SYNTHESIS AND REACTIONS OF ORGANOMETALLIC COMPLEXES CONTAINING TRIFLUOROMETHYLATED PHOSPHINES

A thesis submitted in
partial fulfilment of
the requirements for admission to the degree of

Doctor of Philosophy

by

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PREFACE

This work was carried out in the Department of Organic Chemistry at the University of Sydney during the period February, 1991 to March, 1995. All results and discussion reported in this thesis are my own, except where reference to the work of others is made in the text.

A portion of this work has been published elsewhere :

A new synthesis of 1,2-bis(bis(trifluoromethyl)phosphino)ethane.

Leslie D. Field and Matthew P. Wilkinson, *Tetrahedron Lett.*, **1992**, *33*, 7601-7604.

Portions of this work have also been discussed at Scientific meetings :

Synthesis and coordination properties of fluorinated phosphines

Field, L.D.; Wilkinson, M.P.

RACI 9th National Convention (Monash University, Melbourne)
6-11 December, 1992

Synthesis and properties of $(CF_3)_2PCH_2CH_2P(CF_3)_2$ and $RuH_2(dfmpe)_2$

Field, L.D.; Wilkinson, M.P.

Gordon Conference July 1993

Synthesis and properties of $(CF_3)_2PCH_2CH_2P(CF_3)_2$ and $RuH_2(dfmpe)_2$

Field, L.D.; Wilkinson, M.P.

Australian Symposium on Organometallic Chemistry 1993 (University of New England, Armidale, N.S.W.) 5-8 December, 1993

Fluorophosphine Chemistry

Field, L.D.; Wilkinson, M.P.

Phosphorus Symposium II (University of New South Wales) 29/11/91

Synthesis and coordination properties of trifluoromethylated phosphines

Field, L.D.; Wilkinson, M.P.

RACI NSW Branch Organic Chemistry Group One Day Symposium
(University of Western Sydney, Macarthur) 27/11/92

New Methodology for the Synthesis of Trifluoromethylated Phosphines :
Novel Ligands for the Synthesis of Organometallic Complexes

Matthew Wilkinson

Le Fevre Postgraduate Student Award

November 1993

ABSTRACT

This thesis describes an investigation into the synthesis and coordination properties of trifluoromethylated bisphosphines, and a study of the C-H activation properties of iron and ruthenium complexes containing trifluoromethylated bisphosphines.

The first part of this work describes the development of a convenient, one step procedure for the synthesis of trifluoromethylated phosphines by the low temperature addition of hexaethylphosphorus triamide to a mixture of trifluoromethyl bromide and an appropriate chlorophosphine. 1,2-Bis(bis(trifluoromethyl)phosphino)ethane, (dfmpe), was synthesised in 20% isolated yield by this new method, a significant improvement on previous preparations of this compound.

An investigation of the coordination chemistry of dfmpe with iron was undertaken, however no iron complexes containing dfmpe were obtained. The electron-withdrawing properties of the trifluoromethyl groups on dfmpe make this ligand a poor σ-donor, which rationalises the difficulties encountered in forming complexes with early transition metals.

The coordination chemistry of dfmpe with ruthenium was also investigated. The complexes $RuHCl(CO)(PPh_3)(dfmpe)$, $RuH_2(CO)(PPh_3)(dfmpe)$ and $RuCl_2(CO)(PPh_3)(dfmpe)$ were synthesised and characterised, but were not found to be useful precursors to the target compound, $RuH_2(dfmpe)_2$. The x-ray crystal structure of $RuHCl(CO)(PPh_3)(dfmpe)$ was determined and is presented in this work. $RuHCl(dfmpe)_2$ was synthesised by the reaction of excess dfmpe with $RuHCl(PPh_3)_3$, and was structurally analysed by x-ray crystallography. The direct synthesis of *cis*-$RuH_2(dfmpe)_2$ in 55% yield by reduction of $RuHCl(dfmpe)_2$ is reported.

$RuH_2(dfmpe)_2$ is an air-stable white powder which forms $RuD_2(dