(\pi\text{-}C_5H_5)_2Ti^{III}$ *Compounds in Organic Media*

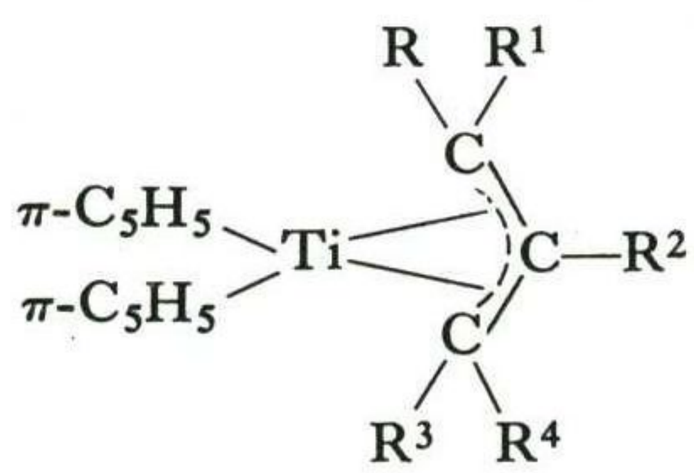
From $(\pi\text{-}C_5H_5)_2TiCl_2$ and Grignard reagents or other strongly reducing reactants, several bis(cyclopentadienyl)titanium(III) compounds have been isolated. Issleib and Häckert (*98*) obtained the bridged phosphido complex (XI), where $R = C_2H_5$ or $n\text{-}C_4H_9$, from $(\pi\text{-}C_5H_5)_2TiCl_2$ and



(XI)

2 moles of $LiPR_2$. The violet compounds are diamagnetic and with methyl iodide give $(\pi\text{-}C_5H_5)_2TiI$ and the dimethyldialkylphosphonium iodide.

By reduction of the titanium(IV) compound with allyl Grignard reagents Jellinek and collaborators have prepared a series of allyltitanium(III) compounds substituted in the 1-, 2-, and 3-positions, of general structure



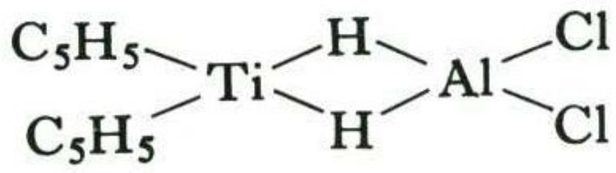
(XII)

(XII) (*83*, *120*). Several of the compounds have been prepared from $(\pi\text{-}C_5H_5)_2TiCl$ with 1 mole of allyl Grignard reagent (*121*), or with isopropylmagnesium bromide in the presence of dienes (*119*, *121*). The compounds are all monomeric and blue to violet in color; they have one unpaired electron per titanium atom. The allylic group occupies two coordination positions on the titanium atom, leading to the stable tetrahedral arrangement so common in compounds of this class.

As intermediates in the formation of these allyl derivatives and also in the reactions of both $(\pi\text{-}C_5H_5)_2TiCl_2$ and $(\pi\text{-}C_5H_5)_2TiCl_2ZnCl_2Ti(\pi\text{-}C_5H_5)_2$ with lithium alkyls and Grignard reagents, it has been suggested (*16*, *121*) that dihydride and dialkyl complexes are formed as intermediates. The evidence for the existence of such complexes, of type $[(\pi\text{-}C_5H_5)_2TiR_2]^-$, where $R = H$, CH_3, C_2H_5, etc., comes from ESR spectra, but as yet no hydride or alkyl derivative of $(\pi\text{-}C_5H_5)_2Ti^{III}$ has been isolated and characterized.

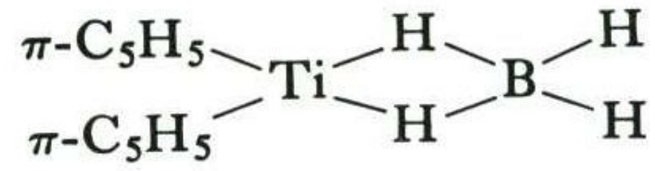
Note added in proof: The titanium(III) hydride $[(\pi\text{-}C_5H_5)_2TiH]_2$ has recently been isolated by Bercaw and Brintzinger as a purple solid from the reaction between gaseous H_2 and solid $(\pi\text{-}C_5H_5)_2Ti(CH_3)_2$ (*8a*).

The bimetallic hydride (XIII) has been suggested by Henrici-Olivé and Olivé as product of the reduction of $(\pi\text{-}C_5H_5)_2TiCl_2$ with sodium in the presence of $AlCl_3$ (*91*). The suggestion was made in order to explain six 1/2/1 triplets in the ESR spectrum of the reaction mixture, apparently due to the splitting by two equivalent hydrogen nuclei of the six-line spectrum caused by interaction of the unpaired titanium(III) electron with the aluminum nucleus ($I=\frac{5}{2}$).



(XIII)

Lithium borohydride in ether will also reduce $(\pi\text{-}C_5H_5)_2TiCl_2$ giving $(\pi\text{-}C_5H_5)_2Ti\cdot BH_4$ (*138*), a volatile compound with double hydrogen bridge between titanium and boron.



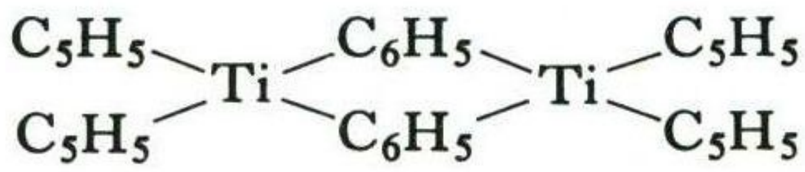
(XIV)

With HCl, HBr, HI, BCl_3, or BBr_3 the borohydride (XIV) is converted to the corresponding titanium(III) halides, $(\pi\text{-}C_5H_5)_2TiX$, while boron trifluoride afforded the tetrafluoroborate, $(\pi\text{-}C_5H_5)_2TiBF_4$, which is bridging through two fluorine atoms (*138*).

Compounds containing metal–metal bonds between elements of Groups IVA and IVB have been prepared. In particular titanium(III)–tin and titanium(III)–germanium compounds were isolated (*37*) as paramagnetic solvated complexes, $(\pi\text{-}C_5H_5)_2TiM(C_6H_5)_3\cdot THF$, where M = Sn or Ge, from the reaction between $(\pi\text{-}C_5H_5)_2TiCl$ and sodium tin triphenyl or lithium germanium triphenyl. The corresponding lead derivative could be formed as a bright green solution in tetrahydrofuran at low temperature but deposition of lead occurred rapidly at room temperature and the compound could not be isolated.

Recently the olive green phenyl derivative, $[(\pi\text{-}C_5H_5)_2TiC_6H_5]_2$ has been isolated (*46*) from the reaction between $(\pi\text{-}C_5H_5)_2TiCl$ and LiPh.

In this case the coordination number of the titanium has been satisfied by dimerization, probably bridging through phenyl groups.



(XV)

Since the magnetic susceptibility of (XV) can be accounted for almost entirely by temperature-independent paramagnetism, spin-pairing of the electrons is quite strong and may involve metal–metal bonding.

The same phenyl derivative has been postulated as an intermediate in the pyrolysis of the titanium(IV) derivative $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$ to give titanocene (*148*), but it was never isolated from this pyrolysis.

The corresponding deep green phenylethynyl derivative, $(\pi\text{-}C_5H_5)_2TiC{\equiv}CC_6H_5$, is claimed from mass spectral evidence to be a dimer with bridging phenylethynyl groups (*169*). Phenylethynyl-bridged aluminum, gallium, indium, zinc, and cadmium derivatives all show C≡C stretching bands in their infrared spectra around 2050–2120 cm^{-1} (*102*), whereas $(\pi\text{-}C_5H_5)_2TiC{\equiv}CC_6H_5$ shows no band in this region. This evidence is not in accord with a bridging dimer, nor is its extreme insolubility in polar solvents (*46*). The presence of a mass spectral peak at *m/e* for a dimer does not necessarily preclude the presence of a higher oligomer. It would seem likely that the triple bond is associated in a much more complex manner than a bridging dimer would require.

The related complexes, black $[(\pi\text{-}C_5H_5)_2TiC{\equiv}CH]_n$ and blue $[(\pi\text{-}C_5H_5)_2TiC{\equiv}CTi(\pi\text{-}C_5H_5)_2]_n$, have been isolated from reaction mixtures of the mono- and dimagnesium bromides of acetylene with $(\pi\text{-}C_5H_5)_2TiCl$ (*104*). Both compounds are air-sensitive and undoubtedly polymeric. Like the phenylethynyl derivative they show no acetylenic bands in their infrared spectra.

A recent communication (*2*) describes the preparation of the dimethylamido-bridged dimer, $[(\pi\text{-}C_5H_5)_2Ti\cdot N(CH_3)_2]_2$, and its use in the synthesis of titanium(III) derivatives by displacement of dimethylamine with protic reagents such as alcohols and metal hydrides, but details are not yet available.

The alkoxides $[(\pi\text{-}C_5H_5)_2TiOR]_n$ are chocolate brown solids which were obtained by Coutts and Wailes from $(\pi\text{-}C_5H_5)_2TiCl$ and the sodium alkoxide in tetrahydrofuran (*36*). The alkoxides are extremely soluble, even in light

petroleum, and are extensively associated. The molecular weight values, in terms of multiples of the monomer are as follows: methoxide, 2.2 to 2.6 depending on concentration in boiling benzene; ethoxide, 2.5; and *tert*-butoxide, 1.4. Magnetic measurements on the methoxide over the temperature range 112° to 293° K reflect this association, the moments ranging from 1.03 to 1.38 BM. The electronic absorption spectrum of the *tert*-butoxide differs somewhat from that of the other homologs (Table III). In tetrahydrofuran a strong band around 16,900 cm^{-1} develops, which is probably caused by irradiation in the spectrophotometer since the same thing happens in sunlight, the color changing to deep blue simultaneously.

The bis(indenyl)titanium(III) halides, $(C_9H_7)_2TiX$, where X = Cl, Br, or I, are known. These are analogous to the cyclopentadienyl derivatives and were prepared by reduction of the corresponding titanium(IV) dihalides with triethylaluminum (*118*). The intermediate green complexes $(C_9H_7)_2TiX_2Al(C_5H_5)_2$ are tabulated in Table VIII, Section IX,A.

C. *Mono(cyclopentadienyl)titanium(III) Compounds*

This field has scarcely been touched and few complexes are known in which one cyclopentadienyl ring is attached to titanium(III). The first was prepared by Bartlett and Seidel (*7*) by the action of di(isobutyl)aluminum chloride on $(\pi\text{-}C_5H_5)_2TiCl_2$. The chlorido ligands remained untouched but one cyclopentadienyl group was removed, giving the purple $\pi\text{-}C_5H_5TiCl_2$.

A rather more convenient preparation in 85% yield is by zinc reduction of $\pi\text{-}C_5H_5TiCl_3$ in benzene in the presence of a stoichiometric amount of tetrahydrofuran (*41*). A purple precipitate of $\pi\text{-}C_5H_5TiCl_2$ appears almost immediately and after filtration can be extracted from unreacted zinc with tetrahydrofuran. Although the insolubility in nonpolar solvents and involatility of this compound would indicate some type of association, its magnetic moment is close to the spin-only value and is virtually independent of temperature (*18*). This behavior would not be expected of, say, a chlorine-bridged oligomer. The compound forms a blue-green crystalline tetrahydrofuranate and a green crystalline triethylamine complex, but these solvents are only weakly coordinated and on pumping under vacuum or washing with ether they are easily removed. The green pyridine complex $C_5H_5TiCl_2 \cdot 2$ py and the blue-gray bipyridyl complex $C_5H_5TiCl_2 \cdot$ bipy are rather more stable and can be isolated as well-defined complexes (*41*).

Differences in their solubilities and spectral properties seem to indicate different structures for these two derivatives.

Cyclopentadienylbis(dimethylamido)titanium(III) is reported to be formed by the action of cyclopentadiene on the tris(dimethylamido) derivative, $Ti(N[CH_3]_2)_3$ (*2*). One of the dimethylamido ligands of π-$C_5H_5Ti[N(CH_3)_2]_2$ is bridging and magnetic interaction between titanium atoms renders the compound virtually diamagnetic.

From $C_5H_5TiCl_3$ or $(C_5H_5)_2TiCl_2$ and the dipotassium salt of cyclo-octatetraene, van Oven and de Liefde Meijer have recently isolated the green volatile titanium(III) derivative $C_5H_5TiC_8H_8$ (*170*). The magnetic moment of this complex is 1.6 BM and it is independent of temperature.

D. Alkyl and Aryl Titanium(III) Compounds

These are usually so thermally unstable that they cannot be isolated. Such is the case with trimethyltitanium, which has been obtained only as deep green solutions in tetrahydrofuran from titanium trichloride and methyllithium at $-50°$ to $-80°$ C. Above $-20°$ C the solutions decompose, giving a gas and leaving a black residue (*26*).

The alkyltitanium dichlorides $RTiCl_2$, where $R = CH_3$ and C_8H_{17}, are mentioned in a French patent (*139*) as products of the reaction between titanium tetrachloride and the appropriate trialkylaluminum. Pyridine adducts of this class of compound, i.e., $RTiCl_2 \cdot 3$ py, where $R = CH_3$ and C_6H_5, were isolated by Japanese workers from the action of Grignard reagents on titanium trichloride in pyridine (*127*). The alkyl derivatives decompose at room temperature but the aryl is more stable. Despite the instability described by most workers, a recent communication from Kühlein and Clauss mentions the isolation of uncomplexed CH_3TiCl_2 for the first time and describes its use in ethylene polymerization (*110*), but details of its preparation and properties are lacking.

A novel complex of titanium has been isolated by Fischer and Röhrscheid (*62*) from titanium tetrachloride heated to 130° C with aluminum powder, aluminum chloride, and hexamethylbenzene. The complex, $(Ti_3[C_6(CH_3)_6]Cl_6)Cl$, has a trinuclear cluster of titanium atoms with two bridging chlorides between each pair and one hexamethylbenzene molecule coordinated to each titanium atom. In line with its formulation as a trinuclear cluster, the violet compound has a magnetic moment of 1.84 BM, i.e., one unpaired electron per trinuclear unit.

From the same reactants in benzene instead of hexamethylbenzene, the complex $C_6H_6TiCl_2 \cdot 2\ AlCl_3$ has been isolated (*122*, *133*, *176*). This is a halogen-bridged titanium(III) complex with benzene coordinated to the central titanium atom. It is active in polymerization and nitrogen fixation and will be dealt with in Section IX,A.

V

ADDITION COMPLEXES OF TITANIUM DIHALIDES

Methods of preparation similar to those used for the trihalide complexes are generally successful, i.e., direct reaction between the dihalide and the donor ligand, but reaction times are necessarily longer and some ligands, e.g., pyridine, do not give clean products. Better results have been obtained by displacing methyl cyanide from $TiX_2 \cdot 2\ CH_3CN$, which can be formed in high yield from the two reactants (*71*). Although this method works

TABLE IV

ADDITION COMPLEXES OF TITANIUM DIHALIDES

Compound	Color	Visible spectra (kK) Solid	Visible spectra (kK) Solution	μ_{eff} (BM, 20°C)	References
		O-Coordinated			
$TiCl_2 \cdot 2$ THF	Dark brown	16.1 22.2	—	1.21	*67*, *71*
$TiCl_2 \cdot 2$ THP	Black	14.3	—	0.99	*67*, *71*
$TiCl_2 \cdot 2$ DMF	Green	—	—	1.17	*55*
		N-Coordinated			
$TiCl_2 \cdot 2\ CH_3CN$	Black	21.8	9.7 14.0	1.05^T	*67*, *71*
$TiCl_2 \cdot 2$ py	Brown	24.4	25.2	1.14	*67*, *71*
$TiCl_2 \cdot$ bipy	Dark blue	20.0	14.0 19.0	1.09	*67*, *71*
$TiCl_2 \cdot$ phen	Dark blue	16.7	18.0	1.11^T	*67*, *71*
$TiBr_2 \cdot 2\ CH_3CN$	Black	9.7	14.0	1.0^T	*67*, *71*
$TiBr_2 \cdot$ bipy	Dark blue	15.4	17.0	1.10	*67*, *71*

reasonably well with the dichloride, little success has been achieved with the bromide. As a result, the methyl cyanide and bypyridyl adducts remain the only *N*-coordinated complexes of $TiBr_2$ so far characterized. All of the dihalide complexes are dark brown or blue in color and are strong reducing agents. They are oxidized by air and react with water to produce hydrogen. Their magnetic moments are all in the range 0.99–1.35 BM, in accord with polymeric structures with bridging ligands, probably forming six-coordinate titanium. Their visible spectra show only weak shoulders superimposed on rising absorption in the ultraviolet region above 10 kK (Table IV).

VI

COMPLEXES OF TYPE $TiX_n \cdot (2—n)L$

A. Alkoxides of Titanium(II)

Titanium(II) alkoxides, $Ti(OR)_2$ where R = benzyl or allyl, are believed to be intermediates in the coupling of benzyl or allyl alcohol to bibenzyl or

TABLE V

COMPLEXES OF TYPE $TiX_n \cdot (2-n)L$

Compound	Probable structure	Color	Visible spectra (kK) Solid	Solution (ϵ)	μ_{eff} (BM, 20°C)	References
β-Diketonates						
$Ti(acac)_2$	Polymeric	Red-brown	—	16.4 (110) 20.8 (207)	0.41[T]	*156*
Amido Derivatives						
$(Ti[N(CH_3)_2]_2)_n$	Polymeric	Black-green	—	—	—	*2*
$(Ti[N(C_2H_5)_2]_2)_n$	Polymeric	Black-green	—	—	—	*2*
$(Ti[N(iso\text{-}C_3H_7)_2]_2)_n$	Polymeric	Black-green	—	—	—	*2*
Phosphido Derivative						
$Ti[P(C_6H_{11})_2]_2$	Monomeric	Black-brown	—	—	—	*99*
Dithiocarbamate						
$Ti[S_2CN(C_2H_5)_2]_2$	—	—	—	—	—	*2*

1,5-hexadiene (*172*). Impure titanium(II) benzoxide was obtained as a black, air-sensitive solid by reduction with metallic potassium, sodium naphthalide, or alkyllithium of the reaction product from $TiCl_3$ or $TiCl_4$ and benzyl alcohol. On being heated in glyme the black alkoxide generated bibenzyl. Coupling of saturated alcohols in the same manner was not successful.

B. β-Diketonate of Titanium(II)

No carboxylates of titanium(II) are known but the bis(acetylacetonato) derivative, $Ti(acac)_2$, was reported by Salzmann in 1968 (*156*). The red-brown product was prepared by reduction of $Ti(acac)_2Cl_2$ with sodium sand in tetrahydrofuran; it is almost diamagnetic and its insolubility and low chemical reactivity probably indicate a polymeric structure.

C. Amido Derivatives of Titanium(II)

Several dialkylamido derivatives have been mentioned in a recent communication (*2*). The green-black pyrophoric compounds, $Ti(NR_2)_2$ where $R = CH_3$, C_2H_5, or iso-C_3H_7, were obtained, as well as the corresponding titanium(IV) compounds, by disproportionation of the trivalent amido compounds $Ti(NR_2)_3$.

D. Bis(diethyldithiocarbamato)titanium(II)

Disproportionation was observed also on attempted insertion of carbon disulfide into $Ti[N(CH_3)_2]_3$. The bis- and tetra(diethyldithiocarbamato)-titanium derivatives were obtained (*2*).

E. Phosphido Derivative of Titanium(II)

On treatment of $TiCl_3 \cdot 3$ THF or $TiCl_4 \cdot 2$ THF with lithium di(cyclohexyl)phosphide, reduction occurred and the titanium(II) compound $Ti[P(C_6H_{11})_2]_2$ was isolated as a black-brown pyrophoric compound which behaves as a monomer in benzene (*99*). With iodine oxidation to the titanium (IV) species $TiI_2[P(C_6H_{11})_2]_2$ and $TiI_3 \cdot P(C_6H_{11})_2$ occurs.

VII

ORGANOMETALLIC COMPOUNDS OF TITANIUM(II)

A Bis(cyclopentadienyl)titanium(II) and Derivatives

1. *Preparation*

Although a preparation of bis(cyclopentadienyl)titanium (titanocene) from titanium dichloride was reported by A. K. Fischer and Wilkinson (*59*) in 1956, no one has yet succeeded in repeating this preparation (*185*). Other syntheses of $(C_5H_5)_2Ti$ are now available but there is some reason to believe that the bonding in the "titanocenes" prepared by the various methods is not consistent.

In 1962 Clauss and Bestian reported (*27*) that solutions of bis(cyclopentadienyl)dimethyltitanium in hexane deposited green crystalline $(C_5H_5)_2Ti$ on exposure to hydrogen at ambient temperatures.

$$(\pi\text{-}C_5H_5)_2Ti(CH_3)_2 + H_2 \rightarrow (C_5H_5)_2Ti + 2\,CH_4 \qquad (4)$$

In fact, a solution of titanocene in tetrahydrofuran may be prepared directly from $(\pi\text{-}C_5H_5)_2TiCl_2$ and 2 moles of methyllithium in a hydrogen atmosphere. On treatment with halogens and other reagents the titanocene was oxidized to known titanium(IV) compounds, which is good reason to believe that both of the rings are π-bonded.

Russian workers have prepared $(C_5H_5)_2Ti$ from the same dimethyl derivative and also from the diphenyl derivative, by pyrolysis in hexane in a sealed tube at 90° C. The yield of green-black $(C_5H_5)_2Ti$ was reported to be 91% (*148*).

A later preparation of $(C_5H_5)_2Ti$ by Watt and co-workers (*186*) used strongly reducing sodium naphthalide to remove the two chloride ions from $(\pi\text{-}C_5H_5)_2TiCl_2$. Modifications of this reductive method employ sodium sand in toluene or tetrahydrofuran (*158*) or sodium amalgam (*162*). Interestingly, with one equivalent of anhydrous hydrogen chloride the "Watt titanocene" is converted fairly rapidly to a purple compound, $[(C_5H_5)_2TiCl]_n$, while a second equivalent slowly forms green, insoluble $[(C_5H_5)_2TiCl_2]_n$. Both of these products differ from the usual forms of the chlorides and these results were interpreted by Salzmann and Mosimann (*158*) as indicating the presence of two different types of ring–metal bonding, i.e., π- and σ-types. Support for this theory came from Köpf and Block (*109*), who used titanocene to split disulfides, diselenides, and iodine, to give

$(C_5H_5)_2TiX_2$, where X = SR, SeR, or I. The low yields of known compounds obtained possibly reflects the different types of ring–metal bonding present and the difficulty of changing to the bis(π-cyclopentadienyl) derivatives. In addition, Calderazzo, Salzmann, and Mosimann (*17*) obtained two different bipyridyl adducts of titanocene according to the method used (see below). The reactions reported below have been carried out using $(C_5H_5)_2Ti$ from reduction of the dichloride. There seems to have been little work done with the corresponding compound of Clauss and Bestian (*27*) or Razuvaev and co-workers (*148*). A comparison between the two should be made.

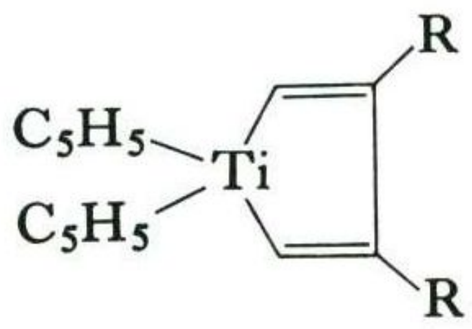
2. *Reactions of* $(C_5H_5)_2Ti$

$(C_5H_5)_2Ti$ is a dark green diamagnetic solid which is dimeric in benzene (*17*, *158*, *186*), although its mass spectrum shows no peaks at *m*/*e* greater than that of the monomer (*168*). The NMR spectrum shows four peaks between τ 3.3 and 4.1 (*158*).

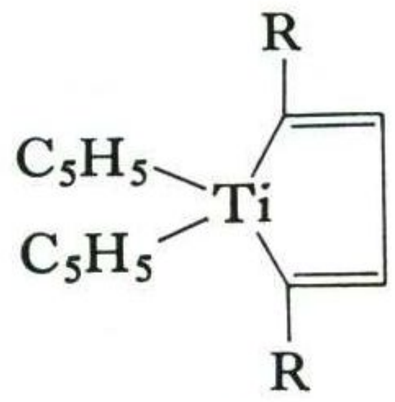
With oxygen the peroxo compound $[(C_5H_5)_2TiO_2]$ was obtained, while nitric oxide produced the hyponitrite $(C_5H_5)_2TiNO$, which appears to be a polymer and is weakly paramagnetic (μ_{eff} 0.43 BM) (*157*).

"Titanocene" absorbs carbon monoxide slowly at room temperature and atmospheric pressure, giving low yields of the known dicarbonyl $(C_5H_5)_2Ti(CO)_2$ (*17*; see below).

Japanese workers have investigated the reactions of titanocene with acetylenes and have found that acetylene itself was readily polymerized at 30°C by $(C_5H_5)_2Ti$, giving red-black "polyacetylene" containing trans double bonds (*192*). Mass spectral evidence suggests (*168*) that the complex



(XVIa)



(XVIb)

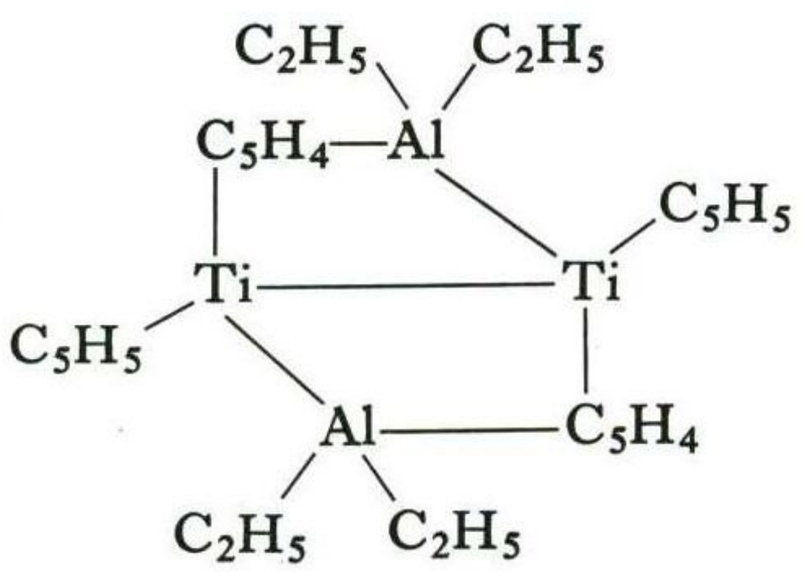
from $(C_5H_5)_2Ti$ and methylacetylene has structure (XVIa) or (XVIb). Similar types of compounds have been isolated from the reactions between diphenylacetylene or phenylacetylene and $(C_5H_5)_2Ti(CO)_2$ (*124*, *164*) or a mixture of titanium tetrachloride and excess sodium cyclopentadienide (*177*).

An interesting reaction between titanocene and boron halides was demonstrated by Nöth and collaborators (*161*); the halides are split giving purple titanium–boron-bonded derivatives as shown in Eq. (5), where

$$[(C_5H_5)_2Ti] + 2\,Y_2BX \longrightarrow (C_5H_5)_2Ti\begin{matrix}X\\BY_2\end{matrix} \qquad (5)$$

X and Y = Cl and C_6H_5, Br and Br, or Cl and Cl.

With triethylaluminum in benzene in a sealed tube at 60° C "titanocene" undergoes an insertion reaction with liberation of ethane (*184*). The purple product obtained is diamagnetic and appears to be identical in every respect with the complex obtained by Natta and co-workers (*29*, *132*) from $(C_5H_5)_2TiCl$ and $(C_2H_5)_3Al$ in boiling benzene, in which aluminum apparently bridges between titanium and the cyclopentadienyl ligand on the neighboring titanium atom as in (XVII).



(XVII)

With trimethylaluminum under the same conditions titanocene forms the analogous methyl compound, $[C_5H_5TiC_5H_4Al(CH_3)_2]_2$ with loss of methane (*184*).

Complexes of $(C_5H_5)_2Ti$ with bipyridyl and pyridine have been obtained in various ways. A 1:1 adduct with 2,2′-bipyridyl was obtained by heating the reactants together at 105° C (*17*) but the blue complex was too insoluble for molecular weight measurements to be made. Another adduct of the same stoichiometry was obtained (*17*) by reduction of the dichloride with dilithium bipyridyl. This compound is dark blue and monomeric, and

$$(C_5H_5)_2TiCl_2 + Li_2bipy \rightarrow (C_5H_5)_2Ti\cdot bipy + 2\,LiCl \qquad (6)$$

is probably the same complex as was isolated by Fischer and Amtmann (*60*) from the action of 2,2′-bipyridyl on the dicarbonyl $(C_5H_5)_2Ti(CO)_2$.

Reduction of $(C_5H_5)_2TiCl_2$ with sodium pyridyl gave a complex of formula $[(C_5H_5)_2Ti]_2\cdot 3$ py (*184*). Oxidation followed by sublimation gave

TABLE VI

ORGANOMETALLIC COMPOUNDS OF TITANIUM(II)

Compound	Color	Visible spectra (kK)		μ_{eff} (BM, 20°C)	References
		Solid	Solution		
$(C_5H_5)_2Ti$	Dark green	—	—	Diamag.	*27, 59, 148, 158, 162, 186*
$(C_5H_5)_2Ti(CO)_2$	Red-brown	—	20.6 (277)	Diamag.	*17, 60, 61, 128*
$(C_5H_5)_2Ti \cdot NO$	Brown	—	—	0.43	*157*
$(C_5H_5)_2Ti \cdot bipy$	Blue-black	—	12.8 (2130)	0.6	*17, 60*
			17.4 (2530)	0.80	
$[(C_5H_5)_2Ti]_2 \cdot 3\ py$	Red-brown	—	—	0.96	*184*
$[(C_5H_5)_2Ti]_2 \cdot py$	Brown	—	—	—	*184*
$[C_5H_5Ti(C_5H_4)Al(C_2H_5)_2]_2$	Purple	—	9.3	Diamag.	*29, 132, 184*
$[C_5H_5Ti(C_5H_4)Al(CH_3)_2]_2$	Purple	—	—	Diamag.	*184*
$(C_5H_5)_2Ti[O{=}C{=}C(C_6H_5)_2]$	Orange-yellow	—	—	—	*97*
$C_5H_5TiC_6H_5 \cdot 2\ O(C_2H_5)_2$	Black	—	—	—	*147, 148*
$C_5H_5TiC_6H_5 \cdot 2\ NH_3$	Black	—	—	—	*147, 148*
$(C_6H_5)_2Ti$	Black	—	—	—	*111, 146*
$(C_6H_5)_2Ti \cdot THF$	Black	—	—	—	*111, 146*
$(C_6H_5)_2Ti \cdot NH_3$	Black	—	—	—	*111, 146*

a mixture of several bipyridyls so that it is not known whether the ligand is coordinated as pyridine or bipyridyl. Titanocene will dissolve on heating in pyridine and from the solution $[(C_5H_5)_2Ti]_2py$ has been isolated (*184*). Both of these complexes have been characterized by elemental analyses and molecular weight determinations.

The fact that complexing of "titanocene" with such donor ligands gives compounds which are not formed by reduction of $(C_5H_5)_2TiCl_2$ by alkali metal derivatives of the same ligands seems further proof that this reduction alters the bonding in the titanocene in some way. Comparison with the $(C_5H_5)_2Ti$ of Clauss and Bestian (*27*) or of Razuvaev and co-workers (*148*) would be of great interest.

3. *Bis(cyclopentadienyl)titanium dicarbonyl*

The only carbonyl of titanium is $(C_5H_5)_2Ti(CO)_2$, which was first prepared by Murray in 1959 (*128*) from titanium tetrachloride [or $(C_5H_5)_2TiCl_2$], excess sodium cyclopentadienide, and carbon monoxide under pressure. The carbonyl has been obtained also from the action of CO on $(C_5H_5)_3Ti$ at 80° C and 150 atm (*61*) and on $(C_5H_5)_2Ti$ at 20° C and atmospheric pressure (*17*). It is a red-brown readily sublimable solid which is pyrophoric in air and behaves as a monomer in benzene. Because of its diamagnetism, the NMR spectrum of the dicarbonyl shows a single sharp proton resonance peak at 5.42 τ in benzene-d_6, or 4.94 τ in acetone-d_6 (*17*).

As was mentioned above, $(C_5H_5)_2Ti(CO)_2$ expels carbon monoxide on treatment with substituted acetylenes and forms green titanium(IV) derivatives of type (XVIa) or (XVIb) (*124*, *164*), and with bipyridyl blue-black $(C_5H_5)_2Ti \cdot bipy$ is formed (*60*). When heated in solution to 160° C with phenanthroline or terpyridyl the Ti^0 complexes $Ti \cdot 3$ phen and $Ti \cdot 2$ terpy were obtained (*8*). These are violet to black in color and are diamagnetic. A similar reaction occurs with diphenylketene (*97*); carbon monoxide is expelled and the orange-yellow crystalline complex $(C_5H_5)_2Ti \cdot [O{=}C{=}C(C_6H_5)_2]$ is obtained.

The carbonyl also acts as a homogeneous catalyst for the hydrogenation of 1-alkynes to 1-alkenes (*164*).

B. Mono(cyclopentadienyl)titanium(II) Compounds

The only compound of this type is cyclopentadienylphenyltitanium which was isolated as an etherate, $C_5H_5TiC_6H_5 \cdot 2\,O(C_2H_5)_2$, by Razuvaev and

colleagues during their work on the pyrolysis of titanium(IV) derivatives of type $(C_5H_5)_nTiR_{(4-n)}$ (*147*, *148*). At 20°C in ether $C_5H_5Ti(C_6H_5)_3$ decomposes with loss of two phenyl ligands, leaving the black etherate. With gaseous ammonia this is converted to a black ammoniate C_5H_5Ti-$C_6H_5 \cdot 2\,NH_3$.

C. Diphenyltitanium(II)

This is the only purely σ-bonded organotitanium(II) compound reported. Tetraphenyltitanium is thermally unstable above −20°C, eliminating two phenyl groups to form black diphenyltitanium. This compound complexes with tetrahydrofuran and also with anhydrous ammonia, giving 1:1 adducts (*111*, *146*).

VIII

COMPLEXES OF TITANIUM IN VALENCIES LOWER THAN TWO

Under strongly reducing conditions in the presence of donor ligands titanium halides form a number of complexes in which the formal oxidation state of the metal is below 2. Breil and Wilke found that when titanium tetrabutoxide was reduced with triethylaluminum in the presence of cyclooctatetraene two complexes were formed depending on the ratio of reactants (*13*). These were $Ti(cot)_2$ and $Ti_2(cot)_3$, both formed in over 80% yield. The complexes are interconvertible and an X-ray crystal structure investigation of $Ti_2(cot)_3$ has shown it to have a double sandwich structure (*50*). The two outer rings are regular octahedrons whose planes are slightly inclined towards the axis of the molecule.

$Ti(cot)_2$ can also be prepared from $TiCl_4$ with 2 moles of disodium cyclooctatetraene. It is believed that the cyclooctatetraene molecules are bonded, at least partly, as quasi-aromatic planar 10 π-electron systems, i.e., as dianions (*13*).

When $(C_5H_5)_2Ti(CO)_2$ was heated to 160°C with phenanthroline or terpyridyl, carbon monoxide and cyclopentadienyl ligands were lost and the titanium(0) complexes $Ti(phen)_3$ and $Ti(terpy)_2$ were obtained (*8*).

TABLE VII

COMPLEXES OF TITANIUM IN VALENCIES LOWER THAN TWO

Compound	Color	μ_{eff} (BM, 20°C)	References
$Ti(cot)_2$	Violet-red	—	*13*
$Ti_2(cot)_3$	Yellow	—	*13*, *50*
$Ti(phen)_3$	Violet-black	Diamag.	*8*
$Ti(terpy)_2$	Black	Diamag.	*8*
$Ti(bipy)_3$	Violet-black	Diamag.	*93*, *94*
$Li[Ti(bipy)_3]3.7$ THF	Blue-violet	1.75	*93*, *94*
$Li_2[Ti(bipy)_3]5.7$ THF	Green	Diamag.	*95*
$Li_3[Ti(bipy)_3]7$ THF	—	1.75	*92*

The dark violet to black compounds, formed in almost quantitative yield, are diamagnetic.

Herzog and co-workers have prepared a tris(bipyridyl) complex of titanium by reduction of titanium tetrachloride with dilithium bipyridyl in the presence of excess bipyridyl (*93*, *94*). Further reduction of this complex with lithium or sodium in tetrahydrofuran or lithium aluminum hydride has given a series of complexes containing titanium in low oxidation states, and nonstoichiometric numbers of coordinated molecules of tetrahydrofuran (*92*, *95*). These appear to be only weakly bonded.

$$\begin{array}{ccc} Ti(bipy)_3 & \underset{\text{Oxid}}{\overset{\text{Li}}{\rightleftharpoons}} & Li[Ti(bipy)_3]\cdot 3.7\ THF \\ & & \Big\uparrow_{\text{Oxid}}^{\text{Li}}\Big\downarrow \\ Li_3[Ti(bipy)_3]\cdot 7\ THF & \rightleftharpoons & Li_2[Ti(bipy)_3]\cdot 5.7\ THF \end{array} \qquad (7)$$

Although it would appear that the titanium reaches an oxidation number of -3, it is more probable that the ligands are being reduced and are functioning as anions (*92*), the electrons being delocalized into the ligand rings.

The bipyridyl complexes are interconvertible and by controlled oxidation the above reduction sequence may be reversed as shown in Eq. (7).

IX

LOWER-VALENT TITANIUM COMPLEXES IN CATALYSIS

A. Olefin Polymerization

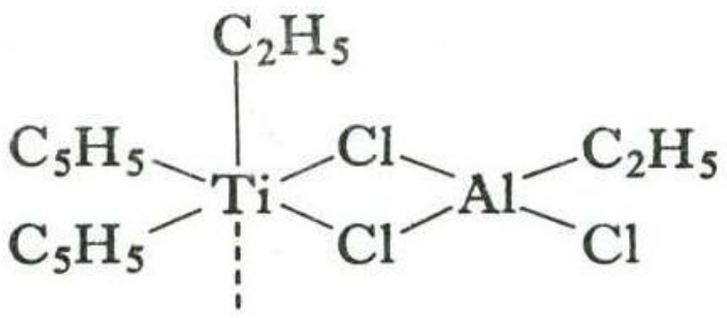
It is not the purpose of this article to review the field of olefin polymerization (see *11*, *57*, *103*, for reviews) but any treatment of titanium(III) derivatives would not be complete without mention of some of the compounds which have been obtained during the search for new polymerization catalysts.

The Ziegler-type catalysts are in general composed of a transition metal compound and an organometallic reducing agent containing a Group I–III metal, the function of which is to alkylate and reduce the transition metal and to complex with it (*103*). Catalysts used in industry generally are prepared from $TiCl_4$ or $TiCl_3$ and triethylaluminum and undoubtedly contain alkyltitanium compounds, but their heterogeneous nature means that the structures and mechanism involved in the polymerization process are difficult to study and are not well understood.

Soluble catalysts for olefin polymerization have been prepared by reaction of $(\pi\text{-}C_5H_5)_2TiCl_2$ with alkylaluminums or alkylaluminum halides and several well-defined titanium complexes have been isolated as a result of this work. In addition, the mechanism of polymerization using these systems has been discussed (*84*) in terms of the theory proposed by Cossee (*30*) for heterogeneous catalysis.

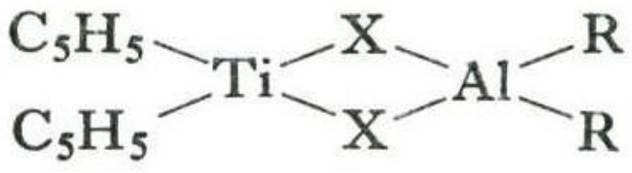
With $(C_5H_5)_2TiCl_2$ and $(C_2H_5)_3Al$ reduction occurs extremely rapidly with evolution of ethane, giving the titanium(III) complex (XIX; X = Cl, $R = C_2H_5$). The fast reduction rate makes this mixture a poor catalyst for polymerization (*84*). With $(C_2H_5)_2AlCl$ or $C_2H_5AlCl_2$ the reduction is slower and the various steps in the reaction can be followed. It is believed that the first step is the rapid formation of a diamagnetic complex (*14*, *84*, *113*), e.g., $(C_5H_5)_2TiCl_2 \cdot (C_2H_5)_2AlCl$, with bridging bonds between the two metals, in which some authors maintain (*84*, *150*), the titanium(IV) ion is in an octahedral environment with one vacant coordination site, e.g., (XVIII).

In the presence of olefins, π-bonding into the vacant site can occur, the double bond is weakened, and polymerization results. In the absence of olefins, hydrogen is transferred from one ethyl group to another on a second



(XVIII)

molecule, probably via the vacant coordination site, giving ethylene and ethane (*84*). As a result the complex slowly loses its activity and changes to a stable paramagnetic complex in which the titanium has been reduced to the trivalent state and is now in a distorted tetrahedral environment. Methylaluminum compounds follow the same reaction course but reduction occurs less readily (*6*, *117*, *132*). An X-ray study of (XIX; X = Cl, R = C_2H_5) has been carried out by Natta, Corradini, and Bassi (*129*) and shows the distorted tetrahedral arrangement around titanium with the bond angles in the central four-membered ring close to 90°.



(XIX)

Complexes of type (XIX) have been prepared also from (π-$C_5H_5)_2TiCl$ and alkyls or halides of aluminum (*131*). By reduction of (π-$C_5H_5)_2Ti(C_3H_7)Cl$ with sodium or potassium in the presence of a Group III trichloride, similar complexes containing boron, gallium, or indium instead of aluminum were obtained (*87–89*). These complexes are tabulated in Table VIII; they are blue to green in color with one unpaired electron per titanium atom. The ESR spectra of some have been recorded (*6*, *87–89*, *117*) and show hyperfine interaction of the unpaired electron of the titanium (III) atom with the magnetic nuclei of the Group III elements.

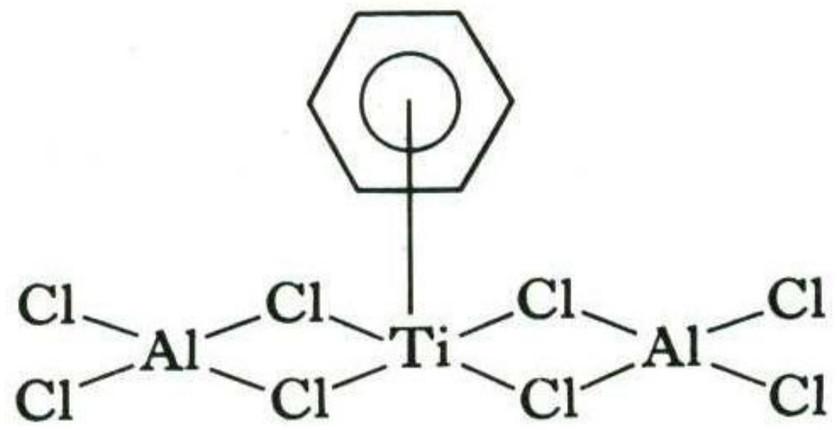
The zinc complex (π-$C_5H_5)_2TiCl_2ZnCl_2Ti(\pi$-$C_5H_5)_2$, is readily prepared by reduction of (π-$C_5H_5)_2TiCl_2$ with metallic zinc and has been mentioned previously (Section IV,B,1).

From titanium tetrachloride, aluminum, and aluminum chloride in benzene an arene-titanium(II) complex, $C_6H_6 \cdot TiCl_2 \cdot 2\ AlCl_3$, was isolated (*122*, *133*, *176*). This has been formulated as the halogen-bridged complex (XX) in which benzene is coordinated to the central titanium ion (*176*); it is an active catalyst for the cyclooligomerization of butadiene (*176*) and is also useful in nitrogen fixation (*178*, *179*),

TABLE VIII

BIMETALLIC COMPOUNDS WITH BRIDGING BONDS

Compound	Color	Visible spectra (kK)		μ_{eff} (BM, 20°C)	References
		Solid	Solution		
$(\pi\text{-}C_5H_5)_2TiCl_2ZnCl_2Ti(\pi\text{-}C_5H_5)_2$	Green	—	7.7 (33) 14.3 (96)	1.71[T]	*155*
$(\pi\text{-}C_5H_5)_2TiCl_2Al(C_2H_5)_2$	Blue	—	—	1.70	*14, 129, 131, 134, 135*
$(\pi\text{-}C_5H_5)_2TiCl_2Al(C_2H_5)Cl$	Blue	—	—	1.56	*84, 130, 131, 132, 135*
$(\pi\text{-}C_5H_5)_2Ti(CH_3)ClAl(CH_3)_2$	—	—	—	—	*132*
$(\pi\text{-}C_5H_5)_2TiCl_2Al(CH_3)_2$	—	—	—	—	*6, 117*
$(\pi\text{-}C_5H_5)_2TiCl_2Al(iso\text{-}C_4H_9)_2$	—	—	—	—	*6, 117*
$(\pi\text{-}C_5H_5)_2TiCl_2MCl_2$ (M = B, Al, Ga, In)	Blue	—	—	1.7	*84, 87, 89, 130, 131, 135*
$[C_5H_5Ti(C_5H_4)\cdot Al(C_2H_5)_2]_2$	Purple	—	9.3	Diamag.	*29, 132, 184*
$[C_5H_5Ti(C_5H_4)\cdot Al(CH_3)_2]_2$	Purple	—	—	Diamag.	*184*
 $Cl_2AlCl_2TiCl_2AlCl_2$	—	—	—	—	*122, 133, 176, 178, 179*
$(C_9H_7)_2TiCl_2Al(C_2H_5)_2$	Dark green	—	—	—	*118*
$(C_9H_7)_2TiBr_2Al(C_2H_5)_2$	Green	—	—	1.68	*118*
$(C_9H_7)_2TiI_2Al(C_2H_5)_2$	Green	—	—	—	*118*



(XX)

The effectiveness of aryltitanium compounds as polymerization catalysts for vinyl chloride has been investigated by Razuvaev and co-workers (*149*). With the introduction of cyclopentadienyl ligands, the activity of the catalyst decreased.

From $(\pi\text{-}C_5H_5)_2TiCl$ and $(C_2H_5)_3Al$ in boiling benzene Natta and co-workers obtained the red complex $[(C_5H_5)Ti(C_5H_4)Al(C_2H_5)_2]_2$ (*156*) which is also active in polymerization. The same compound has been obtained by Wailes and Weigold (*184*) from titanocene and $(C_2H_5)_3Al$; its structure, determined from an X-ray study by Corradini and Sirigu (*29*), is discussed in Section VII,A,2. The methyl analog of this complex, $[(C_5H_5)Ti(C_5H_4)Al(CH_3)_2]_2$, has been obtained in a similar manner from titanocene and trimethylaluminum with liberation of methane (*184*).

The bis(indenyl) derivatives $(C_9H_7)_2TiX_2Al(C_2H_5)_2$ where X = Cl, Br, or I, have been isolated also (*118*) from $(C_9H_7)_2TiCl_2$ treated with triethylaluminum. With trimethylamine the complexes are split to give the corresponding bis(indenyl)titanium(III) halide. The olefin polymerization properties of the indenyl complexes have been explored by Marconi and collaborators (*118*).

B. Nitrogen Fixation

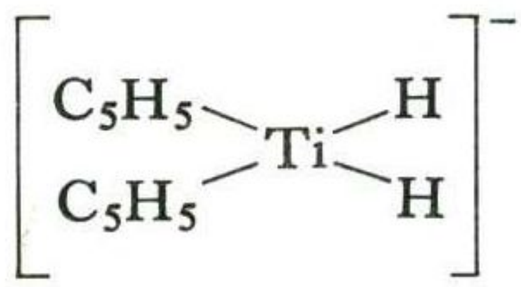
One of the most significant advances in metal-organic chemistry in recent years has been the realization that transition metals with unsaturated coordination sites can react with dinitrogen (N_2), either to form stable coordination complexes or intermediates capable of reacting with a proton source to give ammonia.

The stable dinitrogen complexes are generally found among the elements of higher atomic number and do not concern us here. For fixation of nitrogen the active systems consist of a complex or a salt of a transition metal reduced with Grignard reagents, alkyl or aryl lithiums, alkylaluminums, lithium aluminum hydride, or alkali metal naphthalide. Although chromium, molybdenum, tungsten, iron, cobalt, nickel, and

zirconium are active in fixation, titanium is the most efficient (*178*, *179*), and most of the later experiments have been carried out using this metal.

The ligands around the metal influence its activity appreciably (*180*), as might be expected, but the extent of this influence has not been fully investigated. Most experiments have been carried out using halides, alkoxides, or cyclopentadienyl derivatives of titanium.

In a typical experiment of the type initiated by Vol'pin (*180*) excess ethylmagnesium bromide is added to bis(cyclopentadienyl)titanium dichloride in ether. Evolution of ethane and ethylene occurs immediately, the color changing from red to green to brown. The "reduced solution" will now absorb nitrogen, up to 1 gm atom per mole of titanium complex. High pressure hastens the absorption but does not increase the yield of nitrogen complex (*85*, *126*). The process has been studied by ESR spectroscopy both for Grignard reagents (*15*, *16*) and lithium naphthalide (*86*), and the kinetics of the reactions have been investigated (*125*, *126*). It seems to be agreed that these data indicate the presence of a monomeric titanium(III) hydride such as (XXI) in the "reduced solution," which is probably the intermediate in the fixation process.



(XXI)

Although Nechiporenko maintains that the "reduced solution" loses its nitrogen-fixing ability with time (*136*), other authors found little loss of activity on aging (*126*), but fixation is inhibited by complexing agents which compete with nitrogen, e.g., carbon monoxide and acetylenes (*180*). The function of the Grignard reagent is merely to reduce the metal compound (*126*).

The mechanism of nitrogen complexation which follows formation of the reduced intermediate is not well understood. Since the molar ratio NH_3 : Ti does not exceed 1 in the system under discussion, then two titanium atoms must be involved in any dinitrogen complex. Whether these are contained in two separate molecules or in a dimeric intermediate has not been established. The nitrogen complex shows weak and complex ESR signals from which no conclusions could be drawn (*15*). The simplest explanation is the formation of a titanium nitride complex, as first suggested

by Nechiporenko (*136*), which gives ammonia on hydrolysis (*125*). It is possible that the efficiency of titanium in nitrogen fixation experiments parallels its ready formation of nitrides (*126*).

In the system titanium trichloride and magnesium in tetrahydrofuran under nitrogen, Japanese workers have found nitrides of the type [$TiNMg_2Cl_2 \cdot THF$] (*191*). Tetrahydrofuran and/or magnesium could be replaced without loss of nitrogen by treatment with pyridine, bipyridyl or benzoyl chloride. A hydrogen complex [$TiNMg_4Cl_{1.5}H_2 \cdot 2\,THF$], was also observed. Although all of these complexes are noncrystalline they are believed to be homogeneous and all gave one equivalent of ammonia on hydrolysis

Russian workers found that $(C_5H_5)_2TiR_2$, where $R = CH_3$ or C_6H_5, added nitrogen on heating and the products gave ammonia on hydrolysis (*182*). Since the dimethyl- and diphenyltitanium(IV) compounds give $(C_5H_5)_2Ti$ on pyrolysis at 90°C (*148*), it would seem that titanocene is the active constituent. However, preformed titanocene reacted to a lesser degree, in line with the observations of van Tamelen (*175*).

In attempts to prepare a true catalytic system for nitrogen fixation Vol'pin and co-workers used $TiCl_4$ or $Ti(OR)_4$ reduced with aluminum powder and aluminum bromide at temperatures above 50°C in benzene or molten $AlBr_3$ (*178*, *179*). With ratios of $TiCl_4$:Al:$AlBr_3$ of 1:600:1000 at 130°C and 100 atm of nitrogen, yields of ammonia in the molar ratio NH_3:Ti of 200 or more were obtained. In benzene the stable halogen-bridged complex $C_6H_6 \cdot TiCl_2 \cdot 2\,AlCl_3$ is formed (*122*, *133*, *176*; see Section IX,A) and this is believed to be the active compound. In the absence of aluminum and aluminum bromide the complex reacts with nitrogen at 130°C to give a compound whose analysis is close to that of $C_6H_6(TiCl_2 \cdot 2\,AlCl_3)_3N$ and which gives a stoichiometric yield of ammonia on hydrolysis (*178*).

Vol'pin has shown also that nitrogen can insert between an organic group and titanium (*181*). Thus in reactions of $(C_5H_5)_2TiCl_2$, $TiCl_4$, or $Ti(OR)_4$ with phenyllithium in ether under nitrogen at atmospheric pressure aniline as well as ammonia was obtained on hydrolysis.

Using systems based on titanium alkoxides reduced with alkali metals or alkali metal naphthalide, van Tamelen and co-workers have developed a system for fixation of nitrogen at atmospheric pressure which gives, after addition of a proton source, up to 1.1 for the molar ratio NH_3:Ti per pass (*174*). A typical system consists of titanium tetraisopropoxide reduced

with sodium naphthalide in diglyme in a stream of nitrogen. Two equivalents of alkali metal are required before nitrogen uptake commences, which means that a titanium(II) complex is the active species (*173*). If isopropanol is added as the proton source after nitrogen uptake is complete after 30–60 min, the process becomes a cyclic one provided the ammonia is removed and additional metallic sodium is added to regenerate sodium naphthalide. Over five such cycles a yield of ammonia corresponding to the molar ratio of 3.4 for NH_3:Ti was obtained (*174*). The process may be represented by Eq. (8),

$$N_2 + 6\,e^- + 6\,ROH \rightarrow 2\,NH_3 + 6\,RO^- \tag{8}$$

In addition a significant uptake of nitrogen from air has been observed by van Tamelen using such a system (*174*). Electrolytic reduction of molecular nitrogen to ammonia has been demonstrated using an electrolysis medium of $Ti(O\text{-iso-}C_3H_7)_4$ plus aluminum chloride (1:1.5) in 1,2-dimethoxyethane. Nitrogen was bubbled through the electrolysis cell and after 2 days about 10% yield of ammonia had been collected (*171*).

The authors claim that this system parallels the steps in the simplest biological nitrogen fixation system, namely, interaction of a transition metal in a low oxidation state with dinitrogen, subsequent reduction of the resulting coordinated nitrogen complex, followed by protonation and hydrolysis to give ammonia.

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A P P E N D I X

MONOCYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

II.* COMPLEXES OF NITROGEN-CONTAINING LIGANDS

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Abstract

The complexes $cpTiCl_2$,bipy, $cpTiCl_2$,phm, $cpTiCl_2$,2py, and $cpTiCl_2$,2pic (bipy = bipyridyl, phm = *o*-phenylenediamine, py = pyridine, pic = α-picolylamine, cp = π-cyclopentadienyl) have been prepared by allowing the appropriate nitrogen base to react with $cpTiCl_2$. Spectroscopic, magnetic, and conductivity data are consistent with either non-ionic, six-coordinate dimeric species with pseudo-octahedral symmetry or five-coordinate monomeric species. A complex of the type $cpTiCl_2$,1·5en (en = ethylenediamine) was also formed. Possible structures are discussed.

Introduction

Although a vast chemistry of the addition complexes of inorganic titanium(III) derivatives has developed over the last ten years,[1–3] few references can be found in the literature to organo-titanium(III) compounds which form complexes with neutral ligands.[4–9]

This investigation is part of a general survey of monocyclopentadienyltitanium(III) compounds. Their synthesis and characterization can provide a bridge between the numerous bis(cyclopentadienyl)titanium(III) compounds, with preferred pseudo-tetrahedral stereochemistry, and inorganic titanium(III) derivatives with preferred "octahedral" stereochemistry.

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Monocyclopentadienyltitanium(III) dihalides have been found by us to form complexes with ethers, alcohols, as well as nitrogen chelates.[8–10] The formation of a representative sample of nitrogen chelate complexes with $cpTiCl_2$ will be described in this paper.

Results and Discussion

The complexes were prepared by mixing, under argon, dry oxygen-free tetrahydrofuran solutions of $cpTiCl_2$ and of the ligand. All except the pyridine complex precipitated from dilute THF solutions. Analyses showed (Table 1) that 1 : 2 complexes were formed with monodentate and 1 : 1 complexes with bidentate ligands (except with en). In the case of triethylamine, colour changes in the solution together with its visible spectrum indicated that a complex had formed. However, the product was unstable and decomposed from a green crystalline solid to mauve $cpTiCl_2$ during its isolation.

Table 1

CHARACTERIZATION OF COMPLEXES

Complex	Colour	M.p. (°C)	Found (%) Ti	Cl	N	Calc. (%) Ti	Cl	N
$cpTiCl_2$,2py	deep green	60	14·3	20·9	8·2	14·0	20·7	8·2
$cpTiCl_2$,bipy	grey-blue	225	13·8	21·1	8·3	14·1	20·8	8·2
$cpTiCl_2$,phm	pale green	256	16·1	[a]	9·8	16·4	24·3	9·6
$cpTiCl_2$,2pic	mauve	150	12·0	17·7	13·3	12·0	17·8	14·0
$cpTiCl_2$,1·5en	blue	140	17·6	24·6	15·2	17·5	25·9	15·3

[a] Solution too coloured for end-point to be determined by Volhard's method.

All complexes showed instability in air, oxidizing exothermally to yellow-coloured titanium(IV) compounds; no attempt has been made to characterize these materials. The bipy and en complexes changed only slowly from blue through green to their final yellow colour indicating a greater resistance to oxidation. All of the titanium(III) complexes decomposed without melting and could not be sublimed under high vacuum before decomposition was complete.

In water the complexes hydrolysed rapidly and in this respect they behave more like the inorganic titanium halides than like cp_2TiCl. In water this compound forms a cation, supposedly cp_2Ti^+, which has an extensive aqueous chemistry of its own.[3] In organic solvents the complexes of bidentate ligands were only slightly soluble and although the monodentate complexes showed somewhat greater solubility, in no case was this sufficient for molecular weight determination.

Conductivity Data

With two of the complexes (phm and en) even conductivity measurements were ruled out by lack of solubility. Comparison of molar conductivity of the more soluble complexes in dry methyl cyanide with a typical 1 : 1 electrolyte, tetramethyl-

[10] Coutts, R. S. P., Martin, R. L., and Wailes, P. C., unpublished data.

ammonium bromide, in the same solvent shows that these complexes have low but significant conductivities in solution (see Table 2).

TABLE 2

CONDUCTIVITY DATA IN DRY METHYL CYANIDE

Complex	$10^3 \times$ concn (mol l^{-1})	Λm (Ω^{-1} cm^2)	Complex	$10^3 \times$ concn (mol l^{-1})	Λm (Ω^{-1} cm^2)
$cpTiCl_2$,2py	1·65	39	$cpTiCl_2$,2pic	1·02	58 ± 4[a]
	1·08	44		0·55	68
$cpTiCl_2$,bipy	1·71	20		0·37	84
	0·48	27	$(Me_4N)Br$	2·90	150
				1·27	167

[a] Result obtained from 11 readings over 5 hr.

The values in Table 2 are much lower than those expected for 1 : 1 electrolytes but an equilibrium of the type shown below (eqn (1)), which is not uncommon in methyl cyanide solutions, seems possible:

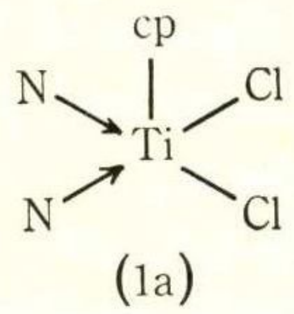
$$cpTiCl_2,2N + MeCN \rightleftharpoons [cpTiCl,2N(MeCN)]^+ + Cl^- \qquad (1)$$

(N = nitrogen of chelating ligand.) We can conclude however that these complexes in the solid state are most likely to be non-ionic and their general insolubility suggests a polymeric structure, probably with bridging chlorides.

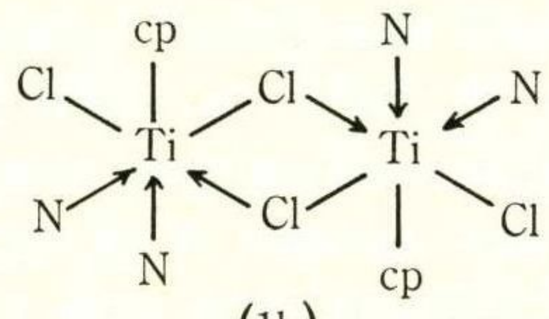
Magnetic Data

In some situations, the presence of chloride bridges can lead to magnetic anomalies, which are diagnostic of polymerization. It is obvious from the data in Table 3 that any interaction is evidently rather small since the compounds follow the normal Curie–Weiss law with low values of θ (see footnotes to Table 3).

The moments at room temperature fall in the range 1·55–1·75 B.M. The lack of a marked temperature dependence implies that should magnetic interaction through halogen bridges be taking place it must necessarily be very weak. This is in marked contrast to the strong interaction found in the dimeric $(cp_2TiCl)_2$ where, however, the stereochemistry is believed to be pseudotetrahedral.[11]



(1a)



(1b)

Generally octahedral complexes of inorganic titanium(III) halides have magnetic moments which can usually be classified as essentially the spin-only value, even though bridging halides are frequently proposed as being present in the solid compounds. Further it is interesting to note that Machin *et al.*[12] found that the five-

[11] Martin, R. L., and Winter, G., *J. chem. Soc.*, 1965, 4709.

[12] Machin, D. J., Murray, K. S., and Walton, R. A., *J. chem. Soc.* (*A*), 1968, 195.

coordinate monomer $TiBr_3,2NMe_3$ had magnetic properties which also fitted very well to the calculations for an octahedral model with rather small distortion. These results emphasize the difficulties of using the magnetic criterion for detailed stereochemical diagnosis in systems such as these. Thus the data in Table 3 do not differentiate between a five-coordinate monomer (1a) or a six-coordinate dimer (1b).

TABLE 3

MAGNETIC DATA

$\mu_{eff} = 2{\cdot}83(\chi'_M.T)^{1/2}$

T (K)	$10^6\chi'_M$ (cm^3 mol^{-1})	μ_{eff} (B.M.)	T (K)	$10^6\chi'_M$ (cm^3 mol^{-1})	μ_{eff} (B.M.)	T (K)	$10^6\chi'_M$ (cm^3 mol^{-1})	μ_{eff} (B.M.)
	$cpTiCl_2,2py$[a]			$cpTiCl_2,bipy$[b]			$cpTiCl_2,1{\cdot}5en$[c]	
290	1303	1·75	291	1028	1·55	286	1038	1·55
263	1446	1·75	264	1239	1·63	263	1174	1·58
233	1613	1·74	234	1400	1·63	239	1318	1·59
203	1843	1·74	203	1581	1·60	201	1515	1·57
170	2133	1·71	170	1842	1·59	170	1770	1·56
142	2571	1·72	142	2195	1·59	140	2107	1·54
113	3142	1·69	113	2723	1·58	113	2644	1·55
100	3461	1·67	100	3043	1·57	102	2832	1·53
	$cpTiCl_2,phm$[d]			$cpTiCl_2,2pic$[e]				
289	1252	1·71	291	1153	1·65			
263	1452	1·76	264	1333	1·69			
233	1639	1·76	234	1534	1·70			
203	1882	1·76	203	1723	1·68			
172	2194	1·75	170	1965	1·64			
142	2619	1·73	142	2333	1·64			
113	3222	1·71	113	2956	1·64			
			100	3190	1·60			

[a] T.i.p. 160×10^{-6} cm^3 mol^{-1}, θ −13 K. [b] T.i.p. 130×10^{-6} cm^3 mol^{-1}, θ −11 K. [c] T.i.p. 130×10^{-6} cm^3 mol^{-1}, θ −12 K. [d] T.i.p. 120×10^{-6} cm^3 mol^{-1}, θ −11 K. [e] T.i.p. 160×10^{-6} cm^3 mol^{-1}, θ −16 K.

Visible Spectral Data

The principal absorption bands of the complexes in the 4000–25000 cm^{-1} region are listed in Table 4. Reflectance spectra were measured for all samples although spectra in solution were recorded only in some cases.

The solid state spectra of all complexes (except $cpTiCl_2,1{\cdot}5en$) contain a high energy band at >20000 cm^{-1} with a broad absorption band centred in the range 15500–12500 cm^{-1}. This latter band sometimes shows an associated shoulder at lower energies (see Fig. 1(*a*)).

The solution spectra for the triethylamine (Et_3N) complex (in pure Et_3N) and the py complex (in methyl cyanide) differ from the solid state spectra in that they show no high energy band and the broad absorptions have moved to higher energy and are much sharper (see Fig. 1(*b*)).

It is possible that in the solid state the high energy band is associated with the halide bridges. The en complex is unlikely to contain halide bridges if the

maximum coordination number of six for titanium is maintained and so does not show this high energy band. To support this proposal, the slow solvolysis of the pic

TABLE 4

ELECTRONIC SPECTRA

ϵ_{max} in parentheses; sh, shoulder; br, broad

Complex	Reflectance Band maxima (cm^{-1})	Solvent	Solution Band maxima (cm^{-1})
$cpTiCl_2$,bipy	20500, 15500, 12000	MeCN	21000 (280), 15500 (254), 11000sh (130)
$cpTiCl_2$,2py	22000sh, 15000br, 10500br	C_5H_5N	21500, 17500
		MeCN	18000 (230)
$cpTiCl_2$,phm	20000sh, 13500, 10500sh		
$cpTiCl_2$,2pic	20000, 17000–7000[a]	MeCN[a]	21000 (300), 20000–7000[a]
		MeCN[b]	16000br
$cpTiCl_2$,1·5en	20000–7000[a]		
$cpTiCl_2$		Et_3N	17500

[a] Unresolved broad band. [b] After 1 hr (see text). [c] After 5 hr (see text).

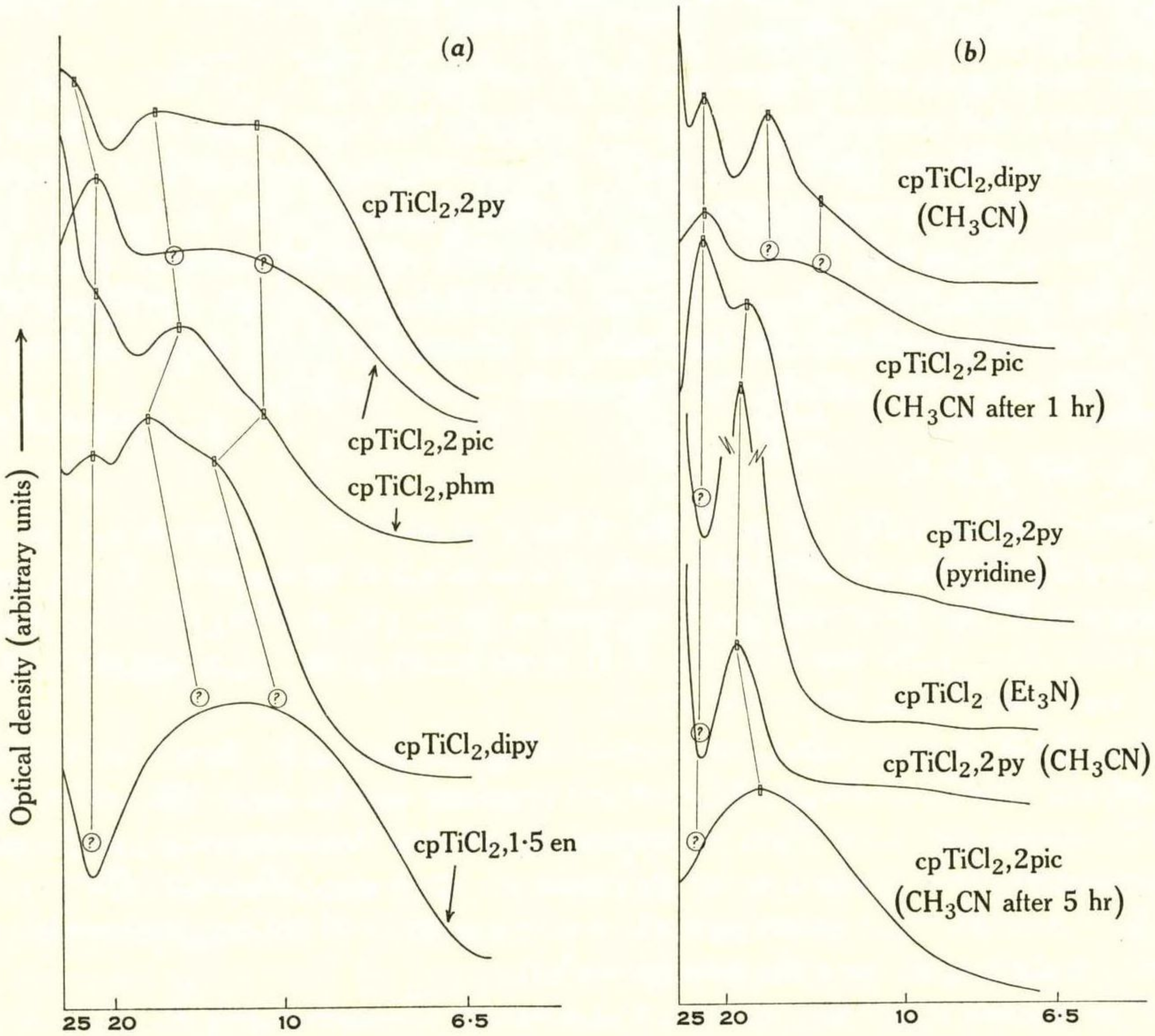


Fig. 1.—Electronic spectra. (*a*) Reflectance; (*b*) in solution (solvent in parentheses).

complex was monitored with time. The experiment involved dissolving the complex in CH_3CN which required approximately an hour, after which time the mauve

complex had formed a red brown solution with a strong band at 21000 cm^{-1} and a broad band at *c.* 15000 cm^{-1}. During the next five hours the peaks gradually coalesced, ultimately forming a single broad band at 16100 cm^{-1}; the solution was now a deep blue colour (cf. Fig. 1(*b*)). The conductivity remained virtually constant (58 ± 4 Ω^{-1} cm^2 mol^{-1}) throughout the experiment, so it was concluded that the reaction did not involve an ionic mechanism such as equation (*1*).

For solvolysis to take place without an ionic mechanism it could be suggested that dissociation of some associated form of the complex has taken place.

Hence, if the red-brown solution with its high energy band contains bridged species, as the solvent ruptures these bridges the blue solution devoid of the band at 21000 cm^{-1} is obtained, but now containing the band at 16000 cm^{-1} in agreement with the solution spectra of Et_3N and pyridine. The fact that the bipy complex has virtually the same spectrum in solid state or in solution can be ascribed to the ability of the chelating dipyridyl ligand to resist solvolysis.

When the pyridine complex was dissolved in pyridine, the solution changed from green to blue after several minutes and showed both the high energy band and the band expected for the solvated species. The spectrum did not change with time and so an equilibrium seems probable. An identical spectrum is obtained by dissolving $(cpTiCl_2)_n$ in pyridine.

In compounds of the type $cp_2Ti^{IV}X_2$ [13,14] (where X = Cl, NCS, OCN), a d^0 system where d–d transitions are not possible, it has been found that the lowest-energy band occurs at 19000 ± 1000 cm^{-1}. This band has been ascribed to a charge-transfer mechanism even though the extinction coefficient was as low as 100–300 units. This suggests that the absorption bands that occur in the region 20000–23000 cm^{-1} in the spectra of the present nitrogen chelates may well originate from a similar charge-transfer mechanism. In this event, the absorption bands in the visible region below 20000 cm^{-1} can probably be attributed to d–d transitions.

Infrared Spectral Data

In the region 4000–250 cm^{-1} the complexes show the expected modifications of the free ligand spectra brought about by coordination to a metal. The spectra of complexes with ligands containing NH_2 groups (phm, pic, and en) showed a decrease in wave number (>100 cm^{-1}) in the N–H stretching modes indicating that all NH_2 groups were attached to the metal atom.

The chelates containing heterocyclic ring systems (py, bipy), displayed the expected observable shifts to higher wave numbers in the 1600–1000 cm^{-1} region. Other bands in the heterocyclic chelates which are most usefully diagnostic of coordination are bands which occur in the free ligands at *c.* 750 cm^{-1}. These shifted 10–20 cm^{-1} to higher wave number and usually a satellite of the band gained intensity and was strongly split from the parent peak.[15]

The present spectra confirmed the absence of uncoordinated ligand, and of cations such as pyridinium and bipyridinium.[16]

[13] Chien, J. C. W., *J. phys. Chem.*, 1963, **67**, 2477.
[14] Burmeister, J. L., Deardorff, E. A., and Van Dyke, C. E., *Inorg. Chem.*, 1969, **8**, 170.
[15] Sirha, S. P., *Spectrochim. Acta*, 1966, **20**, 879.
[16] Mitchell, J., *J. inorg. nucl. Chem.*, 1961, **21**, 382.

The characteristic absorptions due to the presence of the π-cyclopentadienyl ligand were observed in the spectra of the complexes,[17] although some ligands have obscured certain areas due to overlapping absorptions.

Although the region 4000–600 cm^{-1} established the presence of coordinated ligands, it provided little information concerning the stereochemistry of the new complexes.

The most informative area lies below 600 cm^{-1} but, although the spectra for the complexes were recorded down to 250 cm^{-1}, few assignments could be made due to the complexity of this area. This region contains absorptions due to the vibrations of metal–halide, metal–nitrogen, and metal–cyclopentadienyl bonds in addition to internal vibrations for some of the ligands. Unfortunately, the task was further complicated by the conflicting data in the literature concerning the assignment of these vibrations.

TABLE 5

FAR-INFRARED DATA

Assignment	py complex	bipy complex	pic complex	phm complex	en complex
Ti–Cl stretching mode (terminal)	*c.* 250 310m	*c.* 250 315w,sh 325sh	320br,m	*c.* 250 310s 325w,sh	325br,m
Ligand vibrations	335sh 350sh 374s	335sh 340sh 360sh 385s 412w,sh 418sh	340w,sh	340sh 390s	
Ti–cp stretching mode	440s	430m 440m	430m 460sh	430s	430m
—					
—	475	470br,m	470sh	470m	470w,sh 520s
Ti–N stretching mode[a]					
Ligand vibrations			550w 590w	582w	

[a] en complex only.

The metal–nitrogen stretching frequency is dependent upon both the force constant and the mass of the nitrogen donor ligand present in the complex. For metal–ammonia complexes M–N stretching vibrations have been observed at *c.* 500 cm^{-1},[18] while no evidence for M–N stretching vibrations above 200 cm^{-1} have been found for complexes of heavy bidentate nitrogen donor ligands such as 2,2′-bipyridyl or *o*-phenanthroline. An investigation of M–N stretching vibrations of pyridine complexes,[19] a ligand of intermediate mass, suggests that these vibrations occur in the 200–287 cm^{-1} region. It might be expected that complexes of α-picolylamine and

[17] Fritz, H. P., *Adv. organomet. Chem.*, 1964, **1**, 239.

[18] Nakamoto, K., "Infrared Spectra of Inorganic and Coordination Compounds." p. 150. (John Wiley: New York 1963.)

[19] Clark, R. J. H., and Williams, C. S., *Inorg. Chem.*, 1965, **4**, 350.

o-phenanthroline would therefore have M–N stretching bands occurring below 200 cm^{-1}. The ethylenediamine complex on the other hand may well be expected to have an observable M–N stretching vibration in the range studied. The strong band at 520 cm^{-1} (Table 5) could be tentatively assigned to such an absorption. Supporting this assignment is the fact that Clark and Greenfield[20] prepared the complexes $Ti(en)_3Cl_3$ and $Ti(pn)_3Cl_3$ (pn = propylenediamine) and they also tentatively assigned bands at 516 and 528 cm^{-1} to the Ti–N vibration. There has been some conflict over the stoicheiometry of these compounds as Fowles proposed the formation of $Ti(en)_4Cl_3$ under similar reaction conditions.[21] Fowles also observed a strong band at 520 cm^{-1} which was not assigned, but may well be due to the Ti–N stretching mode.

The presence of a medium to strong band in all spectra in the narrow range 310–325 cm^{-1} may be assigned to the terminal Ti–Cl stretching vibrations. Both Clark[20] and Fowles[21] ruled out the presence of covalent metal–chlorine bonds in their complexes due to the absence of any bands at *c.* 300 cm^{-1}. This assignment could have been strengthened by showing that the band was halogen sensitive; fortunately some current work on oxygen chelates[10] tends to validate this proposal. Thus the far-infrared spectra of a range of oxygen chelates contain a strong band at *c.* 320 cm^{-1} which is absent in the analogous complexes of $cpTiBr_2$, although the spectra are identical in all other respects. We ascribe this band at *c.* 320 cm^{-1} to a terminal Ti–Cl stretching vibration.

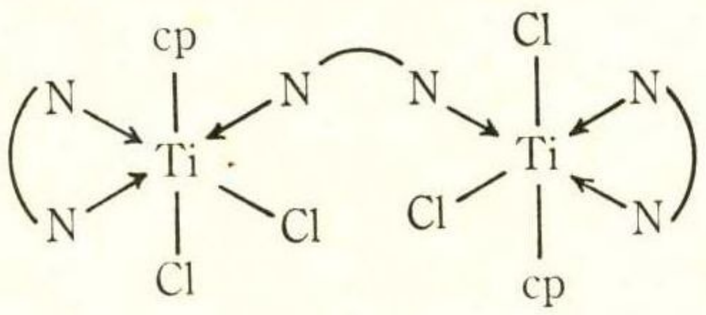
The metal–ring stretching frequencies in monocyclopentadienyltitanium(IV) compounds have been studied by Nesmeyanov *et al.*[22] and the band in the interval 420–441 cm^{-1} has been assigned to the Ti–cp bond vibration. This work differs slightly from the earlier assignment of this mode to a band at 414 cm^{-1}.[17] The spectra of the complexes reported in this paper all show a medium to strong band in the range 430–440 cm^{-1} which is tentatively assigned to the Ti–cp stretching vibration.

All of the data detailed above tends to support the formulation of these complexes as dimers with bridging chlorides (1b) although no definite evidence eliminates the five-coordinate monomeric structures (1a). Conductivity data are in agreement with the value found[23] for $TiBr_3$,bipy (24 Ω^{-1} cm^2). Similarly the electronic spectra of $TiBr_3$,bipy and $cpTiCl_2$,bipy are in close agreement in both solid state and solution. The complex $TiBr_3$,bipy has been formulated as a dimer with bridging bromides; this type of structure (1b) would satisfactorily explain the observed physical properties for the complexes $cpTiCl_2$,2py, $cpTiCl_2$,bipy, $cpTiCl_2$,phm, and $cpTiCl_2$,2pic. In considering the alternative formulation, the spectroscopic method used by Fowles and co-workers[24] to indicate *trans*-trigonal bipyramidal stereochemistry might be relevant if an analogy between our system and inorganic halide complexes can be justified. It was found that the electronic spectra of such complexes contained strong peaks in two regions, 5000–6000 and

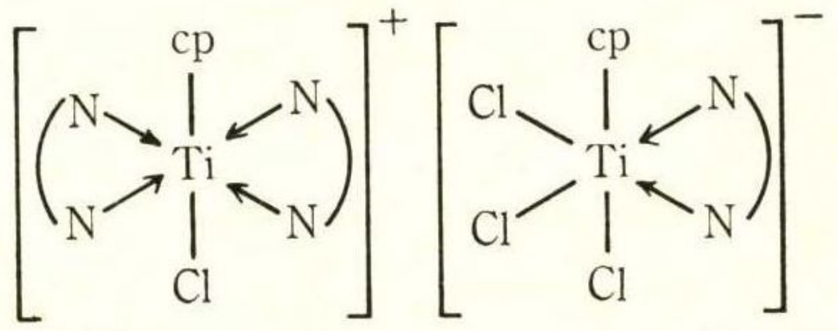
[20] Clark, R. J. H., and Greenfield, M. L., *J. chem. Soc.* (*A*), 1967, 409.
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[23] Fowles, G. W. A., and Lester, T. E., *J. chem. Soc.* (*A*), 1968, 1180.
[24] Crough, P. C., Fowles, G. W. A., and Walton, R. A., *J. chem. Soc.* (*A*), 1968, 2172.

12000–16000 cm^{-1}. Spectra of the complexes under investigation showed no bands in the 5000–6000 region and this might tend to suggest that five-coordinate monomers, if present, are not *trans*-trigonal bipyramidal but perhaps square pyramidal. In this event, the high energy band may be assigned to the five-coordinate species, and the variation in solution spectra attributed to solvation of the sixth coordination site.

The en complex is intractable due to its lack of solubility. Infrared spectra indicate that all NH_2 groups are bonded to titanium atoms. Two of several possibilities which suggest themselves are the neutral dimeric structure (2a) with a bridging en group, and the cation–anion isomer (2b).



(2a)



(2b)

The presence of bridging ethylenediamine molecules has been proposed by other workers,[21] but no case for such behaviour of this ligand has been structurally established.

Structure (2b) would suggest two absorption centres in the visible spectrum. Unfortunately, the broad nature of the single band observed does not permit further speculation.

Experimental

All air-sensitive materials were handled under argon atmosphere or in vacuum. Infrared spectra were measured in KBr disks on a Perkin–Elmer 521 spectrophotometer. Reflection spectra were determined in a sealed cell on a Beckman DK2A spectrophotometer fitted with a reflectance attachment, and solution absorption spectra were recorded on a Beckman DK2 instrument. Magnetic susceptibilities were measured by the Gouy method. Conductivity values were determined in a sealed cell under argon using methyl cyanide distilled under argon from P_2O_5.

Method

Dry oxygen-free tetrahydrofuran solutions of $cpTiCl_2$ and of the nitrogen chelate compound (slight excess) were mixed under argon and the resulting precipitate was filtered off and washed with tetrahydrofuran using the Schlenk tube system.[25]

Acknowledgment

One of the authors (R.S.P.C.) is grateful to the Division of Applied Chemistry, CSIRO, for leave of absence which enabled this work to be carried out at the Department of Inorganic Chemistry, University of Melbourne.

[25] Herzog, S., and Dehnert, J., *Z. Chemie, Lpz.*, 1964, **4**, 1.

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Preliminary communication

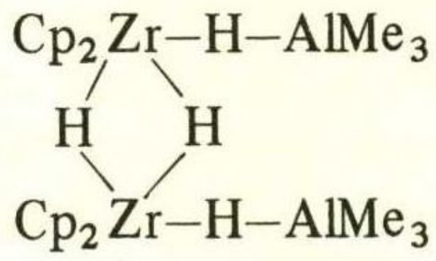
Reaction of dicyclopentadienylzirconium dihydride with trimethylaluminium. Formation of a novel hydride containing both Zr–H–Zr and Zr–H–Al

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(Received July 31st, 1972)

The importance of complexes between alkylaluminiums and compounds of titanium in Ziegler–Natta catalysis prompts us to report some preliminary findings on the reaction of Cp_2ZrH_2 with alkylaluminiums, in particular $AlMe_3$ (Cp = π-cyclopentadienyl).

On dropwise addition of trimethylaluminium in stoichiometric amounts to a stirred slurry of Cp_2ZrH_2 in benzene at room temperature★, a ready reaction ensued to give a clear pale violet solution from which the faintly blue compound



was isolated in almost quantitative yields★★. The C_5H_5 and CH_3 protons showed chemical shifts★★★ of $\delta = 5.50$ and -0.41 ppm respectively in the ^1H NMR spectrum (see Fig.1) with relative intensities in accord with the structure assigned to the complex. The hydridic hydrogens, which are coupled in the NMR spectrum but do not exchange, give rise to bands, also with the appropriate relative intensity, at $\delta = -0.92$ and -2.92 ppm. The triplet nature of these bands is consistent with the proposed structure. Assignment of the peak at $\delta = -0.92$ to the Zr–H–Al hydride can be made on two counts. Firstly, this multiplet is broadened and less well defined than that at higher field, a consequence of coupling with the aluminium. Then, since the chemical shift of the hydride hydrogen in compounds such as diisobutylaluminium hydride[1] and diphenylaluminium hydride[2] lies between $\delta = 2$ and 5 ppm, it would seem that the low field band at $\delta = -0.92$ is more likely to be associated with the hydride attached to the aluminium.

★ Reaction at 5° is very slow.
★★ Satisfactory C, H and total ash analyses were obtained.
★★★ Relative to internal standard hexamethyldisiloxane.

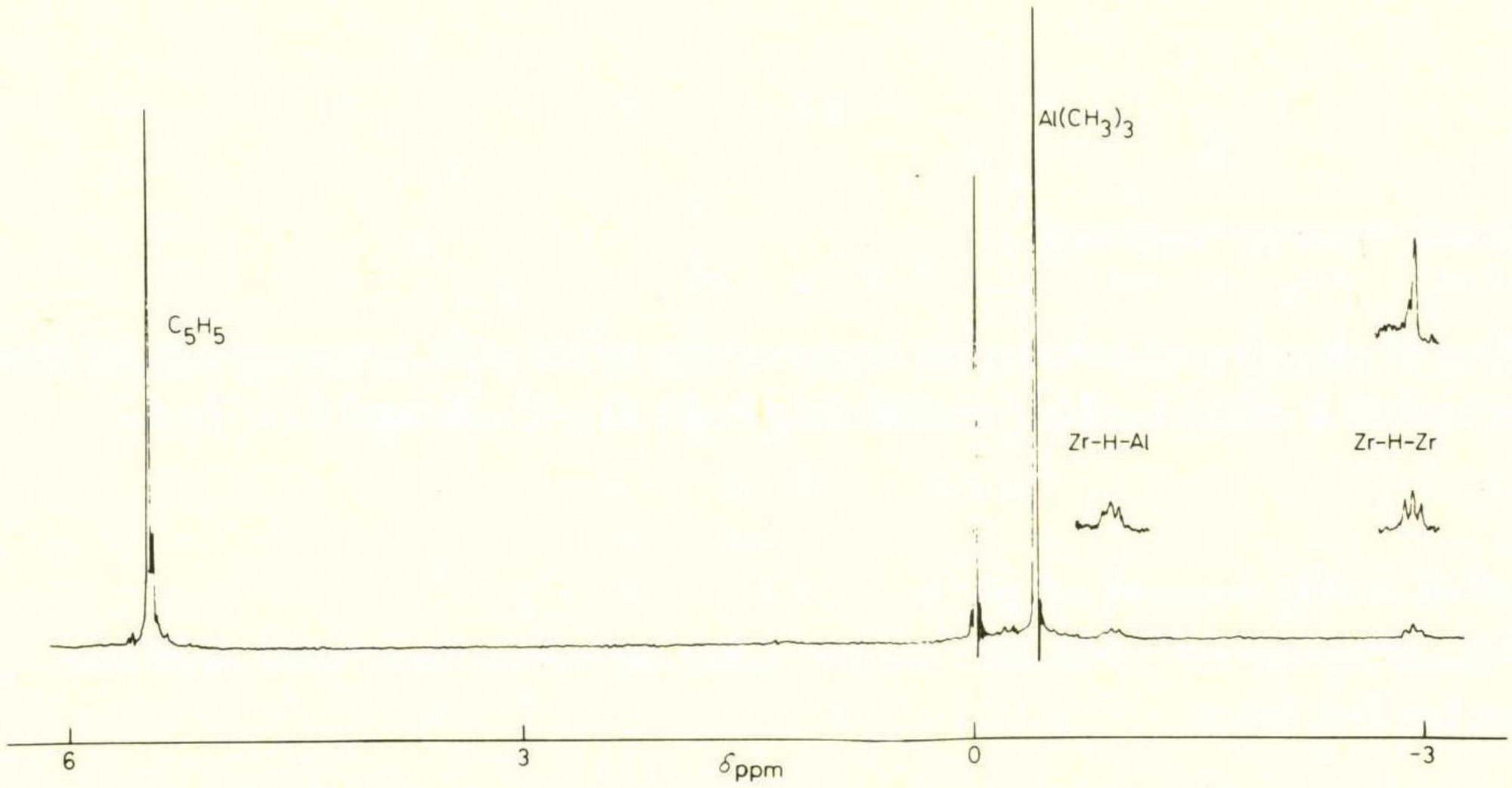


Fig.1. The ^{1}H NMR spectrum of $Cp_2Zr(H)_2AlMe_3$ including the decoupled Zr–H–Zr absorption in benzene-d_6 on an HA-100 spectrometer using hexamethyldisiloxane as internal standard and benzene as lock signal.

That the methyl ^{1}H NMR peak remains a singlet down to −60° (in toluene-d_8) tends to negate the possibility of methyl exchange, a process expected if bridging methyl groups were present.

Although the possibility of coupling between the hydrides and the C_5H_5 protons does exist, no evidence of any interaction between these groups was detected. In the compounds Cp_2MF_2, M = Ti, Zr or Hf, it was found[3] that the C_5H_5 hydrogens were not NMR

TABLE 1

INFRARED FREQUENCIES (cm^{-1}) OF SOME DICYCLOPENTADIENYLZIRCONIUM HYDRIDES AND DEUTERIDES

	Assignment	*Hydride*	*Deuteride*	*Reference*
$Cp_2Zr(H)_2AlMe_3$				
	Zr–H–Zr	1350	980	This work
	Zr–H–Al	1780	1290	
$Cp_2Zr(H)AlH_4$	Zr–H–Zr	1425	1055	4
	AlH_4	1790, 1700	1310, 1260	
$Cp_2Zr(H)BH_4$	Zr–H	1945		5
Cp_2ZrH_2	Zr–H–Zr	1520, 1300	1100, 960	4
$Cp_2Zr(H)Cl$	Zr–H–Zr	1390	1020	4
$Cp_2Zr(H)CH_3$	Zr–H–Zr	1500	1090, 965	4

equivalent (triplet, J = 1.7 Hz) in the case of the titanium compound, but were equivalent in the case of M = Zr or Hf.

The infrared spectra of this compound and its deuterido analogue have been measured in nujol and halocarbon oil (see Table 1). Reaction with KBr prevented the use of this material as a support. All of the hydrido and deuterido adsorptions were broad and the ratio γ(M–H)/γ(M–D) was 1.38 for both types of hydrido groups.

The compound is thermally unstable decomposing even at room temperature to a crimson compound with the evolution of methane and hydrogen. The methyl groups react here with a bridging hydride rather than abstracting a proton from the cyclopentadienyl ring since on warming the deuterido compound, CH_3D was detected in the gaseous decomposition products. Its low thermal stability would also account for the low (found 376, calc. 591.0) dimer molecular weight observed ebulliometrically in benzene. Cryoscopically, in the same solvent, the value determined was 510. Dimerization through Zr–H–Zr bridges may be expected since this behaviour occurs in the parent compound[4]

$Cp_2Zr(H)Cl$ also reacts with aluminium trimethyl, but the products are unstable at room temperature.

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Preliminary communication

Hydrido complexes of zirconium
IV. Reactions with olefins

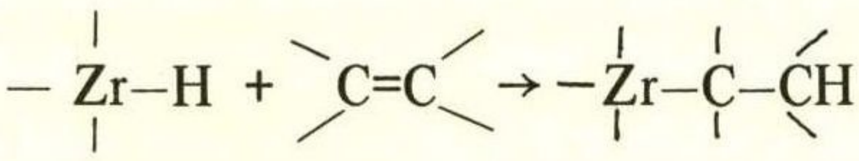
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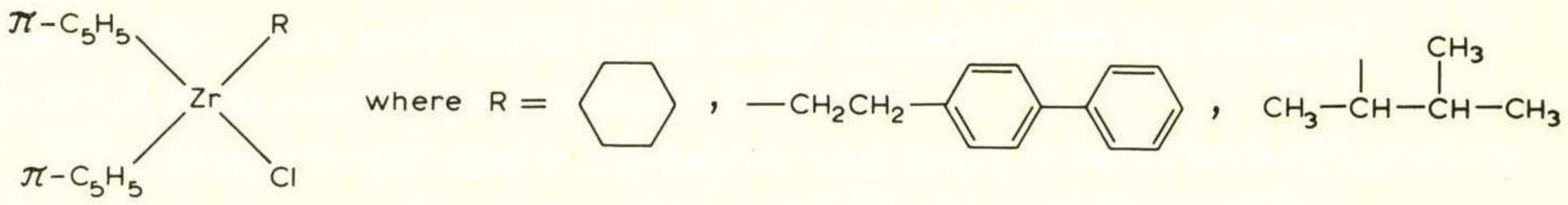
(Received July 31st, 1972)

Part III of this series[1] described the addition of the zirconium hydrides $(\pi\text{-}C_5H_5)_2ZrH_2$ and $(\pi\text{-}C_5H_5)_2Zr(H)Cl$ to acetylenes to give alkenylzirconium derivatives. We now report the reactions of these hydrides with olefines to give saturated compounds.

The difficulty in preparing alkyl derivatives of transition metals is connected with their thermal instability and general lability which renders their isolation difficult. Thermal instability of alkyls is in many cases due to ease of β-elimination of hydrogen[2-4] which explains why methyl derivatives of zirconium, *e.g.* $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$ and $(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$, are relatively stable[5,6] while the corresponding ethyl derivatives are considerably less so (in fact only $(\pi\text{-}C_5H_5)_2Zr(C_2H_5)Cl$ has been isolated[7]). It was to be expected, therefore, that under the conditions used for the preparation of alkenylzirconium derivatives, namely addition of $(\pi\text{-}C_5H_5)_2ZrH_2$ and $(\pi\text{-}C_5H_5)_2Zr(H)Cl$ to acetylenes in boiling benzene[1], alkyl derivatives formed from these hydrides and olefins would not be isolable, since the method of preparation ensures the presence of a β-hydrogen atom.

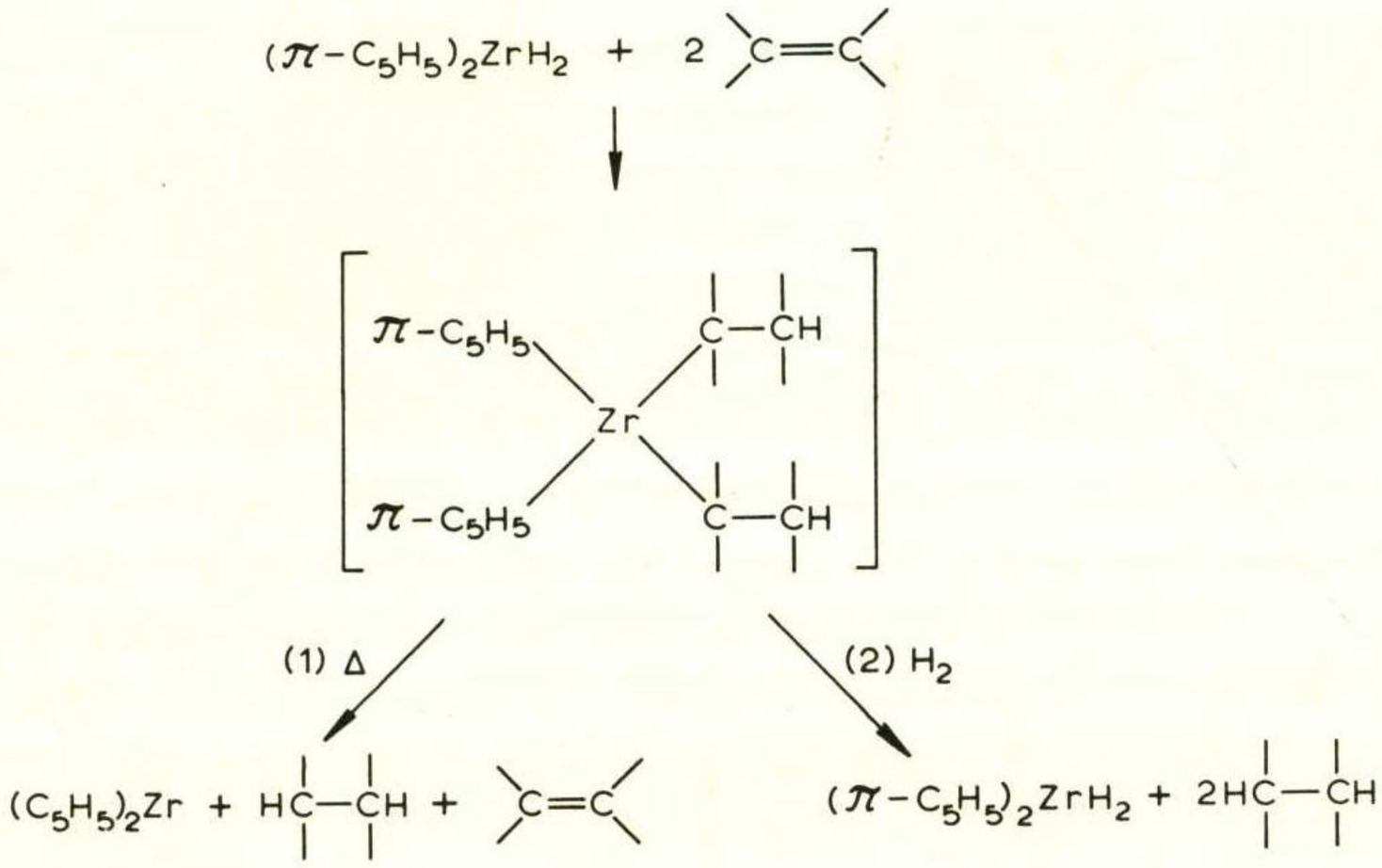


Such has proved to be the case but by using lower temperatures and longer reaction times (typically, room temp. for several hours) it has been found possible to prepare the monoalkyl derivatives shown below from the monohydride, $(\pi\text{-}C_5H_5)_2Zr(H)Cl$ and the appropriate olefin, *viz.* cyclohexene, 4-vinyldiphenyl or 2-methyl-2-butene:



Satisfactory analyses have been obtained for these compounds. The point of attachment of zirconium in the second and third compounds is not known with certainty; the ^{1}H NMR spectra are complicated by overlapping multiplets in the aliphatic region. These alkyl derivatives are of marginal stability and decompose slowly in the solid state and more rapidly in solution.

The instability of compounds such as this can be used to advantage; *e.g.* for the synthesis of derivatives of lower-valent zirconium by pyrolysis or hydrogenolysis;



Reaction 1 occurs with the dihydride and stoichiometric amounts of olefin (2 moles); the formation of the intermediate unstable complex is shown by the dissolution of the insoluble dihydride to give a dark solution which decomposes with precipitation of a dark solid identified as zirconocene. The formation of alkane and alkene in this reaction has been demonstrated in the reaction with 4-vinyldiphenyl. Equal amounts of ethyldiphenyl and vinyldiphenyl (the latter complexed with zirconocene) were identified in the reaction product by NMR spectroscopy.

When a pressure of hydrogen was applied during the reaction of cyclohexene with the zirconium dihydride it was found that hydrogen was absorbed and the metal hydride was reformed together with cyclohexane (Reaction 2). The hydrogenation is therefore catalytic; it appears to be a general reaction for olefinic hydrocarbons (and also acetylenes) (see Table 1).

The catalyst darkens considerably during some of these hydrogenations, possibly due to the formation of zirconocene by pyrolysis of alkyl derivatives.

The monohydride $(\pi\text{-}C_5H_5)_2Zr(H)Cl$, although not tested as extensively as the dihydride, will also reduce these olefins, but longer reaction times and/or higher temperatures are necessary. This lower activity is no doubt connected with the increased stability of the intermediate organozirconium derivative.

Other zirconium and titanium derivatives were found to be active hydrogenation catalysts under similar conditions, *viz.* $(\pi\text{-}C_5H_5)_2Zr(CH_3)Cl$, $(\pi\text{-}C_5H_5)_2Zr(CH_3)_2$, $(\pi\text{-}C_5H_5)_2Ti(CH_3)Cl$, $(\pi\text{-}C_5H_5)_2Ti(C_6H_5)_2$, $(C_5H_5)_2Zr$ and $(C_5H_5)_2Ti$. This behaviour

TABLE 1

CATALYTIC HYDROGENATION USING $(\pi\text{-}C_5H_5)_2ZrH_2$ (H_2 press. 50–100 atm)

Unsaturated compound	*Temp. (°C)*	*Product (yield is quantitative)*
Cyclohexene	80	Cyclohexane
trans-Stilbene	100	1,2-Diphenylethane
cis-Stilbene	100	1,2-Diphenylethane
Styrene	120	Ethylbenzene
Vinylcyclohexane	120	Ethylcyclohexane
2-Methyl-1-butene	120	2-Methylbutane
2-Methyl-2-butene	120	2-Methylbutane
cis-Hept-2-ene	120	Heptane
Phenylacetylene	120	Ethylbenzene
3-Hexyne	120	Hexane

was not unexpected in view of the ability of titanocene[8] (and presumably zirconocene) to form hydrides and the facile displacement of alkyl groups from these metals under the hydrogenation conditions.

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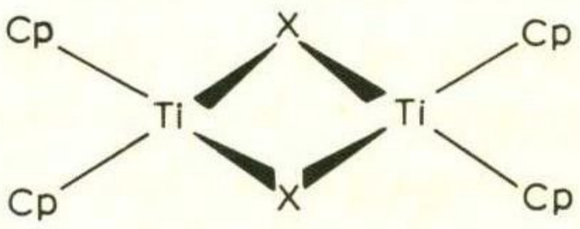
DIMERIC DICYCLOPENTADIENYLTITANIUM(III) HALIDES

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SUMMARY

The synthesis and characterization of dicyclopentadienyltitanium(III) fluoride completes the series $(Cp_2Ti^{III}X)_2$ [where Cp = π-cyclopentadienyl; X = F, Cl, Br or I]. Two new methods of preparation are reported for the other members of the series.

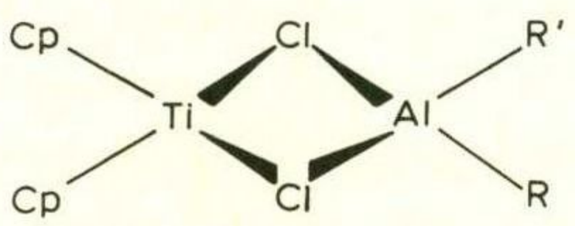
Structural investigation by means of molecular weight determinations, spectroscopic, and magnetic susceptibility measurements confirm the dimeric model shown below.



(X=F,Cl,Br and I)

INTRODUCTION

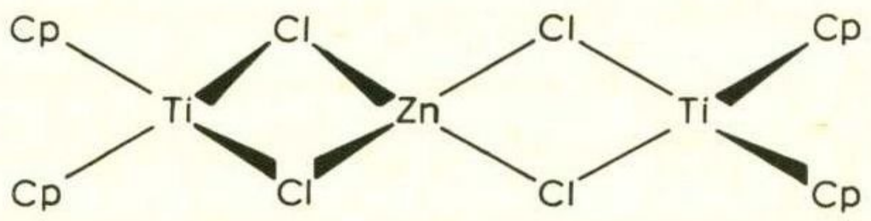
The reduction of dicyclopentadienyltitanium(IV) compounds with a range of reductants, including metals (Na, Zn, Mg, Al), Grignard reagents, lithium aluminium hydride, aluminiumalkyls, etc. has been used in the preparation of many lower-valent cyclopentadienyltitanium derivatives[1], including phosphides[2], allylic compounds[3], borohydride[4], as well as the extensive series of bimetallic compounds of general type[5–8] (I).



(R or R'= alkyl or halide)

(I)

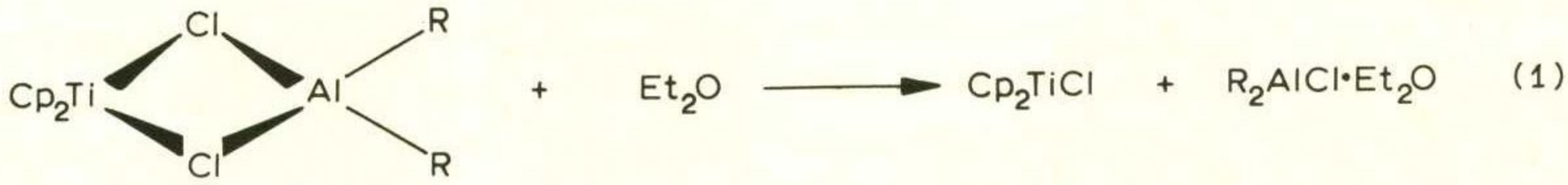
The original preparation of the chloride, $Cp_2Ti^{III}Cl$, was by reduction of Cp_2TiCl_2 with zinc dust in tetrahydrofuran (THF) as solvent[9]. The low yield in this preparation was later shown to be due to the formation of a bimetallic complex (II) which could not be easily decomposed[10].



(II)

The absence of evidence for Ti–Ti interaction in the ESR spectrum of zinc-reduced Cp_2TiCl_2 was originally attributed[11] to the presence of a solvated monomer of Cp_2TiCl. However, it has now been shown that the complex (II) is formed under these conditions[10]. Furthermore, there is no Ti–Ti interaction present and the magnetic susceptibility obeys a Curie law[10].

The bimetallic complexes of type (I) can be used to prepare Cp_2TiCl in good yield by complexing the aluminium with triethylamine or ether[5,12] according to eqn. (1).



(1)

The bromide and iodide derivatives of $Cp_2Ti^{III}X$ have not been isolated by reduction of $Cp_2Ti^{IV}X_2$ (X = Br or I). Reduction of Cp_2TiCl_2 with allylmagnesium bromide in ether has been claimed[3] to give solutions of $Cp_2Ti^{III}Br$ although the only evidence offered was a characteristic band in the visible spectrum and the appearance of an uncharacterized green precipitate. We find the compound to be red-brown in colour in agreement with the original synthesis report[13].

The polarographic reductions of $Cp_2Ti^{IV}X_2$ (X = F, Cl, Br and I) in both protic and aprotic solvents have been studied[14]. However, the titanium–halide bonds did not reduce cleanly; the reactions were complicated by hydrolysis, complexation or specific solvation, and no compound was isolated.

The chloride, bromide, and iodide members of the Cp_2Ti^{III} halide series have been prepared from the borohydride, Cp_2TiBH_4, by ligand exchange reactions with hydrogen halides[13] (eqn. 2), and also with boron trihalides[13] (eqn. 3). However the use

$$Cp_2Ti^{III}BH_4 + HX\ (Cl, Br \text{ or } I) \rightarrow Cp_2Ti^{III}X + H_2 + \tfrac{1}{2}(BH_3)_2 \quad (2)$$

$$3\ Cp_2Ti^{III}BH_4 + BX_3\ (X = Cl \text{ or } Br) \rightarrow 3\ Cp_2Ti^{III}X + 2\ (BH_3)_2 \quad (3)$$

of boron trifluoride did not give the expected fluoride derivatives but instead the borofluoride (eqn. 4). Few physical properties have been reported for these compounds.

$$3\ Cp_2Ti^{III}BH_4 + 4\ BF_3 \rightarrow 3\ Cp_2Ti^{III}BF_4 + 2\ (BH_3)_2 \quad (4)$$

It was our intention to synthesize the outstanding fluoride derivative and then examine the physical properties of the completed series, in particular the magnetic behaviour. The dimeric[6] chloride shows antiferromagnetic behaviour[15,16] due to intramolecular titanium–titanium interaction probably via the bridging chloride atoms[15].

This series offers an unusual opportunity to study the effect of the availability of orbitals of the bridging halide atom on metal–metal interaction in dimeric systems such as these.

RESULTS AND DISCUSSION

Polarographic data for $Cp_2Ti^{IV}F_2$ ($-E^1_{\frac{1}{2}}$ 1.21 V) in DMF as compared to Cp_2TiCl_2, Cp_2TiBr_2 or Cp_2TiI_2 ($-E^1_{\frac{1}{2}} < 0.6$ V)[14], indicated the need for stronger chemical reductants than say zinc ($-E^0_{red}$ 0.76 V) if $Cp_2Ti^{III}F_2$ was to be chemically

reduced. The use of Mg or Na ($-E^0_{red} > 1.75$ V) might be expected to cause further reduction to Ti^{II} compounds. Such was the case when Cp_2TiF_2 or Cp_2TiCl_2 was treated with magnesium metal activated with iodine, the black-brown products were extremely reactive with chemical behaviour indicative of a probable oxidation state of +2. No characterization was attempted.

It was found that aluminium ($-E^0_{red}$ 1.67 V) would effect the reduction of Cp_2TiF_2 only if much care was used in activating the surface of the metal (see Experimental).

In the cases when X = Cl, Br, or I, activation was not necessary to produce total reduction.

The reduction of Cp_2TiX_2, where X = Cl, Br or I with aluminium foil in THF resulted in a solution of $Cp_2Ti^{III}X$*. The solution could be filtered free of the excess reductant and then pumped to low bulk and the precipitate formed washed free of aluminium halide using diethyl ether.

In the case of Cp_2TiF_2 however the reduction of the yellow compound with activated aluminium foil in THF resulted in a deep blue solution and a light blue precipitate. When this mixture was pumped to dryness and then sublimed at ≈250° at 10^{-4} mmHg, a green crystalline sublimate was obtained in 40% yield which was identified as $Cp_2Ti^{III}F$. The original blue compound is believed to be a bimetallic complex and is still under investigation.

The reduction of Cp_2TiI_2 with aluminium was somewhat anomalous in that the product always contained strongly coordinated ether in approximately 1/1 ratio. It was found that an alternative ligand exchange reaction provided a better product. The chloride could be used to prepare bromide or iodide by treatment with boron trihalides (eqn. 5). Again difficulty was encountered with the iodide reaction. It was

$$3\ Cp_2Ti^{III}Cl + BX_3 \rightarrow 3\ Cp_2Ti^{III}X + BCl_3 \qquad (X = Br \text{ or } I) \tag{5}$$

found in several preparations that $Cp_2Ti^{IV}I_2$ was forming probably by dissociation of BI_3 into I_2 which then oxidized some of the $Cp_2Ti^{III}I$ (eqn. 6)

$$2\ Cp_2Ti^{III}I + I_2 \rightarrow 2\ Cp_2Ti^{IV}I_2 \tag{6}$$

When aluminium foil was added to this ligand exchange reaction oxidation was eliminated and pure $Cp_2Ti^{III}I$ could be isolated in good yields (≈70%).

Properties

The fluoride is coloured green; chloride; green brown; bromide, red brown; and iodide, black. On exposure to air all are oxidized to yellow-orange solids although the fluoride tends to show a decreased sensitivity to oxygen. All but the iodide can be purified by sublimation without decomposition taking place. All are soluble in air-free water, in THF, and in benzene, although the dissolution of the fluoride in organic solvents is very slow. Ebulliometric molecular weight determinations in benzene confirm the predicted dimeric structure.

Infrared data

The spectra of the four Cp_2TiX derivatives are closely similar in the region 4000–600 cm^{-1} as the metal to halogen stretching frequencies fall below 600 cm^{-1}.

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* Preparation of Cp_2TiCl by this method had been developed in these laboratories by Dr. Weigold[25].

This similarity is consistent with the presence of the common Cp_2Ti^{III} moiety. Thus all the compounds showed bands associated with the π-C_5H_5 ring[17], at 3100, 1440 ± 3, 1130 ± 10, 1015 ± 10, and 800 ± 10 cm^{-1}, which are assigned to CH in-plane stretching, CC in-plane skeletal stretch, CH out-of-phase deformation, CH in-plane deformation, and CH out-of-phase deformation.

In recent times, interest has been shown in the far infrared spectra of some dicyclopentadienyltitanium(IV) derivatives, in particular $Cp_2Ti^{IV}X_2$ (where X= halide). However the spectra are extremely difficult to interpret.

Fritz[17] assigned a weak peak at 595 cm^{-1} in the spectrum of Cp_2TiCl_2 to a metal–ring tilting vibration, whereas Maslowsky and Nakamoto[18] assign it to a cyclopentadienyl ring vibration due to its constant position as metal or halogen atom is changed. In going from F to I we observed no appreciable change in this frequency and so favour the latter assignment to a ring vibrational mode. The only other bands observed between 600–300 cm^{-1} in the spectra of all four members of the series was a strong band at 395 ± 3 cm^{-1} for X = Cl, Br or I; which moved to 380 cm^{-1} for the fluoride derivative, and a medium to weak band at 355 cm^{-1} which appeared as a weak shoulder at 360 cm^{-1} in the fluoride. In the series $Cp_2Ti^{IV}X_2$ bands at 416 ± 5 cm^{-1} and 370 ± 20 cm^{-1} were assigned to the asymmetric and symmetric metal–ring stretching vibrations respectively; again the higher energy band was strong relative to the lower energy band[18].

Since the pseudo-tetrahedral symmetry of Cp_2TiX_2 derivatives exists also around the titanium atom of the compounds under investigation, the metal–cyclopentadienyl stretching frequencies would be expected to occur in the same area. The decrease in frequency of some 20 cm^{-1} observed may be attributed to the lower oxidation state of the metal.

The metal–halogen stretching frequencies for bridging halides are expected below 250 cm^{-1} for chloride, bromide and iodide and were not observed in the range studied. The only other absorption present was a strong band at 470 cm^{-1} in the spectrum of the fluoride derivative, which must be assigned to a bridging titanium–fluoride stretching frequency.

Electronic spectral data

The spectra of the compound were measured, both as solid reflectance and in benzene solution, over the range 25000–5000 cm^{-1} (Table 1). The data is in close agreement for both solid and solution state so we can assume that the dimeric structure persists in benzene (as established by molecular weight determinations).

Magnetic data

The measurements of the variation of paramagnetic susceptibility with temperature were recorded between 80 and 380 K. In the case of the fluoride derivative no maximum in susceptibility was observed over the temperature range studied. However, a plot of effective magnetic moment per titanium atom *vs.* temperature immediately revealed a well-defined temperature dependency, suggesting that some exchange interaction may well be present (Table 2).

With the remainder of the halide series (X = Cl, Br or I) the susceptibility was observed to pass through a maximum value and then fall rapidly at lower temperatures.

TABLE 1

ELECTRONIC SPECTRAL DATA

Compound	*Medium*	*Assignments*				
		Charge transfer	*d–d transition* [ε_{max}]			
Cp_2TiF	Solid	22200			12500	8700
	Benzene				12900 (br)	8900 (br, sh)
Cp_2TiCl	Solid	21000	14500		12100 (sh)	8700
	Benzene		14500 [40]		12100 [32] (sh)	8700 [7.5]
Cp_2TiBr	Solid	20300			14300	12100	8160
	Benzene				14300 [42]	12100 [27]	8160 [8.6]
Cp_2TiI	Solid	20000	16700		15400 (sh)	12100 (sh)	7700
	Benzene		16700 [550]		14900 (sh)		8160 [7.5]

TABLE 2

MAGNETIC DATA

Compound	μ_{eff}				*Observed J*
	360 *K*	260 *K*	160 *K*	100 *K*	(cm^{-1})
Cp_2TiF	1.65	1.63	1.56	1.45	
Cp_2TiCl	1.54	1.47	1.18	0.85	140–170[a]
Cp_2TiBr	1.39	1.23	0.87	0.45	250
Cp_2TiI	1.51	1.41	1.20	0.80	150–160[a]

[a] Some reproduceable scattering is evident near the maxima suggesting phase changes may be taking place at the Néel temperature.

Extrapolation to temperatures >400 K should produce effective magnetic moments close to the "spin only" value (1.73 BM) for a single unpaired electron. Reduction of temperature to 80 K causes the magnetic moment to decrease monotonically, indicating that the dimers will become diamagnetic at lower temperatures (Table 2). These observations support the previous proposals of a thermal equilibrium between singlet and triplet states. As the temperature is lowered, the singlet state becomes progressively populated at the expense of the triplet level, so that the susceptibility and magnetic moment both decrease steadily, eventually to zero.

The experimental results from $\chi_M(T)$ and $\mu_{eff}(T)$ curves can be compared with the theoretical curves derived from eqn. (1), which is appropriate to the singlet–triplet model[19], where J is the separation between singlet and triplet states.

$$\chi_M = \frac{N \cdot \beta^2}{3k \cdot T} \cdot g^2 \cdot \left[1 + \tfrac{1}{3} \exp\left(\frac{-J}{k \cdot T}\right)\right]^{-1} \quad (1)$$

The experimental data is being extended to helium temperatures and the interpretation will be discussed elsewhere.

EXPERIMENTAL

General

Manipulations of air-sensitive materials were carried out in a nitrogen-filled glove-box or in vacuum, and all reactions were effected in a stream of purified argon. Infrared spectra were run in KBr disks protected by pure KBr pressed in either side of the sample, on a Perkin–Elmer 521 spectrophotometer. Visible spectra were measured in benzene solution on a Beckman DK2 spectrophotometer, or in the solid state by using a reflectance attachment on a Beckman DK2A spectrophotometer. Magnetic susceptibilities were determined by the Gouy method. Molecular weight values were obtained in a Gallenkamp ebulliometer modified to take a 3.5 ml cell under argon atmosphere.

Analysis

Titanium was estimated by ashing a hydrolysed, sulphated pellet of the sample. Carbon, hydrogen and halide were determined by the Australian Microanalytical Service, Melbourne, by treating weighed pellets sealed in aluminium capsules.

Materials

Cp_2TiF_2[24], Cp_2TiCl[23], Cp_2TiBr_2[24] and Cp_2TiI_2[24] were prepared by published methods, while Cp_2TiCl_2 was available commercially. The solvents THF and diethyl ether were purified by distillation from $LiAlH_4$ under argon.

Activation of aluminium foil

The activation of the metal surface is critical and not all attempted reductions of Cp_2TiF_2 would go to completion. The following method proved the most successful.

A large excess of aluminium foil was cut up into pieces $\approx 1\ cm^2$ and placed under argon. A hot saturated solution of mercurous nitrate in degassed water was then added. After ca. 30 sec the mixture reacted vigorously and the foil formed a shining surface due to amalgamation; the liquid was removed under argon by means of a hypodermic syringe. Immediately the foil was swamped with dry deoxygenated THF and shaken vigorously. The liquid was removed and the washing repeated 4–5 times. After removing the last washing the foil was used immediately or dried and kept under dry argon.

$(Cp_2TiF)_2$

Yellow Cp_2TiF_2 (10 g) was stirred in THF (50 ml) with activated aluminium. At room temperature a green colouration was evident after 1 h. After 24 h, a light blue solid and an intense blue solution were present. The reaction mixture was pumped to dryness and the residue was heated in a sublimation apparatus at ca. 250°C (10^{-4} mmHg) giving dicyclopentadienyltitanium(III) fluoride (4.1 g, 41% yield) as a green crystalline sublimate. (Found: C, 60.9; H, 5.2; Ti, 23.9; mol.wt. ebulliometric in benzene, 404. $C_{10}H_{10}FTi$ calcd.: C, 61.0; H, 5.1; Ti, 24.3%; mol.wt. dimer, 394.)

$(Cp_2TiCl)_2$ *and* $(Cp_2TiBr)_2$

General method. The dihalide Cp_2TiX_2 (X = Cl or Br) was stirred in THF with

excess activated aluminium foil until reduction was complete (generally 1 to 2 h). The excess aluminium was removed by filtration and the filtrate was pumped to dryness, then extracted several times with diethyl ether to remove aluminium halide as the etherate. $(Cp_2TiCl)_2$, yield 85%. (Found: Cl, 16.7; Ti, 21.8; mol.wt. ebulliometric in benzene, 410. $C_{10}H_{10}ClTi$ calcd.: Cl, 16.7; Ti, 22.4%; mol.wt. dimer, 426.) $(Cp_2TiBr)_2$, yield 79%. (Found: C, 46.3; H, 4.6; Br, 30.6; Ti, 18.5; mol.wt. ebulliometric in benzene, 447. $C_{10}H_{10}BrTi$ calcd.: C, 46.5; H, 3.9; Br, 31.0; Ti, 18.5%; mol.wt. dimer, 516.)

Synthesis of $(Cp_2TiI)_2$

Method I. Attempted reduction of Cp_2TiI_2 with activated aluminium in THF resulted in a dark brown slurry. The solution was decanted after settling and the mother-liquor was treated with diethyl ether. A red brown solid resulted which was extremely air-sensitive. The IR spectrum suggested that ether was still present even after prolonged pumping at $\approx 50°$. At higher temperatures decomposition occurred. The compound is believed to be the etherate $Cp_2TiI \cdot Et_2O$. (Found: C, 41.2; H, 5.7; I, 32.3; Ti, 13.9%. $C_{12}H_{20}IOTi$ calcd.: C, 44.2; H, 5.3; I, 33.5; Ti, 12.7%.)

Method II. Cp_2TiCl (2.1 g) was stirred with BI_3 (1.4 g) in benzene (60 ml) in the presence of aluminium foil. The mixture was stirred overnight at room temperature and the resulting red-brown solution was filtered to remove Al and the filtrate was reduced to low bulk. The red brown precipitate of dicyclopentadienyltitanium-(III) iodide (2.1 g, 69% yield) was collected by filtration under argon and was washed with diethyl ether then pumped dry. (Found: C, 39.7; H, 3.3; I, 38.4; Ti, 15.8; mol.wt. ebulliometric in benzene, 590. $C_{10}H_{10}ITi$ calcd.: C, 39.4; H, 3.3; I, 41.5; Ti, 15.7%; mol.wt., 610.)

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MONOCYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

III.* COMPLEXES OF OXYGEN-CONTAINING LIGANDS

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Abstract

Complexes of the type $cpTiX_2,nL$ [where cp = π-cyclopentadienyl; X = Cl or Br; $n = 1$ when L = 1,2-dimethoxyethane (dme); $n = 2$ when L = ethanol (EtOH), or methanol (MeOH)] have been prepared. Various physical properties, including magnetism and electronic spectra, have been measured and interpreted on the basis of six-coordinate titanium(III) atoms. The magnetic moments of all complexes approximate to the spin-only value.

Reactions with dioxan did not result in the formation of stoichiometric complexes, while β-diketones caused rupture of the cp–Ti bonds as well as the halide–titanium bonds giving known tris-β-diketonates of titanium(III).

INTRODUCTION

Monocyclopentadienyltitanium(III) dichloride has been found to form complexes with a range of nitrogen donor chelates.[1] Due to lack of solubility the physical measurements employed for the characterization of these compounds were limited in scope. It was hoped that the oxygen donor chelates would prove to be more soluble and so allow more extensive characterization.

It has already been reported that the monocyclopentadienyltitanium(III) dihalides form 1 : 1 complexes with tetrahydrofuran (thf).[2,3] They are believed to be monomers, involving a pseudotetrahedral stereochemistry about the central titanium atom.

No other references to oxygen complexes of organotitanium(III) halide derivatives could be found in the literature. There is however, an extensive chemistry of inorganic titanium(III) halides complexed with a range of oxygen chelates.[4–8]

RESULTS AND DISCUSSION

A range of complexes with oxygen-containing ligands was prepared by dissolving the monocyclopentadienyltitanium(III) dihalides, $cpTiX_2$ (X = Cl or Br), or

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their tetrahydrofuran complexes, $cpTiX_2$,thf, in the dry, oxygen-free ligands (see Experimental).

The bidentate dme forms 1 : 1 complexes, pale green in colour and virtually insoluble in the parent ligand. The alcohols form 2 : 1 complexes with the dihalides. These complexes are also various shades of green, very soluble in the parent ligand, and may be isolated as crystalline products by pumping to dryness, or by precipitation from concentrated solutions using diethyl ether.

The complexes are thermally unstable, and if the alcohol complexes are heated to $>70°$ they start to revert to free alcohol and $cpTiX_2$. All complexes are rapidly hydrolysed in oxygen-free water to blue $Ti(OH)_3$ and all oxidize exothermally to yellow-orange titanium(IV) compounds.

When the halides were left in alcoholic solution for about 1 week at room temperature, or if the solutions were refluxed for about 1 hr, the green solutions turned yellow-brown and yielded inorganic titanium(III) polymers. Alcoholysis had removed the π-cyclopentadienyl ligand as cyclopentadiene, and polymers of empirical formulae $[(RO)TiX_2,2(ROH)]_n$ formed, where R = Me or Et, X = Cl or Br.[9] The question of association in this type of polymeric compound has been discussed in two earlier publications.[7,10]

Molecular Weight Data

The complexes were too insoluble in non-coordinating (e.g. benzene, toluene) solvents for ebulliometric or cryoscopic molecular weight determinations. Ebullio-metric determinations in tetrahydrofuran for the ethanol and dme complexes gave values equal to or greater than the empirical formulae, suggesting that the complexes may be associated.

The molecular weights of the methanol compounds, $cpTiX_2$,2MeOH where X = Cl, Br, could not be determined in boiling thf because methanol was displaced causing boiling point depression.

Unfortunately the appropriate alcohols could not be used for molecular weight determinations as alcoholysis occurred rapidly giving the alkoxide-bridged polymers mentioned earlier.

Infrared Data

The spectra of the complexes were recorded over the range 4000–250 cm^{-1}. The complexes $cpTiX_2$,thf (X = Cl or Br) were also examined below 600 cm^{-1}, a region not reported in earlier investigations.[2,3]

In the region 4000–600 cm^{-1} the data in each case indicated the presence of coordinated ligands, and π-bonded cyclopentadienyl groups.

The band at 1110 cm^{-1} in free dme, corresponding to a C–O–C stretching mode, was shifted to 1090 ± 5 cm^{-1} in the complexes, suggesting that both oxygen atoms of the ligand are attached to a titanium atom.[11] A similar effect on the C–O–C stretching frequency in tetrahydrofuran has been reported for the tetrahydrofuran complexes $cpTiX_2$,thf (X = Cl, Br, and I).[2,3] The alcohol complexes showed the expected

[9] Coutts, R. S. P., Martin, R. L., and Wailes, P. C., unpublished data.
[10] Winter, G., *Inorg. nucl. Chem. Lett.*, 1966, **2**, 161.
[11] Fowles, G. W. A., Greene, P. T., and Lester, T. E., *J. inorg. nucl. Chem.*, 1967, **29**, 2365.

shifts of the free ligand bands due to coordination to a metal. The band due to the C–O stretch at 1030 cm^{-1} in the free alcohol shifted to lower wavenumber by some 30 cm^{-1} in each case. Covalently bound but symmetrically disposed π-cp ligands can be identified by the simultaneous appearance of bands at 815 ± 5, 1020 ± 5, 1440, and 3100 ± 10 cm^{-1}, although in some spectra various bands are obscured by the presence of overlapping absorptions from the oxygen ligands. The presence of a band at approx. 1130 cm^{-1} could not be confirmed. This absorption due to C–H deformation (perp.) gives some indication of the degree of ionic bonding between the metal and the cyclopentadienyl ring.[12] In $cpTi^{IV}Cl_3$ and $cpTi^{IV}Br_3$ the band was not observed which would tend to suggest that the monocyclopentadienyl derivatives are more ionic than the biscyclopentadienyltitanium(IV) dihalides which usually show low-intensity bands in this region.[12]

Below 600 cm^{-1} absorptions are expected due to the vibrations of metal–halide, metal–oxygen, and metal–cyclopentadienyl bonds in addition to some internal vibrations of the ligands. To assign such absorptions without a normal coordinate analysis is difficult but the tentative assignments shown in Table 1 are based on comparison with earlier data.[1–3]

TABLE 1

INFRARED DATA (<600 cm^{-1})

Assignment	$cpTiCl_2$, 2MeOH	$cpTiBr_2$, 2MeOH	$cpTiCl_2$, 2EtOH	$cpTiBr_2$, 2EtOH	$cpTiCl_2$, dme	$cpTiBr_2$, dme	$cpTiCl_2$, thf	$cpTiBr_2$, thf
Ti–O str	570m,br	560br	590br	565br	540m	540m	575br	580w
	—	480w,br	480w	470m	470	470	—	475w
Ligand bands			450sh	450vw,sh				
			435m					
Ti–cp	410m,br	405br	400m	410br	416m	416m	415s	400s
							330m[a]	330m[a]
Ligand bands					376	376		
					340sh	335w		
Ti–Cl str	332	—	330m	—	326s	—		
Ligand band					320w,sh	318w		

[a] These absorptions obscuring the Ti–Cl stretching region are discussed in the text.

The assignment of the titanium–chloride stretching vibration is strengthened by showing that the band is halogen-sensitive. In the alcohol complexes a medium intensity band occurs at 332 and 330 cm^{-1} respectively in the methanol and ethanol derivative of $cpTiCl_2$, but is absent in the $cpTiBr_2$ complexes. A strong band occurs in $cpTiCl_2$,dme at 326 cm^{-1} which is replaced by a weak band at 318 cm^{-1} in $cpTiBr_2$,dme. This latter band was evident as a weak shoulder in the chloride complex, and has been assigned to a ligand band. Metal–halogen stretching frequencies have been reported for many complexes of trivalent metals including $TiCl_3,3CH_3CN$[13] (330 cm^{-1}, strong band) and $(pyH)_3[TiCl_6]$[14] [300 cm^{-1} (strong), and 287 cm^{-1} (strong)] in agreement with the present tentative assignments. The tetrahydrofuran complexes appear to be anomalous in that a band occurs in both the chloride and the bromide complex at 330 cm^{-1}. Unlike the previous complexes, the tetrahydrofuran derivatives are believed to be monomeric tetrahedral compounds and so this variance may be of a stereochemical nature. It is interesting to note that $cpTi^{IV}Cl_3$ and

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[14] Fritz, H. P., Griffith, W. P., Stefaniak, G., and Tobias, R. S., *Z. Naturf.* (*B*), 1970, **25**, 1087.

$cpTi^{IV}Br_3$, also of tetrahedral stereochemistry, have absorptions at 330 cm^{-1} which are proposed as arising from ring tilting modes.[15] This mode may not be observable in the proposed pseudooctahedral symmetry of the complexes under investigation.

A recent report of a five-coordinate Ti^{III} complex $TiCl_3,2(Et_2O)$[16] assigns the sym Ti–Cl stretch at 460 cm^{-1} and the asym Ti–Cl stretch at 530 cm^{-1}. These assignments seem unlikely due to the fact that Ti–Cl stretching frequencies never occur above 500 cm^{-1} even in Ti^{IV} tetrahedral molecules, and some reduction in frequency would be expected in this case due to both decrease in oxidation state and increase in coordination number. The same workers assign bands at 453 and 518 cm^{-1} to the corresponding Ti–O stretching frequencies. The spectrum of the complex is included in the publications and it would seem more realistic to report the absorptions as two in number one at 518 with a slight shoulder at 530 cm^{-1} the other at 453 with a shoulder at 460 cm^{-1}. These could then be assigned to Ti–O stretching modes experiencing some minor distortions. Absorptions at <400 cm^{-1} could then be assigned to the Ti–Cl stretching frequencies.

Kriegsmann and Leicht[17] have assigned Ti–O vibrational modes in titanium(IV) alkoxides in the range 650–400 cm^{-1}. Adams *et al.*[18] reported the far-infrared spectra of the methoxides of some first-row transition metals, and suggested the relative positions of the pair of M–O stretching frequencies are dependent on the d shell population. For d^5–d^8 divalent metal methoxides the bands were generally below 430 cm^{-1}. For both d^4 and d^9 systems two bands occurred at *c.* 520 and *c.* 450 cm^{-1}. This suggestion was supported by other findings with Cu^{II} methoxides (d^9; 535 ± 15 and 430 ± 20 cm^{-1}),[19] and Cr^{III} chloroalkoxides (d^3; 555 ± 5 and 445 ± 5 cm^{-1}).[20] It may be surmized that the d^1 system of Ti^{III} will fall into this latter category. The spectra of the complexes studied do in fact show two absorptions in the ranges 565 ± 25 cm^{-1} and 475 ± 5 cm^{-1}, and these have been tentatively assigned to the M–O stretching frequencies. In support of this assignment it should be said that the polymeric alcoholysis products[9] only show two bands between 800–300 cm^{-1}. These occur as strong broad bands at *c.* 550 cm^{-1} and 470–490 cm^{-1} in agreement with the above proposal.

The Ti–cp stretching mode expected in these monocyclopentadienyltitanium(III) complexes occurs as a broad weak–medium intensity band for the dme and alcohol complexes at 410 ± 10 cm^{-1}. In the thf complexes the band is much stronger, and associated with it is a medium intensity band at 330 cm^{-1}. It may be that this latter band is due to a ring tilt mode, as suggested earlier.

Conductivity Data

Conductance was measured in methanol solution at 25°C for the alcohol complexes using a range of concentrations (Table 2). The bromide derivatives were

15 Maslowsky, E., Jr, and Nakamoto, K., *Appl. Spectrosc.*, 1971, **25**, 187.
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17 Kriegsmann, H., and Leicht, K., *Z. Elektrochem.*, 1958, **62**, 1163.
18 Adams, R. W., Martin, R. L., and Winter, G., *Aust. J. Chem.*, 1967, **20**, 773.
19 Adams, R. W., Barraclough, C. G., Martin, R. L., and Winter, G., *Aust. J. Chem.*, 1967, **20**, 2351.
20 Dubicki, L., Kakos, G. A., and Winter, G., *Aust. J. Chem.*, 1968, **21**, 1461.

found to have higher values of conductance than the analogous chlorides. The equivalent conductance (Λ_e) was plotted against $C^{1/2}$ (where C is the concentration in equiv. cm^{-3}).

TABLE 2

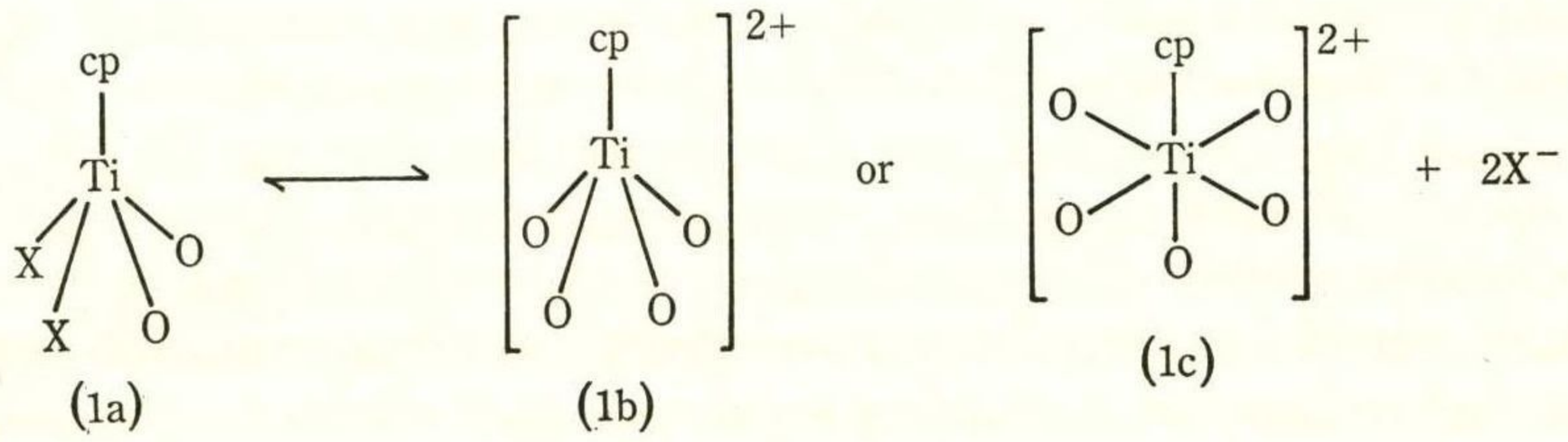
CONDUCTANCE DATA

C in mol l^{-1}; Λ in Ω^{-1} cm^2 mol^{-1}

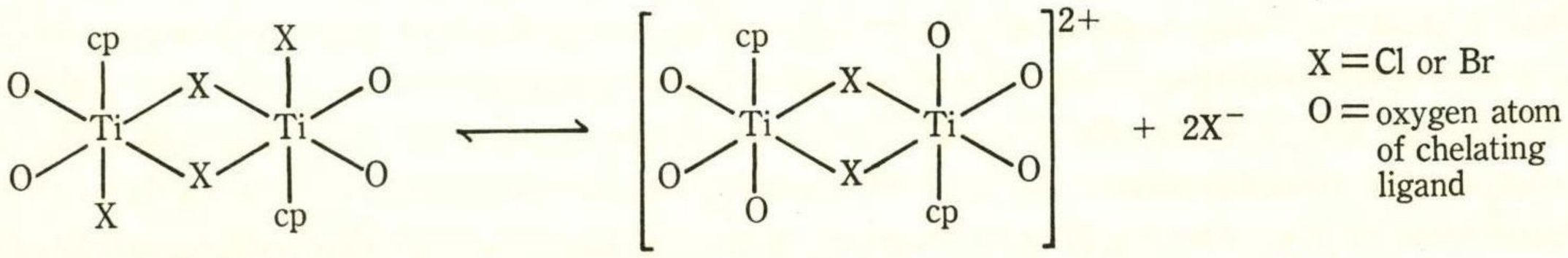
$cpTiCl_2$,2EtOH		$cpTiBr_2$,2EtOH		$cpTiCl_2$,2MeOH		$cpTiBr_2$,2MeOH	
10^3C	Λ_e	10^3C	Λ_e	10^3C	Λ_e	10^3C	Λ_e
4·28	110	7·40	180	7·35	80	3·80	169
2·40	134	3·25	202	2·63	103	1·72	183
0·86	180	0·74	250	1·63	135	1·10	194
0·43	253	0·07	435	0·56	194	0·55	206

At low concentrations Λ_e started to increase rapidly suggesting solvolysis was much faster in dilute solution. The values of Λ_e at high concentration were much greater than the values found for the polymeric alcoholysis products[9] at comparable concentration, so it was considered that ionization was taking place before alcoholysis had progressed to any extent.

The values for Λ_e, for the alcohol complex $cpTiX_2$,2ROH, taken at the concentration $1{\cdot}0\times10^{-3}$M were 176 (X = Cl, R = Et), 242 (X = Br, R = Et), 162 (X = Cl, R = Me), and 200 (X = Br, R = Me). This data compared extremely well with the range 160–220 Ω^{-1} cm^2 mol^{-1} suggested by Geary[21] for a 2 : 1 electrolyte in methanol at such a concentration.



(1a) (1b) (1c)



(2a) (2b)

The possibility of five-coordinate monomeric species, structure (1a), should be considered although molecular weight determinations in conjunction with the conductance data tend to favour some associated form in the solid state such as a halogen bridged dimer, structure (2a). Either structure could lead to the observed 2 : 1 electrolytic behaviour (see above).

[21] Geary, W. J., *Coord. Chem. Rev.*, 1971, **7**, 81.

Visible Spectral Data

The principal absorption bands of the complexes in the 5000–25000 cm^{-1} region are listed in Table 3. Reflectance spectra were measured for all samples and solution spectra for the alcohol complexes were recorded in the appropriate alcohol.

TABLE 3

ELECTRONIC SPECTRAL DATA

Complex	Solid state			Solution		
$cpTiCl_2$,dme	25000sh	13800	*c.* 9100sh			
$cpTiBr_2$,dme	24100sh	13650	*c.* 9100sh			
$cpTiCl_2$,2EtOH	23600w,sh	13500	*c.* 10000	—	12600	*c.* 10000
$cpTiBr_2$,2EtOH	—	13500	*c.* 9700sh	—	13300	*c.* 10000
$cpTiCl_2$,2MeOH	23000vw,sh	13300	*c.* 10500	23800	13300	*c.* 10300
$cpTiBr_2$,2MeOH	23600sh	13700	*c.* 10500	—	13700	*c.* 10300

The solid state spectra for the complexes contain a weak shoulder at *c.* 24000 cm^{-1} on the edge of the charge transfer absorptions. The main absorption band occurs in the narrow range 13300–13800 cm^{-1}. Associated with this strong absorption band is a pronounced shoulder at *c.* 9000–10000 cm^{-1}.

The interpretation of the spectra of similar complexes of nitrogen-containing ligands was discussed at some length in Part II. It suffices to say that the band at 24000 is mostly likely charge transfer in origin possibly associated with the halide bridge, while the band at *c.* 13500 cm^{-1} with its associated shoulder is attributable to the ligand field band of a Ti^{III} atom in a pseudo-octahedral environment. The decrease in frequency of the ligand field band of the oxygen complexes compared with that of the nitrogen complexes is in keeping with the findings obtained with other metal ions when used to order various ligands into a spectrochemical series.

The d–d bands occur at almost the same position as in the solid state spectra indicating that the ligand field environment is virtually unchanged. Complexes of structures (1a) and (2a) in alcoholic solution may give rise to species (1b) or (1c) and (2b). The environments of (1b) or (1c) are such that a shift to higher frequency would be expected, due to the effect of the rule of average environment proposed by Jørgensen.[22] The effect is less in (2b), so this latter structure is favoured. A large shift was observed in the nitrogen complexes and was attributed to rupture of the halide bridge.[1] Since the d–d bands of the alcoholysis products appear in both solution and solid state spectra[9] at *c.* 10000 cm^{-1}, it would appear that alcoholysis of the complexes is slow and is not taking place during measurement of their spectra.

Magnetic Data

The proposed associated nature of the complexes (from molecular weight and spectroscopic data) requires the presence of bridging groups, a situation which can

[22] Jørgensen, C. K., "Absorption Spectra and Chemical Bonding in Complexes," p. 109 (Pergamon: New York 1962).

lead to magnetic anomalies. It is obvious from the data in Table 4 that any interaction through such a bridging group is evidently rather small since the compounds follow the normal Curie–Weiss law with relatively low values of θ.

TABLE 4

MAGNETIC DATA

$\mu_{eff} = [8\chi'_M(T)]^{1/2}$. The magnitude of t.i.p. was obtained from the intercept of a χ'_M against $1/T$ plot for the complexes, as the plot was linear. θ was obtained from the intercept of a $1/\chi'_M$ against T plot and is defined by the expression $\chi'_M = \text{constant}/(T-\theta)$

T (K)	$10^6\chi'_M$ ($cm^3\ mol^{-1}$)	μ_{eff} (B.M.)	T (K)	$10^6\chi'_M$ ($cm^3\ mol^{-1}$)	μ_{eff} (B.M.)	T (K)	$10^6\chi'_M$ ($cm^3\ mol^{-1}$)	μ_{eff} (B.M.)
	$cpTiCl_2$,dme[a]			$cpTiBr_2$,dme[b]			$cpTiCl_2$,2EtOH[c]	
290	1520	1·89	290	1280	1·73	291	1015	1·54
263	1678	1·89	263	1444	1·75	261	1144	1·55
233	1845	1·88	202	1801	1·71	232	1279	1·55
205	2070	1·85	172	2100	1·71	200	1449	1·53
171	2368	1·81	141	2480	1·68	165	1698	1·50
140	2797	1·78	111	3084	1·66	136	2003	1·48
109	3425	1·73				105	2482	1·45
						94	2727	1·44
	$cpTiBr_2$,2EtOH[d]			$cpTiCl_2$,2MeOH[e]				
295	982	1·53	298	1020	1·57			
260	1155	1·56	262	1192	1·59			
231	1282	1·55	232	1312	1·59			
200	1458	1·53	205	1496	1·57			
168	1693	1·51	168	1722	1·53			
137	2014	1·49	140	2033	1·52			
107	2436	1·45	109	2424	1·46			

[a] T.i.p. $380\times10^{-6}\ cm^3\ mol^{-1}$, θ −38 K. [b] T.i.p. $240\times10^{-6}\ cm^3\ mol^{-1}$, θ −16 K. [c] T.i.p. $260\times10^{-6}\ cm^3\ mol^{-1}$, θ −26 K. [d] T.i.p. $240\times10^{-6}\ cm^3\ mol^{-1}$, θ −26 K. [e] T.i.p. $160\times10^{-6}\ cm^3\ mol^{-1}$, θ −24 K.

The moments at room temperature fall in the range from 1·53 to 1·89 B.M. The lack of a marked temperature dependence implies that should magnetic interaction through, say, halogen bridges be taking place it must necessarily be very weak.

The dme complexes have much higher moments than do the alcohol derivatives. This is in keeping with the magnetic studies of Machin *et al.*[23] which showed that the blue adduct $TiCl_3$,1·5dme has a much higher room-temperature moment (1·86 B.M.) than any of the other Ti^{III} compounds which they studied.

It appears that the magnetic data is consistent with pseudooctahedral stereochemistry. This situation is depicted in structure (2a) in which the two halide atoms are bridging.

The complex $cpTiBr_2$,2MeOH was found to be of a waxy nature and extremely difficult to pack into the Gouy tube; only a room temperature reading was recorded; a value of *c.* 1·3 B.M. was observed.

[23] Machin, D. J., Murray, K. S., and Walton, R. A., *J. chem. Soc.* (*A*), 1968, 195.

Experimental

General

All manipulations were carried out in a nitrogen-filled evacuable glove box, or in a stream of purified argon using a Schlenk system. Infrared spectra were run in KBr discs, on a Perkin–Elmer 521 spectrophotometer. Visible spectra were measured in solution on a Beckman DK2 spectrophotometer and in the solid state on a Beckman DK2A spectrophotometer with a diffuse reflectance attachment. Magnetic susceptibilities were determined by the Gouy method and molecular weight values were obtained in a Gallenkamp ebulliometer modified to take a 3·5 ml cell, under anaerobic conditions.

Analyses

Titanium was estimated as TiO_2 by ashing a sulphated pellet of the sample. Carbon, hydrogen, and halide were determined by the Australian Microanalytical Service, Melbourne, using weighed pellets sealed in aluminium capsules.

Table 5

Analytical data

Compound	Colour	Found (%)				Calc. (%)			
		C	H	Hal	Ti	C	H	Hal	Ti
$cpTiCl_2$,dme	pale green	37·1	5·1	26·0	17·2	39·5	5·5	25·9	17·5
$cpTiBr_2$,dme	pale green	28·5	4·2	44·2	13·6	29·8	4·2	44·0	13·2
$cpTiCl_2$,2MeOH	pale green	31·9	5·1	28·2	19·7	33·9	5·3	28·6	19·3
$cpTiBr_2$,2MeOH	bright green	24·2	3·8	47·5	14·4	25·0	3·9	47·5	14·2
$cpTiCl_2$,2EtOH[a]	bright green	38·1	5·9	25·8	17·4	39·2	6·2	25·6	17·4
$cpTiBr_2$,2EtOH[b]	bright green	29·9	4·9	43·6	12·8	29·6	4·7	43·9	13·1

[a] Mol. wt (ebulliometry, in thf) 373 (theor. 276). [b] Mol. wt 406 (theor. 365).

Reagents

$cpTiX_2$ and $cpTiX_2$,thf (X = Cl or Br) were prepared from the cyclopentadienyltitanium(IV) trihalides by reduction with zinc.[3] Dioxan and dimethoxyethane were purified by allowing them to stand over molecular sieves, and then distilling them under anaerobic conditions. Methanol and ethanol were purified by reaction with magnesium metal and distillation under anaerobic conditions.

Reactions

(i) *General method.*—Reactions were carried out by treating about 1–2 g of the appropriate dihalide or dihalide tetrahydrofuran with excess of the ligand (10–15 ml) at room temperature. In the case of dme the complexes were formed over some hours as evidenced by the gradual changes of colour of the suspended reactants. With the alcohol complexes the reactants formed deep green solutions in minutes and could only be isolated by pumping to dryness, or by reducing to low volume and precipitating with diethyl ether. Table 5 summarizes the analytical data.

(ii) *Reactions with dioxan.*—When the blue tetrahydrofuran complex $cpTiCl_2$,thf (1·0 g) was treated with dioxan (*c.* 20 ml) a mauve solid formed immediately. This was identified by infrared spectrum, and titanium ash, as $cpTiCl_2$ (Found: Ti, 25·8. Calc. for $cpTiCl_2$: Ti, 26·0%). When a sample of the dihalide was sealed in a glass tube with dioxan and heated at 95° for *c.* 16 hr, only slight dissolution took place to give a green-brown colour; even after 24 hr most of the dihalide remained unchanged. No complex could be isolated. A similar reaction with $cpTiBr_2$,thf did show some reaction after 16 hr refluxing but no stoichiometric complex was isolated from the deep green solution formed.

(iii) *Reactions with β-diketones.*—$cpTiCl_2$ or $cpTiCl_2$,thf (1–2 g) was treated in dilute thf solution with a thf solution of the β-diketone (acetylacetone, benzoylacetone, and dibenzoylmethane). In all cases the highly coloured crystalline products were identified by titanium ash and infrared spectra as the tris-β-diketonates of titanium(III).

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THE UNEXPECTED FORMATION OF TITANOXANES

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Monocyclopentadienyltitanium(III) dihalides [$CpTi^{III}X_2$, where Cp = π-cyclopentadienyl, X = Cl, Br, or I] form normal coordination complexes with ethers, (1,2), alcohols (2), and a range of nitrogen-containing ligands (3). With aldehydes or ketones "redox" reactions take place after several minutes in a THF/diethyl ether solvent mixture to yield yellow crystalline titanium IV compounds believed to be of the type shown in Fig. 1 (4).

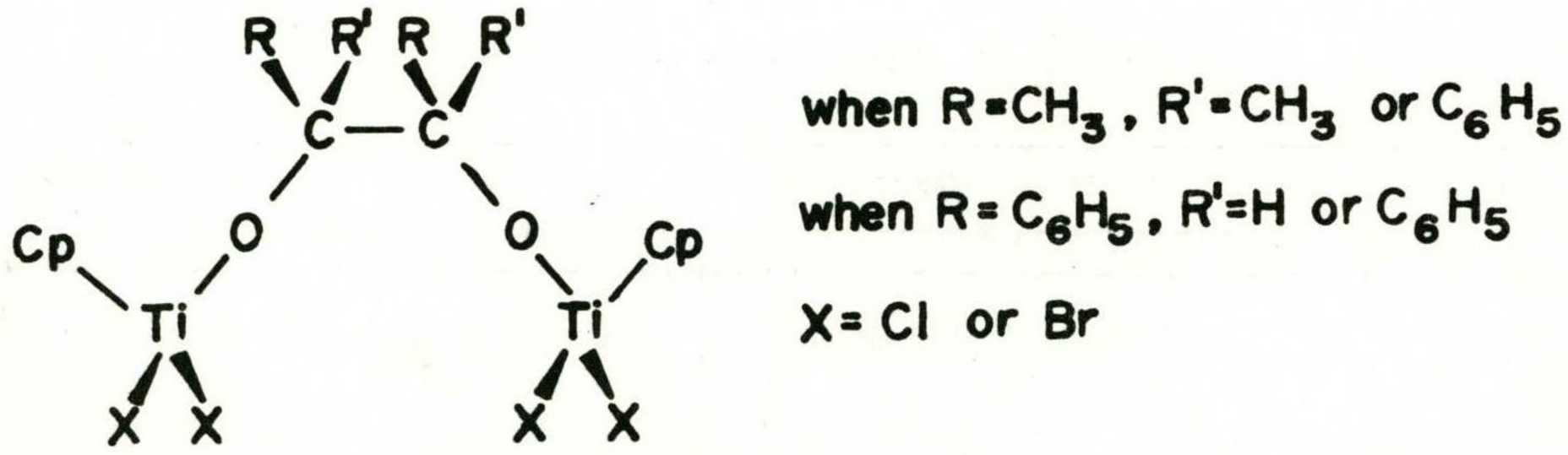
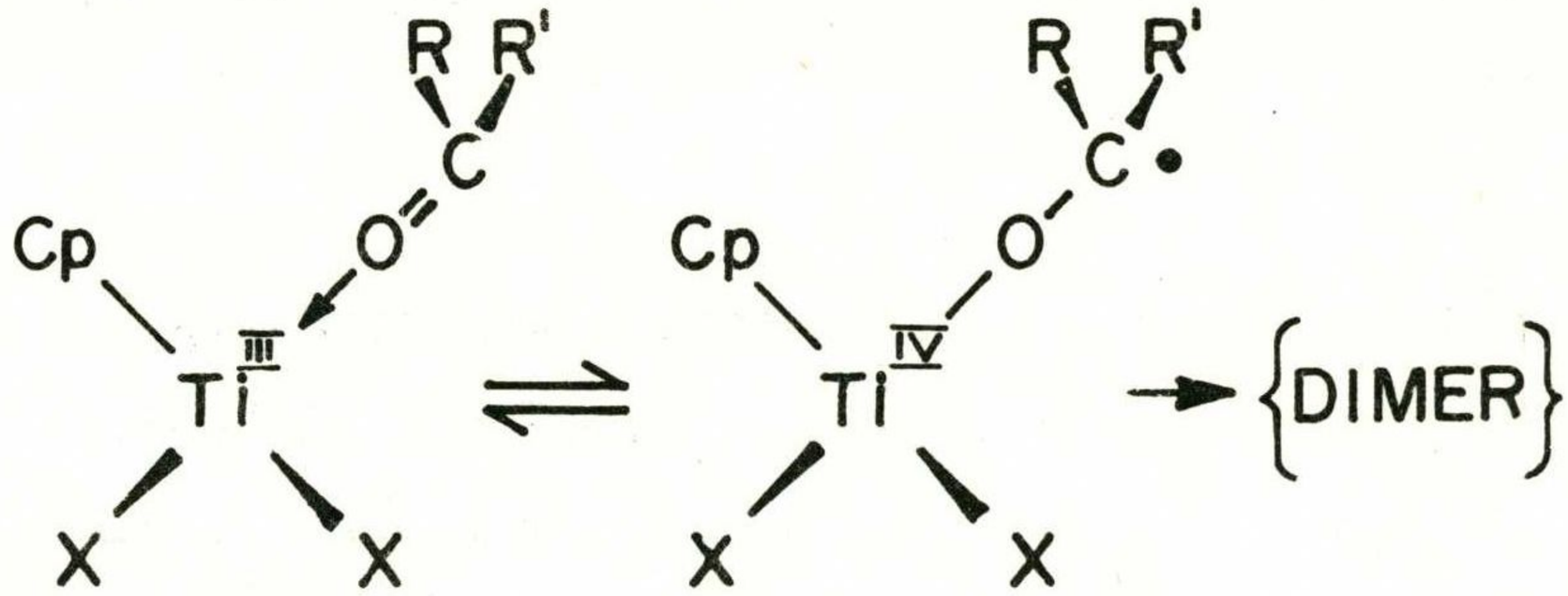


FIGURE 1.

The formation of these dimers in ethereal media may well proceed via the following free radical intermediate:



In this event, formation of the dimer should be inhibited in those solvents which are susceptible towards radical attack. To test this hypothesis, the solvent THF/diethyl ether was replaced by acetone.

Interestingly no normal ketone or aldehyde complexes of $CpTi^{III}X_2$ have been isolated although such complexes readily form with titanium(III) trihalides (5,6), or titanium(IV) tetrahalides (7,8).

When the dihalides are dissolved in pure dry acetone under anaerobic conditions, a brown solution forms from which yellow crystals slowly precipitate over several days. These crystalline products were found to be $(CpTi^{IV}XO)_n$ [X = Cl, Br, or I] see Tables 1 and 2.

TABLE 1. Analytical Data

Compound	ANALYSIS %				NMR (δ)
	C	H	Ti	Halide	
$(CpTiClO)_4$	Found 37.2 Calc. 36.8	3.2 3.1	29.3 29.1	21.5 21.6	6.63
$(CpTiBrO)_n$	Found 28.5 Calc. 28.7	2.4 2.4	23.2 23.0	37.5 38.2	6.71
$(CpTiIO)_n$	Found 24.6 Calc. 23.5	2.0 1.9	19.2 18.8	- 49.6	6.78

TABLE 2. Infra Red Data

$(CpTiClO)_4$	$(CpTiBrO)_n$	$(CpTiIO)_n$	Compound Assignment
3090 (w-m)	3090 (w-M)	3095 (w)	C-H stretching mode
1430 (m-s)	1430 (m-s)	1435 (m mult)	C-C stretching mode
1020 (s)	1020 (s)	1020 (s)	C-H wagging mode (II)
	870 (sh)	885 (sh)	
800 (v vs bd)	840 (sh) }	850 (sh) }	C-H wagging mode (I)
	790 (vs)	810 (vs)	and Ti-O vibrations
600 (w-m)	600 (w-m)	600 (w-m)	ring deformation mode
430 (s)	-	-	Ti-Cl stretching mode
415 (s)	415 (m)	415 (m)	Ti-Cp stretching mode
330 (s)	-	-	Ti-Cl stretching mode
305	310 (w)	310 (w)	

Only the chloride derivative $(CpTiClO)_4$ has been reported previously (9,10). The earlier preparations involved hydrolysis of $CpTi^{IV}Cl_3$. Due to its limited solubility in organic solvents, cryoscopic and ebulliometric molecular weight determinations could not differentiate between a trimeric product or some higher oligomer (9). It was later established by light scattering methods that the product is a tetramer (10). This has since been confirmed by crystal and molecular structure studies (11).

We found the new compounds, X = Br or I, were also too insoluble for molecular weight determinations. The iodide derivative is sensitive to light and starts to decompose to an orange-brown solid after 1-2 days. The compounds, X = Br or I, could also be prepared by the hydrolysis of $CpTi^{IV}X_3$.

As the reactions were conducted under anaerobic conditions the acetone must be the source of oxygen and so must itself be reduced. It was established by two phase gas chromatography that the major byproduct from the

reaction is mesityl oxide, the expected product from condensation of acetone.

Although not normally obtained under such mild conditions, it is believed that the carbonyl group is activated by electron donation from the titanium(III) compound (d^1 system), as shown in equation , giving a titanium(IV) intermediate with a carbonyl group sufficiently activated to condense with another acetone molecule. Mesityl oxide is formed with elimination of water which is then available to hydrolyse the titanium(IV) intermediate.

Acknowledgement

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MONOCYCLOPENTADIENYLTITANIUM(III) COMPOUNDS

IV.* CARBOXYLATES

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[Manuscript received 2 November 1972]

Abstract

Two methods of preparing monocyclopentadienyltitanium(III) carboxylates of general formula $cpTi(O_2CR)_2$ ($cp = \pi$-cyclopentadienyl; $R = CF_3$, CH_3, CH_2CH_3, $CH_2CH_2CH_3$, C_6H_5) have been investigated. Although titanium(III) has the configuration 3d,[1] the green or brown dimers are virtually diamagnetic. The diamagnetism probably arises from a superexchange interaction between titanium atoms through the π-system of the carboxylate bridges although the possibility of some direct metal–metal interaction cannot be excluded at this stage. Spectroscopic data are reported for all compounds.

Bis(cyclopentadienyl)titanium(III) carboxylates of general formula $cp_2Ti(O_2CR)$ ($R = H$, CH_3, CH_2CH_3) were formed when $cpTi(O_2CR)_2$ were vacuum sublimed at *c.* 180°C.

Introduction

The preparation of the organotitanium(III) carboxylates of formula $cpTi(O_2CR)_2$ was carried out as part of a general survey on monocyclopentadienyltitanium(III) derivatives.[1–4] A preliminary account of the derivatives $R = CH_3$, CH_2CH_3, and C_6H_5 was reported in 1970.[5] About this same time Razuvaev *et al.* reported the unexpected formation of the derivative where $R = C_6H_5$ in approximately 40–50% yield by reaction of $cp_2Ti^{IV}(C_6H_5)_2$ with benzoyl peroxide. Although a similar reduction occurred with acetyl peroxide these workers were unable to isolate the product.[6,7] Current interest in this area of organometallic chemistry[5–10] has prompted this investigation.

* Part III, *Aust. J. Chem.*, 1973, **26**, 47.

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[1] Coutts, R. S. P., Martin, R. L., and Wailes, P. C., *Aust. J. Chem.*, 1971, **24**, 1079.

[2] Coutts, R. S. P., Martin, R. L., and Wailes, P. C., *Aust. J. Chem.*, 1971, **24**, 2533.

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[10] Kalinnikov, V. T., Larin, G. M., Ubozhenko, O. D., Zharkikh, A. A., Latyaeva, V. N., and Lineva, A. N., *Dokl. Akad. Nauk SSSR*, 1971, **199**, 95.

Results and Discussion

Preparation and Properties

Monocyclopentadienyltitanium(III) dichloride, $cpTiCl_2$, was treated with sodium salts of the carboxylic acids under anaerobic conditions in tetrahydrofuran:

$$cpTi^{III}Cl_2 + 2NaO_2CR \rightarrow cpTi^{III}(O_2CR)_2 + 2NaCl \qquad \text{(Method A)}$$

The reaction solution was reduced to dryness and the residue was sublimed at *c.* 180°C. Green sublimates formed in the cases R = CF_3, CH_3, CH_2CH_3, although in the last two instances the sublimates were contaminated with occluded $cp_2Ti^{III}(O_2CR)$. This could be removed by repeated resublimation at *c.* 80°C. In the case of R = H only $cp_2Ti^{III}(O_2CH)$ was formed in very low yield (<5%). It seems that the temperature of sublimation was sufficient to cause some pyrolysis to take place, possibly by the rearrangement reaction below. This reaction is still under investigation:

$$2cpTi^{III}(O_2CR)_2 \xrightarrow{\text{heat}} cp_2Ti^{III}(O_2CR) + Ti^{III}(O_2CR)_3$$

To overcome the necessity to sublime the desired product from the reaction mixture, an alternative synthesis was sought. $cpTiCl_2$ was dissolved in tetrahydrofuran and treated with the appropriate carboxylic acid in the presence of a suitable base. For the virtually insoluble products (R = CF_3, CH_3) n-butylamine was used as this afforded a soluble amine hydrochloride byproduct which remained in solution, the desired product being precipitated. For the more soluble products (R = CH_2CH_3, $CH_2CH_2CH_3$, or C_6H_5) triethylamine was used as base and was precipitated as the hydrochloride, leaving the soluble carboxylate in solution:

$$cpTi^{III}Cl_2 + 2RCO_2H + 2amine \rightarrow cpTi^{III}(O_2CR)_2 + 2amine,HCl \qquad \text{(Method B)}$$

Method B afforded the desired product in 70–90% yield based on the amine hydrochloride formed (Table 1).

TABLE 1

ANALYTICAL DATA

Compound	Colour	Subl. temp. (°C)	Prepn method	Found Mol. wt	Found (%) Ti	C	H	Calc. Mol. wt	Calc. (%) Ti	C	H
$cpTi(O_2CCF_3)_2$	dark green	180	A	insol.	13·7	31·9	1·5	339	14·1	31·9	1·5
$cpTi(O_2CCH_3)_2$	green	180	A	insol.	20·8	47·2	4·7	231	20·7	46·8	4·8
$cpTi(O_2CCH_3)_2$	green	—	B	insol.	20·5	47·4	4·5	231	20·7	46·8	4·8
$cpTi(O_2CCH_2CH_3)_2$	green	180	B	520	18·9	51·1	6·0	259	18·5	51·0	5·8
$cpTi(O_2CCH_2CH_2CH_3)_2$	green	—	B	579	17·0	53·7	6·6	287	16·7	54·4	6·7
$cpTi(O_2CC_6H_5)_2$	brown	—	A	insol.	13·1	64·9	4·9	355	13·5	64·3	4·3
$cpTi(O_2CC_6H_5)_2$	brown	—	B	insol.	13·5	—	—	355	13·5	64·3	4·3
$cp_2Ti(O_2CH)$	green	100	A	[a]	21·3	59·0	5·0	223	21·4	59·3	5·0
$cp_2Ti(O_2CCH_3)$	blue	60	A	[a]	20·3	59·2	5·2	237	20·2	61·0	5·5
$cp_2Ti(O_2CCH_2CH_3)$	blue	80	A	258	18·9	62·2	5·8	251	19·1	62·3	6·0

[a] Monomer; see ref. 8.

A comparison of the monocyclopentadienyltitanium(III) and the bis(cyclopentadienyl)titanium(III) carboxylates is of some interest.

As mentioned above, pyrolysis of $cpTi(O_2CR)_2$ compounds caused apparent rearrangement, the extent of which varied with the particular derivative and became more extensive with increasing chain length. Whereas the trifluoroacetate, $cpTi(O_2CCF_3)_2$, could be sublimed unchanged at 180°C, the acetate under similar

conditions produced a sublimate containing traces of blue $cp_2Ti(O_2CCH_3)$, and the propionate sublimate contained a significant amount of blue $cp_2Ti(O_2CH_2CH_3)$. The butyrate could not be sublimed satisfactorily. All of the $cp_2Ti(O_2CR)$ derivatives were exceptionally volatile and stable under the conditions of sublimation. As mentioned earlier when method A was used the sublimates could be freed of the $cp_2Ti(O_2CR)$ contaminants by resubliming at lower temperatures (for $R = CH_3$ *c.* 60°C, $R = CH_2CH_3$ *c.* 80°C).

The sensitivity to oxidation was far less for $cpTi(O_2CR)_2$ derivatives, which slowly formed yellow-orange titanium(IV) derivatives after several minutes in the air, than for the $cp_2Ti(O_2CR)$ derivatives which were extremely sensitive, some samples inflaming spontaneously when exposed in a densely packed form.

Molecular Weight Data

The $cp_2Ti(O_2CR)$ derivatives were soluble in benzene allowing ebulliometric molecular weight determination.[8] In the case of $cpTi(O_2CR)_2$ derivatives the products $R = CF_3$ and CH_3 were too insoluble for molecular weight determinations in benzene, toluene, or the more polar tetrahydrofuran. Ebulliometric determinations in benzene for the higher, more soluble, homologues ($R = CH_2CH_3$ and $CH_2CH_2CH_3$) showed the derivatives to be dimeric.

Razuvaev *et al.*[7] reported that the compound, $R = C_6H_5$, isolated from their method of preparation was readily soluble in benzene, yet they report a molecular weight of 512, 515 (expected value for a dimer is 710). The molecular weight was determined cryoscopically, presumably in benzene. We find the product from our preparation (method A or B) too insoluble in benzene for cryoscopic determination of molecular weight, and insufficiently soluble in the more polar tetrahydrofuran to obtain meaningful ebulliometric results.

The new derivative $cp_2Ti(O_2CCH_2CH_3)$ was found to be monomeric in benzene solution, in keeping with the earlier work on this type of compound.[8]

Magnetic and E.P.R. Data

The monocyclopentadienyltitanium(III) compounds $R = CF_3$, CH_3, CH_2CH_3, and C_6H_5 are virtually diamagnetic over the temperature range 100–300 K with molar susceptibilities below 150×10^{-6} cm^3 mol^{-1}. The more soluble compounds ($R = CH_2CH_3$, $CH_2CH_2CH_3$, and C_6H_5) are sufficiently paramagnetic in C_6D_6 or tetrahydrofuran to cause line broadening over a wide range of δ values in the n.m.r. spectra.

The presence of pronounced magnetic exchange between pairs of titanium atoms (electron configuration $3d^1$) within each $[cp_2Ti_2(RCO_2)_4]$ dimer, is clearly indicated by X-band electron spin resonance studies on the polycrystalline materials (Fig. 1). At room temperature absorptions were observed both well above and well below the region ($g_{eff} \approx 2$), where signals are normally found for magnetically dilute compounds of titanium(III) with an $S = 1/2$ ground state.

The main features of the line shape can be accommodated in terms of the model employed by Wasserman, Snyder, and Yager[11] for interpreting the spectra of randomly oriented organic triplets. We assign the weak peaks near 2785 and 3937 G as the

[11] Wasserman, E., Snyder, L. C., and Yager, W. A., *J. chem. Phys.*, 1964, **41**, 1763.

$\Delta m = 1$ transitions H_{z1} and H_{z2} from which we obtain $g_{\parallel} = 1{\cdot}94$. From the peaks of the z-axis absorptions (marked by $\times$ in Fig. 1) the most probable value of the zero field splitting parameter D ($E = 0$) is $0{\cdot}051$ cm^{-1}, which is much smaller than $g\beta$H when the observations are made at X-band ($h\nu \approx 0{\cdot}3$ cm^{-1}). The pair of bands at 3003 and 3538 G are assigned to the $\Delta m = 1$ transitions H_{xy1} and H_{xy2} from which we obtain $g_{\perp} = 1{\cdot}99$ and $D = 0{\cdot}050$ cm^{-1}. It appears that the E parameter is very small, for splitting of the xy absorption bands is not observed even down to 170 K.

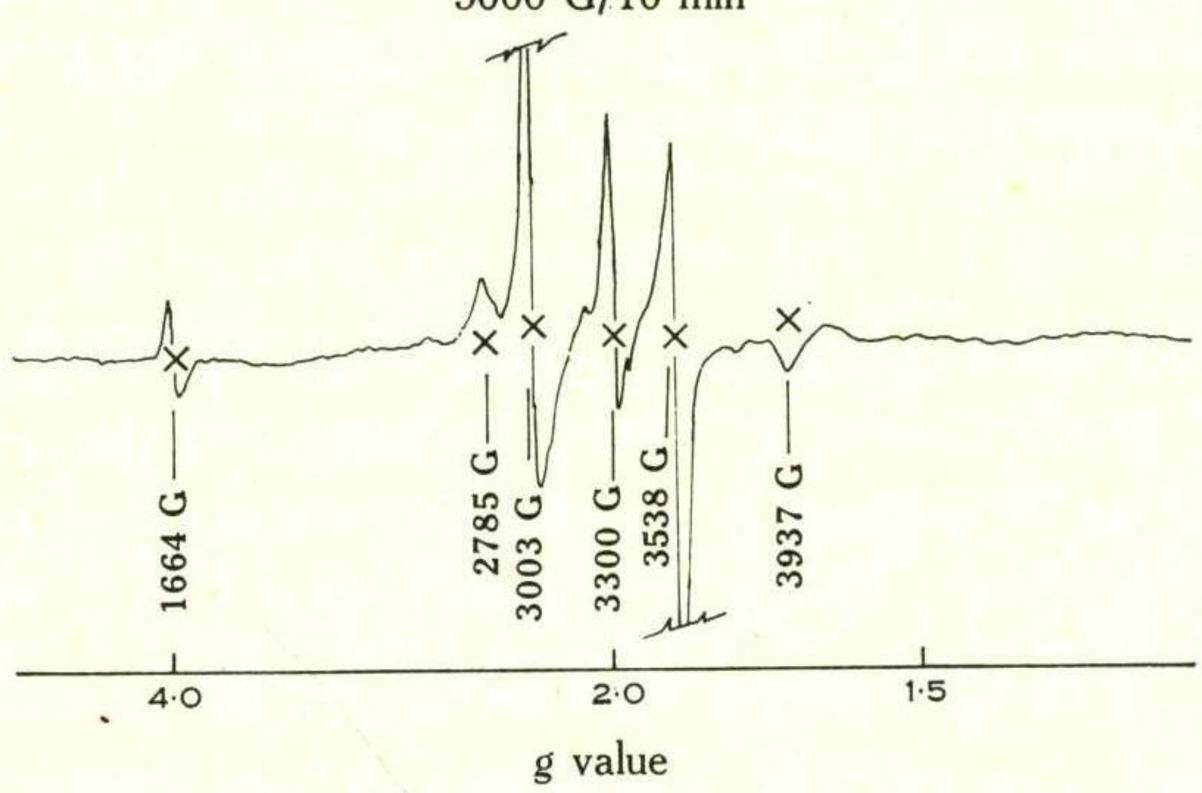


Fig. 1.—E.s.r. spectrum of $[cpTi(O_2CCH_3)_2]_2$.

The peak at 1664 G appears to be the "forbidden" $\Delta m = 2$ double quantum transition ($g_{\text{eff}} = 3{\cdot}91$) which has been observed as strong lines for organic molecules in triplet states and weaker lines for the inorganic copper(II) carboxylates.[12–14]

The remaining band at 3300 G cannot be assigned unequivocally but appears to be due to the presence of a monomeric titanium(III) impurity with a ground state $S = 1/2$ and $g_{\text{eff}} = 1{\cdot}97$. A more detailed description of the temperature dependence of the e.s.r. spectra of all the present compounds, both in solution and polycrystalline states, will be given elsewhere.

It is interesting to note that the Ti–Ti exchange interaction in these binuclear carboxylates must be several times greater than that found for the corresponding copper(II) carboxylates ($-2J \approx 300$ cm^{-1}). If the crude approximation is made that each titanium atom lies in a roughly octahedral field and that the odd electron occupies the d_{xy} (t_2 sub-set) orbital, then this orbital is correctly oriented to overlap with the π-system of the four bridging acetate groups[15] and strong antiferromagnetic coupling is expected through the Ti(d_{xy})–π(acetate)–Ti(d_{xy}) superexchange pathway. This π-superexchange mechanism is not available in copper(II) carboxylates since the corresponding metal d_{xy} orbital is fully occupied.

The near diamagnetism of the present dimers seems unlikely to arise from direct metal–metal bonding. The V–V distance in the corresponding $[cp_2V_2(CF_3CO_2)_4]$ dimer is $3{\cdot}7$ Å which is too large for significant overlap of 3d orbitals based on the

[12] Bleaney, B., and Bowers, K. D., *Proc. R. Soc.* (*A*), 1952, **214**, 451.
[13] Wasson, J. R., Shyr, C. I., and Trapp, C., *Inorg. Chem.*, 1968, **7**, 469.
[14] Goodgame, D. M. L., and Price, K. A., *Nature*, 1968, **220**, 783.
[15] Dubicki, L., and Martin, R. L., *Inorg. Chem.*, 1966, **5**, 2203.

metal atoms.[16] However, a crystal structure determination is required to evaluate these alternative mechanisms for spin coupling.

Electronic Spectral Data

Electronic spectral data were recorded in the region 4000–25000 cm^{-1}. Reflectance spectra were measured for all samples, and the solution spectra in benzene were recorded for all but the trifluoroacetate derivative (Table 2). The spectra are

TABLE 2

ELECTRONIC SPECTRAL DATA (cm^{-1})

Solution spectra in benzene; ε_{max} in parentheses

Compound	Reflectance			Solution	
$cpTi(O_2CCF_3)_2$	—	16700	*c.* 12960sh		
$cpTi(O_2CCH_3)_2$	20800	15400	12300	14300sh	12500
$cpTi(O_2CCH_2CH_3)_2$	20000sh	15600	*c.* 12500sh	14600 (98·6)	12500sh
$cpTi(O_2CCH_2CH_2CH_3)_2$	20000sh	16000	*c.* 12500sh	14600 (94·5)	12500sh
$cpTi(O_2CC_6H_5)$	20000	15400sh	13300sh	—	*c.* 12500sh

substantially the same in solid state or in solution (Fig. 2) suggesting the same absorbing species are present in both cases. Thus we may assume the dimeric unit is present in the solid state as indicated by the magnetic data.

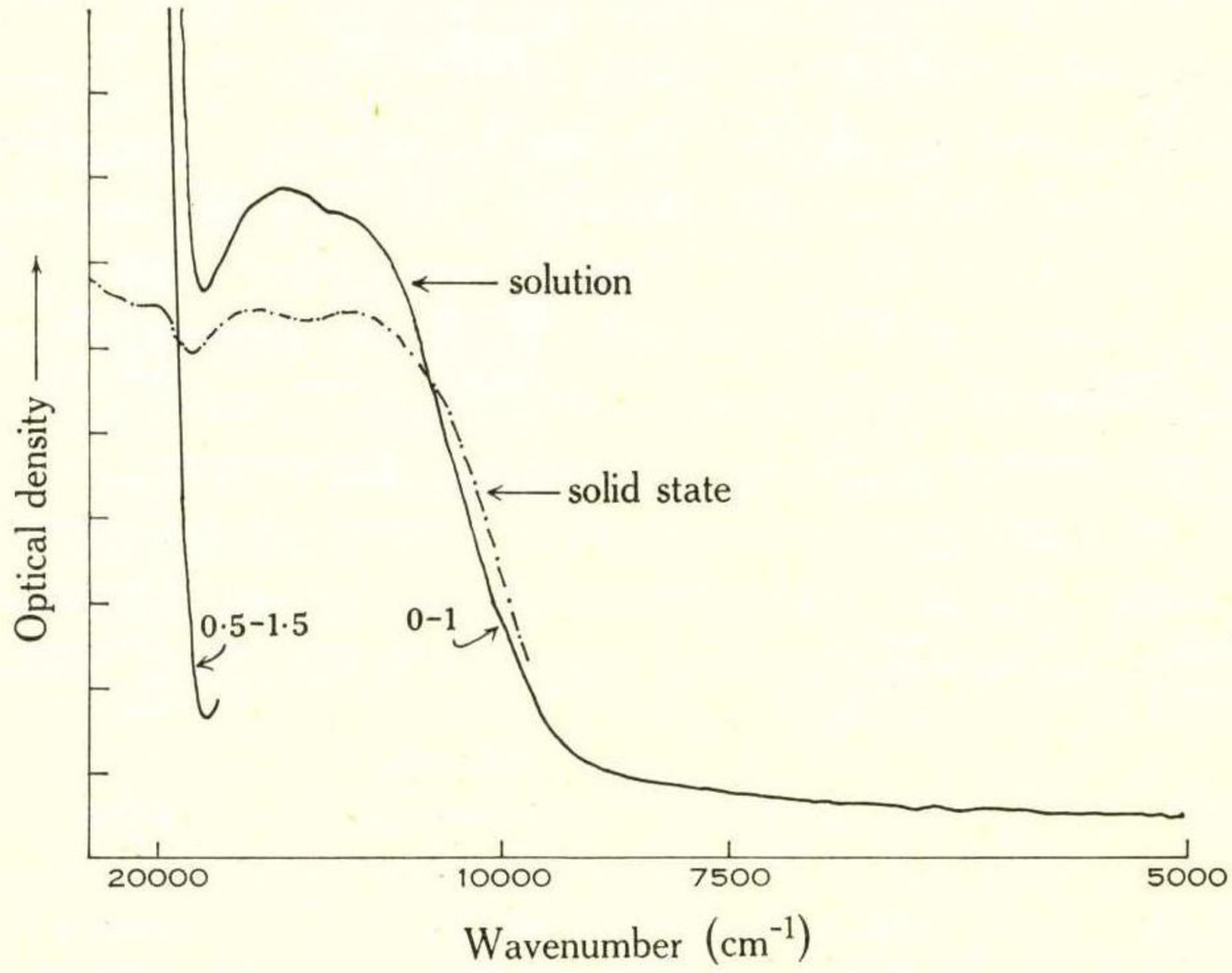


Fig. 2.—Electronic spectra of $[cpTi(O_2CCH_2CH_3)_2]_2$. Numbers indicate instrument optical density scale settings.

Infrared Data

The infrared spectra of all samples were recorded over the range 4000–250 cm^{-1}. Table 3 shows the data for the compounds $cpTi(O_2CR)_2$ ($R = CH_3$, CH_2CH_3, $CH_2CH_2CH_3$, and C_6H_5).

[16] Larin, G. M., Kalinnikov, V. T., Aleksandrov, G. G., Struchkov, Yu. T., Pasnskii, A. A., and Kolobova, N. E., *J. organomet. Chem.*, 1971, **27**, 53.

In some areas of the spectra there is considerable overlap between bands due to the cyclopentadienyl ligand and bands due to alkyl groups, and care must be taken in making some assignments.

TABLE 3

INFRARED DATA FOR THE COMPOUNDS $cpTi(O_2CR)_2$

R = CH_3	R = CH_2CH_3	R = $CH_2CH_2CH_3$	R = C_6H_5	Assignment
			*3100*w,sh	(CH stretch) C_5H_5
*3115*br,m	*3110*w,br	*3100*w,br	3070m	
	2980m	2960s	3035w,sh	R group vibrations
	2945sh	2940sh		
	2880w,sh	2870sh		
			1602s	C_6H_5
*1595*vs	*1595*vs	*1595*m–s	*1566*s	CO_2 asym. stretch
		1550br,sh		
	1465m			
	1435w,sh		1440sh	(C–C stretch) C_5H_5
*1425*vs	*1425*vs	*1420*br,ms	*1400*vvs	CO_2 sym. stretch
	1370m	1370sh		
1340w		1340sh		
	1300s	1310m–s	1310w	
		1260m	1260w	
		1200br,m	1170m	R group vibration
			1155w	
			1100br,m–w	
	1078m	1070br,s–m	1070m	
1030sh			1020sh	
*1015*m–s	*1015*m–s	*1015*s–m	*1015*m–s	(CH deform (‖)) C_5H_5
			970w,sh	
			930w	
—	880sh	880sh	870sh	(CH deform (⊥)) C_5H_5
860br,sh	—	860sh	840sh	
*815*s	*815*sh	*815*sh	*815*sh	
*790*s	*795*vs	*790*vs	*795*s	
			710s	
			690m–s	
645m	650sh	650w,sh	670s	
*610*w–m	*620*w–m	*620*m	*605*w	(ring deformation) C_5H_5
		580br,sh		
530	540br,m	535br,m–s	470s	
		420br,m	440sh	
*400*sh	*400*sh	*400*sh	*405*vw	Ti–cp
*375*vs	*380*br,s	*360*m	*370*m–s	Ti–O
			335m–s	

The four strongest bands in the fundamental spectra which are indicative of the π-cp group appear at *c.* 800, *c.* 1010, *c.* 1450, and 3100 cm^{-1} and are assigned to CH out-of-plane bending, CH in-plane bending, CC stretching, and CH stretching frequencies respectively.[17] In all of the spectra recorded a strong band occurred at *c.* 790 cm^{-1} with an associated shoulder at 815 cm^{-1} which is attributed to the CH

[17] Fritz, H. P., *Adv. organomet. Chem.*, 1964, **1**, 239.

out-of-plane bending mode of the π-cyclopentadienyl ligand. Similarly a medium-to-strong band at 1015 cm^{-1} and a weak band at *c.* 3100 cm^{-1} were assigned to the appropriate π-cp vibrations. Unfortunately the CC stretching mode (*c.* 1450 cm^{-1}) could not be distinguished due to vibrational overlap with the OCO vibration.

The aliphatic and phenyl groups of the carboxylate ligands showed the usual alkane and monosubstituted benzene vibrations.[18]

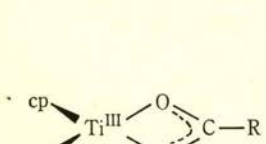
In all carboxylate complexes of metals the symmetrical (ν_2) and unsymmetrical (ν_2) carboxyl stretching vibrations are of interest since their position and the separation between them can assist in determining the type of bonding between the ligand and metal.[19]

In some earlier work on bis(cyclopentadienyl)titanium(III) carboxylates, the unsymmetrical stretching frequency was observed at 1520 cm^{-1} while the symmetrical stretching frequency was assigned to a band at *c.* 1460 cm^{-1}.[8] Similarly $cp_2Ti(O_2CCH_2CH_3)$, prepared in this investigation, showed strong bands at 1515 and 1465 cm^{-1}, attributed to unsymmetrical and symmetrical stretching modes respectively of the OCO entity. The separation ($\nu_2 - \nu_1$) is small in this class of compound (*c.* 60 cm^{-1}) in keeping with the presence of the proposed bidentate symmetrically bound carboxylate ligand (structure (1)).

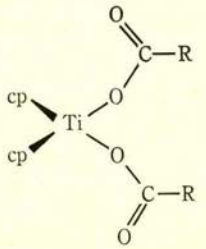
A recent paper[9] on the infrared vibrational spectra of cyclopentadienyltitanium carboxylates has proposed different assignments to the bands in the spectrum of $cpTi^{III}(O_2CC_6H_5)_2$. The band at 1602 cm^{-1} was assigned to the OCO group while the band at 1566 cm^{-1} was assigned to a C_6H_5 vibration.

It was observed, in our earlier work,[8] that the asymmetrical band of the carboxylate group containing an alkyl substituent was at 1522 ± 3 cm^{-1}, whereas in the case of the phenyl substituent the band was *c.* 20 cm^{-1} lower at 1505 cm^{-1}; similarly the symmetrical stretching mode was at 1460 cm^{-1} for alkyl-substituted derivatives and at 1425 cm^{-1} for the phenyl substituent, again some 35 cm^{-1} to lower frequency.

Due to the fact that the symmetrical stretching frequency in our spectrum of $cpTi(O_2CC_6H_5)_2$ is at 1400 cm^{-1}, *c.* 20 cm^{-1} lower than in the related alkyl derivatives (see Table 3), we assume that the asymmetrical stretching frequency corresponding to that at 1595 cm^{-1} in alkyl-substituted derivatives is the lower energy band at 1566 cm^{-1} in the phenyl-substituted and not the band at 1602 cm^{-1} as proposed by Vyshinskii *et al.*[9] Thus from these assignments we again find the separation ($\nu_2 - \nu_1$)



(1)



(2)

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is constant for the range of derivatives studied, being $168 \pm 3\ cm^{-1}$. This value suggests a lowering of symmetry by comparison with structure (1).

Two publications[9,20] which assign the infrared bands for compounds of the type $cp_2Ti^{IV}(O_2CR)_2$ show the separation $(\nu_2 - \nu_1)$ is greater than $300\ cm^{-1}$. This is in keeping with the fact that only one of the oxygen atoms of the carboxylate group is actually bound to titanium (structure (2)).

The progressive increase in the separation $(\nu_2 - \nu_1)$ as we go from the highly symmetrical $cp_2Ti^{III}O_2CCH_3$ (*c.* $60\ cm^{-1}$) to the unsymmetrical carboxylate group of $cp_2Ti^{IV}(O_2CCH_3)_2$ (*c.* $300\ cm^{-1}$) is exemplified in Figure 3. The carboxylates under investigation fall into an intermediate category with a separation of *c.* $170\ cm^{-1}$. This magnitude of separation has been proposed as an indication of a carboxylate group bridging two metal atoms.[21–23]

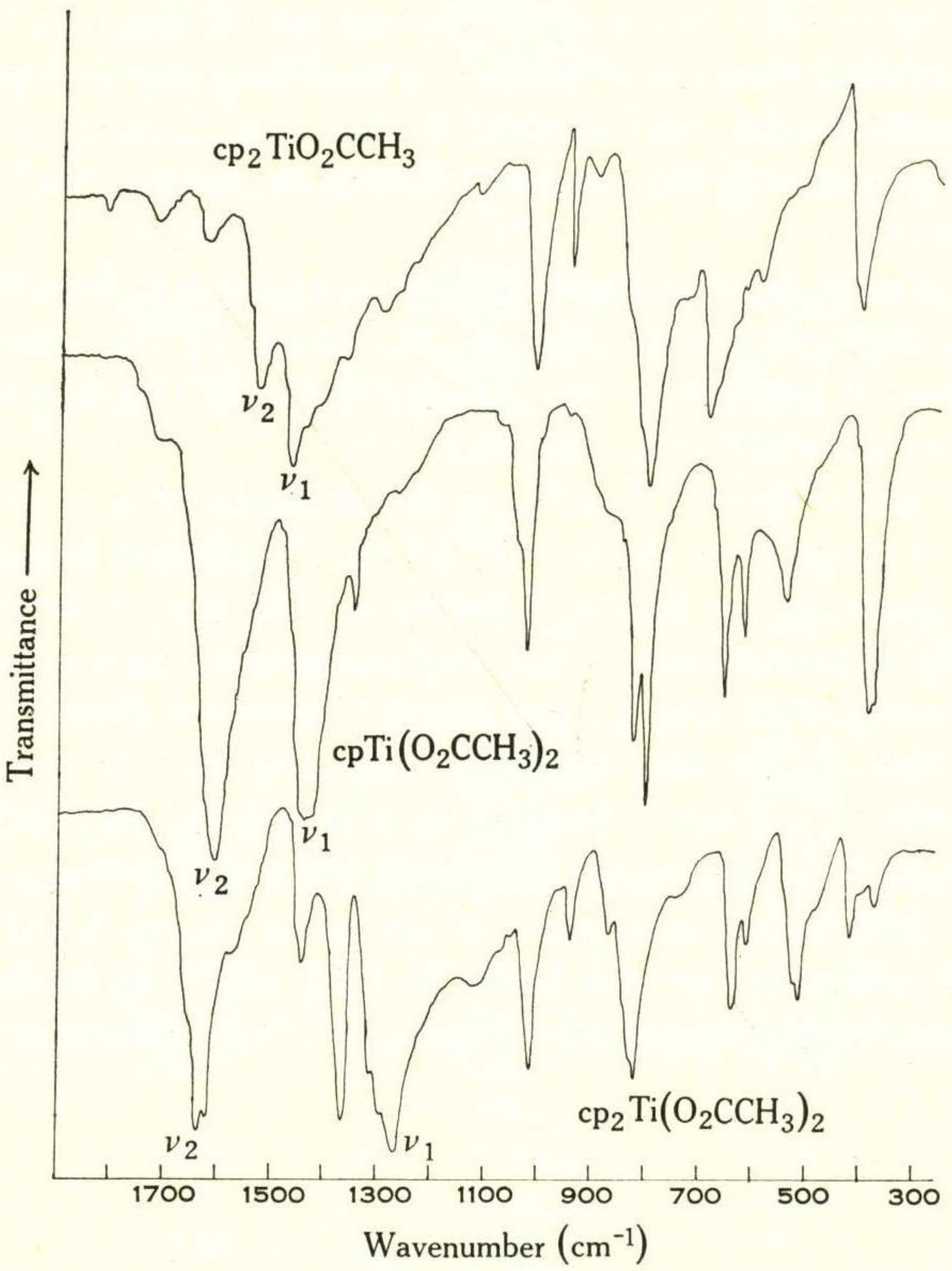


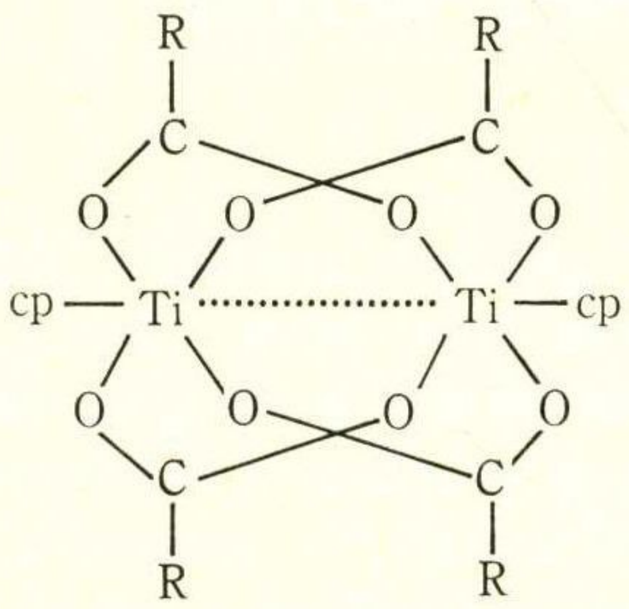
Fig. 3.—Infrared spectra.

The major bands in the infrared spectrum of $cpTi(O_2CCF_3)_2$ are as follows: 1685vs, 1460m, 1445sh, 1205vs, 1160vs, 1020m, 855m, 820vs, 780m, 725s, 630w, 525m, 480m, 400m, 355m cm^{-1}. Due to the extreme electronegativity of the fluoride group

[20] Dvoryantseva, G. G., Sheinker, Yu. N., Nesmeyanov, A. N., Nogina, O. V., Lazareva, N. A., and Dubovitskii, V. A., *Dokl. Akad. Nauk SSSR*, 1965, **161**, 603.
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correlation between the CF_3 and CH_3 derivatives is not feasible, with regard to the OCO stretching frequencies. However, comparison between $cpTi(O_2CCF_3)_2$ and $cpV(O_2CCF_3)_2$[16] shows almost identical absorptions, which leads one to conclude that a similar structural skeleton is present. The crystal structure of the latter compound has been reported recently,[16] and it was established that the compound has a dimeric unit with four bridging trifluoroacetate groups, with a V–V separation of 3·7 Å.

From the dimeric nature of the more soluble derivatives (as shown by molecular weight determinations), the constant pattern for the OCO vibrational modes in the infrared spectra (except for $R = CF_3$), and the supporting e.s.r. data, it is proposed that all the present compounds are dimers with bridging carboxylate groups (structure (3)), analogous to the vanadium compound $cpV(O_2CCF_3)_2$.[16]



(3)

However, unlike the vanadium analogue these compounds are virtually diamagnetic showing no development of paramagnetism over the range 100–300 K. The interaction of vanadium atoms was considered to take place via the π-system of the carboxylate bridges, the distance between metal atoms (3·7 Å) being too great for direct overlap of 3d orbitals. The possibility of direct metal-to-metal bonding cannot be discarded in the case of the titanium analogue at this stage. It is hoped that further elucidation of the exchange mechanism may emerge from the more detailed quantitative treatment of the e.s.r. data.

Experimental

General

All air-sensitive materials were handled under argon atmosphere or in vacuum. Infrared spectra were measured in KBr discs on a Perkin–Elmer 521 spectrophotometer. Reflection spectra were determined in a sealed cell on a Beckman DK2A spectrophotometer fitted with a reflectance attachment, and solution absorption spectra were recorded on a Beckman DK2 instrument. Magnetic susceptibilities were measured by the Gouy method. Molecular weight values were obtained in a Gallenkamp ebulliometer modified to take a 3·5 ml cell under argon flow.

E.s.r. spectra were obtained with a modified Varian V-4501 X-band spectrometer using 100-kHz modulation and a 6-in. electromagnet. The frequency was monitored with a H.P. X532b frequency meter. The magnetic field was taken direct from a "Fieldial". Cylindrical quartz sample tubes were used.

Analyses

Titanium was estimated by ashing a hydrolysed, sulphated pellet of the sample. Carbon and hydrogen were determined by the Australian Microanalytical Service, Melbourne, by burning weighed pellets sealed in aluminium capsules.

Materials

Monocyclopentadienyltitanium(III) dichloride was prepared by a published method.[2] The sodium salts of the carboxylic acids were AnalaR grade which were dried at high temperature under high vacuum. The carboxylic acids were used after degassing without any further purification, while triethylamine and n-butylamine were distilled under argon.

Acknowledgments

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NOVEL REACTIONS OF MONOCYCLOPENTADIENYLTITANIUM(III) DIHALIDES WITH ORGANIC CARBONYL GROUPS

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SUMMARY

Cyclopentadienyltitanium(III) dihalides, $CpTiX_2$ (where X = Cl or Br), or their tetrahydrofuranates, $CpTiX_2 \cdot THF$, have been brought into reaction with organic compounds containing the carbonyl group (benzophenone, acetophenone, acetone, and benzaldehyde). The physical and chemical properties of the yellow crystalline products suggest that organotitanium(IV) derivatives are formed by an intramolecular "redox" process. Evidence for reversibility of the reaction is offered in the case of benzophenone complexes.

INTRODUCTION

Monocylopentadienyltitanium(III) dihalides have been shown to form normal coordination type complexes with ethers[1,2], alcohols[2], and a range of nitrogen donors[3]. It was expected that ketones and aldehydes would form coordination complexes similar to those of both titanium(IV)[4–6] and titanium(III) halides[7,8]. The reaction of ketones with titanium(III) chloride[7,8] gives complexes of general formulae $TiCl_3 \cdot nR_2CO$ (R = Me, Et, and Ph; $n = 2$ or 3). These compounds have visible spectral, and magnetic data consistent with octahedral titanium(III) species. Coordination results in a lowering of the carbon–oxygen stretching frequency ($\approx$ 50–100 cm^{-1}) in the C=O region. This characteristic lowering of the carbonyl stretching frequency has been observed also in the spectra of the keto complexes formed by titanium(IV) chloride[4–6].

RESULTS AND DISCUSSION

The reaction of a ketone or aldehyde with $CpTiX_2$ or $CpTiX_2 \cdot THF$ (X = Cl or Br) in a mixed solvent of THF/diethyl ether resulted in a colour change from mauve or blue, for $CpTiCl_2$ or $CpTiBr_2$, and from blue or green, for $CpTiCl_2 \cdot THF$ or $CpTiBr_2 \cdot THF$, to a brown solution and a yellow crystalline precipitate. The yellow precipitates, after washing with ether and drying, analysed for 1/1 complexes (see Table 1). The complexes, apart from those formed from benzophenone, were slightly

TABLE 1

ANALYTICAL DATA

Compound	*Colour*	*Analysis found (calcd.) (%)*				*Mol. wt. found (calcd.)*
		C	*H*	*Halide*	*Ti*	
$[CpTiCl_2 \cdot (CH_3)_2CO]_2$ (I)	Yellow	40.1 (39.7)	4.7 (4.6)	29.8 (29.3)	19.9 (19.8)	(484)
$[CpTiBr_2 \cdot (CH_3)_2CO]_2$ (II)	Yellow	29.2 (28.9)	3.4 (3.3)	48.0 (48.2)	14.6 (14.5)	618 (662)
$[CpTiCl_2 \cdot Ph(CO_3)CO]_2$ (III)	Yellow	51.2 (51.4)	4.2 (4.3)	23.1 (23.3)	15.9 (15.8)	554 (608)
$[CpTiBr_2 \cdot Ph(CH_3)CO]_2$ (IV)	Yellow	38.2 (39.7)	3.3 (3.3)	39.6 (40.7)	11.9 (12.2)	791 (786)
$[CpTiCl_2 \cdot Ph_2CO]_h$(V)	Greenish yellow	59.1 (59.1)	4.1 (4.1)	18.9 (19.4)	13.1 (13.1)	[a] (366)
$[CpTiBr_2 \cdot Ph_2CO]_h$(VI)	Greenish yellow	43.0 (47.5)	3.9 (3.3)	36.9 (35.1)	10.7 (10.5)	[a] (455)
$[CpTiCl_2 \cdot PhCHO]_2$(VII)	Yellow	49.9 (49.7)	3.8 (3.8)	24.0 (24.4)	16.6 (16.5)	544 (580)
$[CpTiBr_2 \cdot PhCHO]_2$(VIII)	Yellow	37.8 (38.0)	2.9 (2.9)	40.9 (42.2)	12.7 (12.7)	702 (758)

[a] See text.

soluble in THF, $CHCl_3$ and toluene or benzene, and virtually insoluble in diethyl ether and petrol. All were considered hydrolytically unstable and were therefore handled under anaerobic conditions.

Solid state reflectance spectra in the visible and UV regions displayed no absorptions attributable to *d–d* transitions. In THF the yellow benzophenone complexes dissolved to give green solutions with spectra similar to $CpTi^{III}X_2 \cdot THF$ (X = Cl or Br), the remainder of the complexes dissolved to give yellow solutions with spectra again devoid of *d–d* bands. All compounds were virtually diamagnetic with χ_M, values < 120.

Ebulliometric molecular weight determinations in toluene showed the compounds to be dimeric although the benzophenone complexes showed anomalous behaviour. In the boiling solvent thermal decomposition took place, and in the case of compound (V) an insoluble purple material remained (probably $CpTiCl_2$, see later in discussion), and a deflection was registered equivalent to the approximate molecular weight of the free ketone (benzophenone). The toluene solution from the molecular weight determination was taken off with a syringe and reduced to dryness. An IR spectrum of the residue showed the presence of C=O groups, suggesting that the reaction is reversible [eqn (1)].

$$n\,CpTiCl_2 + n\,Ph_2CO \overset{\Delta}{\rightleftarrows} (CpTiCl_2 \cdot Ph_2CO)_n \qquad (1)$$

Infrared data

Infrared spectra were recorded for the eight compounds in the range 4000–250 cm^{-1} using KBr disks. The total absence of the strong ν(C=O) stretching band,

which occurs in the free ligand spectra at $\approx 1700\ cm^{-1}$, is the most significant item of evidence observed. This excludes the possibility of a normal coordination type complex involving attachment to the metal via the oxygen atom of the carbonyl group, as such interactions have been reported to cause maximum shifts of the C=O stretching frequency of the order of $150\ cm^{-1}$ [4-6]

The region $1200–1600\ cm^{-1}$ in which the free ligand exhibits rich absorption, was also depleted of many bands; in particular, the strong to very strong bands between $1200–1270\ cm^{-1}$ which are also associated with contributions from C–O stretching modes. As is exemplified in Fig. 1, the spectra of the new complexes show no strong bands above $1200\ cm^{-1}$, and most of the new absorptions associated with C–O frequencies occur in the narrow range $1000–1150\ cm^{-1}$, a region in which the metal alkoxides absorb strongly.

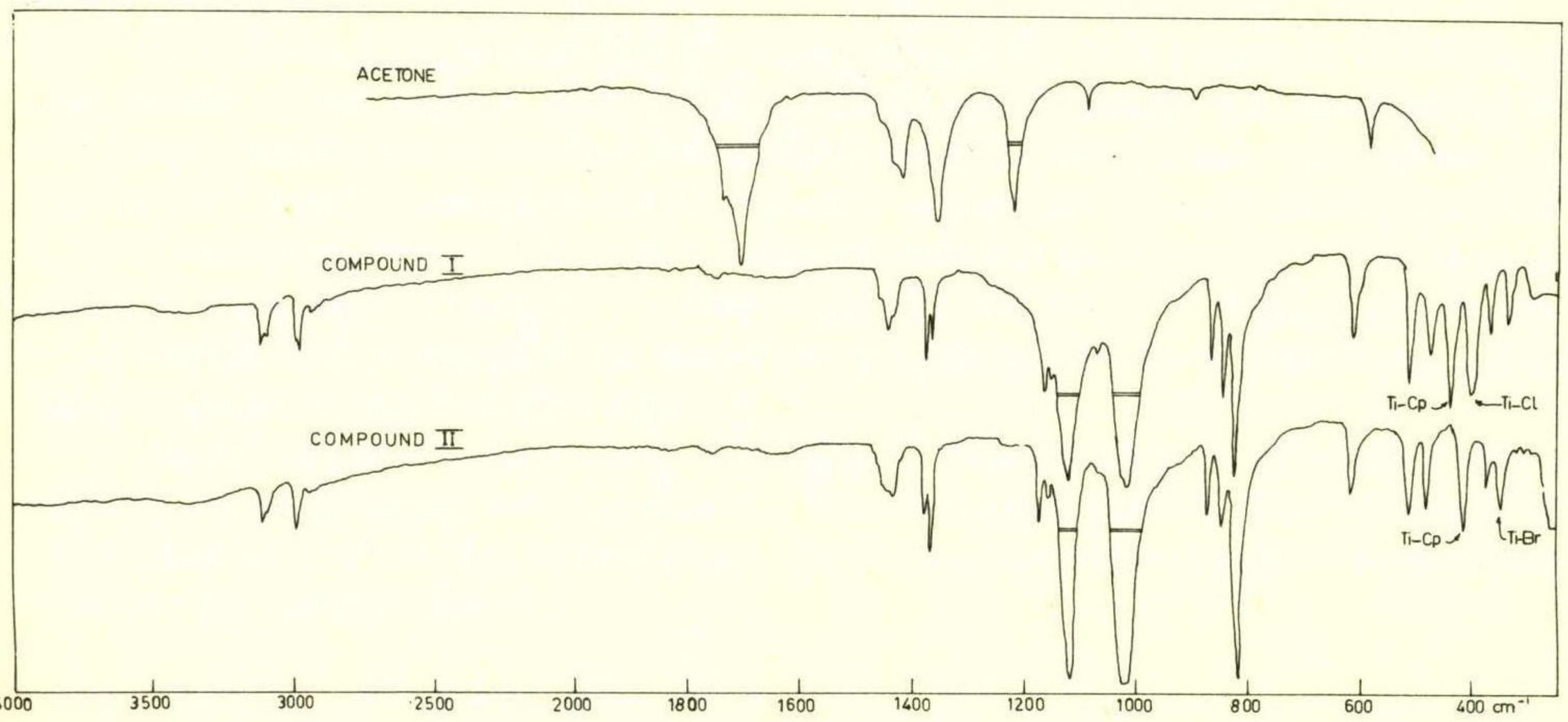


Fig. 1. Infrared spectra of acetone complexes.

The presence of π-bonded cyclopentadienyl ligands was shown by the simultaneous appearance of four bands in the regions $3100–3000\ cm^{-1}$ (C–H stretch), $1400–1450\ cm^{-1}$ (C–C skeletal stretch), 1000 ± 20 (C–H deformation), and $780 \pm 70\ cm^{-1}$ (C–H deformation)[9]. The C–H deformation band normally found at $1010 \pm 16\ cm^{-1}$ was masked by strong absorptions due to other ligand vibrations.

Below $600\ cm^{-1}$ absorption bands due to the vibrations of metal–halide, metal–oxygen, and metal–cyclopentadienyl are expected in addition to bands due to internal vibration of the ligands. Tentative assignments in this region are given in Table 2.

The assignment of the titanium–halogen stretching vibration is strengthened by the fact that the chloride derivatives show a very strong band at $404 \pm 4\ cm^{-1}$ which is absent in all bromide derivatives. The usual range quoted for Ti^{IV}–Cl stretching modes is $360–390\ cm^{-1}$ for six-coordinate compounds, and one could expect some rise in frequency due to decrease in coordination number. The bromide derivatives on the other hand possess a medium to strong band at $335–370\ cm^{-1}$ which is not present in the chloride derivatives.

There are few reports of infrared data for monocyclopentadienyltitanium(IV) derivatives in this low wavelength region; however a recent publication[10] has made

TABLE 2

INFRARED DATA

Compound	*Band position*[a]						
	Ti–O	*Ti–O*	*Ti–Cp*	*Ti–Cl*	*Ligand bands*	*Ti–Cl*	*TiBr*
(I)	516 s	480 m	442 s	406 s	373 m	340 m	
(II)	512 s	484 s	415 s		373 m		350 m
(III)	528 s	465 m	423 s	400 vs 410 (sh)	378 m	330 vw	
(IV)	536 s	472 m (br)	445 m 425 w		394(sh) 385 m		345 m–s
(V)	522 m–s 506 w	470 m	449 s	408 vs	390 (sh) 365 m	325 w–m	
(VI)	522 s 508 w–m	470 s	425 s		390 m 380 (sh) 365 m 360(sh)		335 m–s
(VII)	540 m 525 m	460(sh) 450(sh)	440 s	404 vs 410(sh)		350 vw	
(VIII)	540 w(sh) 535 s	470 m (br)	425 s				370 s 345(sh)

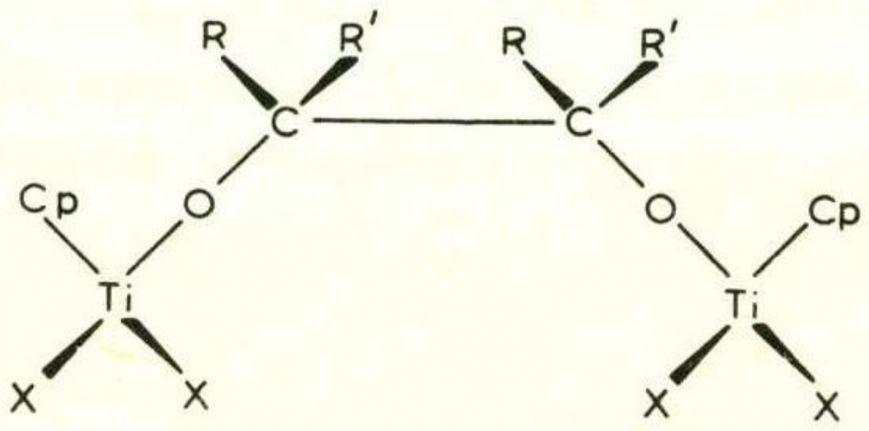
[a] With tentative assignments.

assignments to the IR bands of $CpTiCl_3$ using approximate normal coordinate analyses. The strong bands at 412 and 332 cm^{-1} were assigned to metal–chloride stretching vibrations in good agreement with the data above. The very strong band at 345 cm^{-1} in the spectrum of $CpTiBr_3$ can be assumed to be the Ti–Br stretching mode, once again in agreement with the results of the present study.

Russian workers have made an extensive study of the metal–Cp stretching frequency in compounds of the general formula $CpTi(OEt)_nCl_{3-n}$, where $n=0$–3[11], and have established that in such compounds the Ti–Cp band occurs between 420–441 cm^{-1}. Further work showed the effect of halogen exchange on such compounds. In going from $CpTiCl_3$ to $CpTiBr_3$ the band at 441 shifted to 425 cm^{-1}; the bands assigned to Cp–Ti stretch in $CpTi(OEt)Cl_2$ and $CpTi(OEt)Br_2$ similarly showed a shift of 18 cm^{-1} to lower frequency. These results are confirmed by the present findings.

The alcoholate[2], and etherate[1,2] complexes of $CpTi^{III}X_2$ were shown to have weak bands in the regions 565 ± 25 and 475 ± 5 cm^{-1}, assigned to metal–oxygen stretching frequencies. Some polymeric titanium(III) compounds also show two bands at ≈ 550 cm^{-1} and between 470–490 cm^{-1} which have been tentatively assigned as Ti–O stretching bands[12]. Kriegsmann and Leicht have assigned Ti–O vibrational modes in titanium(IV) alkoxides in the range 650–400 cm^{-1}[13]. Again such assignments would tend to support the tentative assignments to Ti–O stretching modes (Table 2) given in this investigation.

Analytical, molecular weight, and infrared data are thus in agreement with a dimeric, 1/1 ratio compound containing alkoxide-type ligands. The structure of compounds (I)–(IV), (VII) and (VIII) can thus be considered to be of the type shown below, or its isomeric forms.



NMR data confirmed that isomeric forms exist for these compounds and attempted isolation of the individual isomers is in progress.

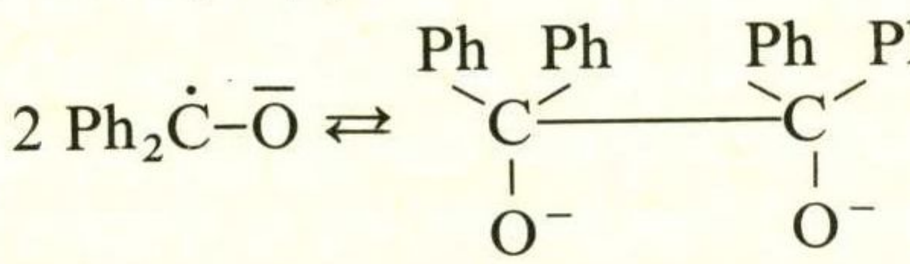
Compounds (V) and (VI) differ from the others in their chemical behaviour. It has been established by IR and NMR that the hydrolysis or alcoholysis of these compounds yield benzophenone, whereas hydrolysis of say compound (I) yields pinacol (IR, NMR), the expected dialcohol from the dimeric structure above. Similarly, compounds (V) and (VI) dissolve in THF to give $CpTiX_2 \cdot THF$ (X = Cl or Br) and free benzophenone, whereas all of the other compounds dissolve without reaction. Thermally, (V) and (VI) decompose even in benzene or toluene at 40° to $CpTiX_2$ (X = Cl or Br) and benzophenone (as demonstrated in attempted ebulliometric molecular weight determinations), whereas all of the other products gave dimeric values for their molecular weight at 110° (boiling toluene).

The reduction of carbonyl groups in aldehydes and ketones has been extensively studied in organic chemistry and a comprehensive literature is available[14]. These reductions have been effected mainly with Group I, II or III metals. The re-

duction of organic carbonyl compounds accompanying the dissolution of Na in liquid ammonia has also been widely explored[15,16]. The addition of an electron results in an anion radical [eqn. (2)].

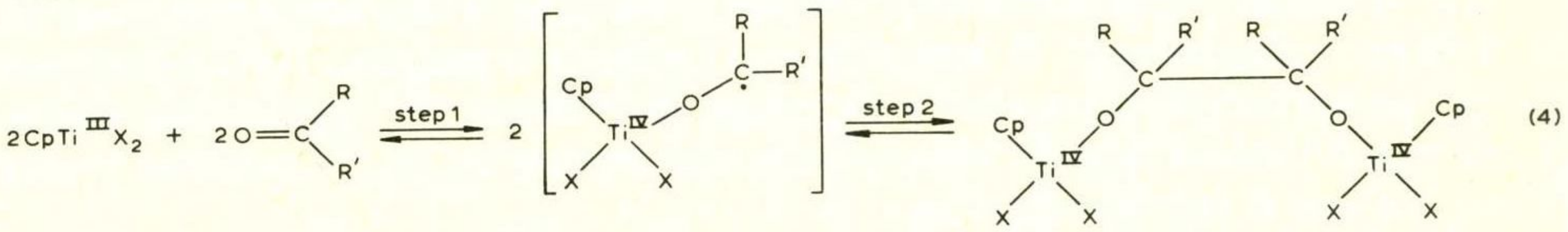
$$\rangle C{=}O + e^- \rightleftarrows \rangle \dot{C}{-}O^- \qquad (2)$$

An aromatic or non-enolyzable aliphatic ketone can react to give a "ketyl" (which is a radical ion). The solution is paramagnetic and in the case of benzophenone a series of complex equilibria has been shown to exist in solution. One such equilibrium is shown in eqn. (3):



(3)

In the present investigation one can consider the organotitanium(III) derivative (d^1 system) as a source of electron donation. The formation of the dimeric products obtained can then be explained using the steps in eqns. (2) and (3) [see eqn. (4)].



(4)

In the cases in which stable intermediates are not expected, the reaction goes to completion via step 2, and can be considered irreversible [compounds (I)–(IV), (VII) and (VIII)]. When the ketone is benzophenone [(V) and (VI)], the intermediate ketyl can be stabilized by electron delocalization and offers an opportunity to reverse step 2 under suitable conditions. This may well explain the anomalous behaviour of compounds (V) and (VI), and their ability to regenerate the C=O group after formation of the alkoxide type bond to the metal.

EXPERIMENTAL

General

All manipulations were carried out in an N_2-filled evacuable glove box, or in a stream of purified argon, using a Schlenk system. Infrared spectra were run in KBr disks, on a Perkin–Elmer 521 spectrophotometer. Visible spectra were measured in solution on a Beckman DK2 spectrophotometer and in the solid state on a Beckman DK2A spectrophotometer with a diffuse reflectance attachment. Magnetic susceptibilities were determined by the Gouy method.

Analysis

Titanium was estimated by ashing a sulphated pellet of the sample. C, H and halide were determined by the Australian Microanalytical Service using weighed pellets sealed in Al capsule.

Reagents

$CpTiX_2$ or $CpTiX_2 \cdot THF$ (X = Cl or Br) were prepared from $CpTiX_3$ by

reduction with Zn[1]. Acetone and acetophenone were purified by drying over molecular sieves and distilling under argon. Analytical grade benzophenone was used without further purification as was a fresh sample of benzaldehyde. Diethylether and THF were distilled from $LiAlH_4$ under argon.

Reactions

1. *General method*

Reactions were carried out by the addition of approximately 1–2 g samples of the solid halide or tetrahydrofuranate to a solution of the ketone or aldehyde ($\approx 50\%$ in excess of 1/1 mole ratio) in 30 ml of diethyl ether and 10 ml of THF, at room temperature. The reaction mixture was stirred, and usually within several minutes the solid had dissolved to give a brown solution, after which slow precipitation of yellow crystalline products occurred. The crystalline precipitates were filtered off and washed several times with ether, and then pumped dry. The yields of pure product ranged from 15–90%. (Table 1 gives the analytical data).

2. *Reversibility of benzophenone reaction with $CpTiX_2$*

(*A*). $(CpTiCl_2 \cdot Ph_2CO)_n$ (3.0 g) was dissolved in THF (30 ml) giving a green solution and blue crystals. The latter were filtered off, washed with diethyl ether (3×10 ml) and then pumped dry, giving 0.5 g of mauve solid which was identified as $CpTiCl_2$ by IR and Ti analysis. (Found : Ti, 25.8. $CpTiCl_2$ calcd. : Ti, 26.0%.) The green filtrate on pumping to low bulk precipitated a yellow solid which was filtered off and washed with benzene. This solid was an impure sample of the original adduct. The benzene/THF filtrate was pumped dry and extracted with diethyl ether to give 0.5 g of impure $Ph_2C{=}O$ identified by IR and NMR spectra.

The ratio of $CpTiCl_2/Ph_2C{=}O$ is approximately 1/1, in agreement with the proposed stoichiometry. Obviously there is an equilibrium reaction which accounts for the incomplete reversal.

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ORGANOMETALLIC CHEMISTRY OF TITANIUM, ZIRCONIUM AND HAFNIUM

by

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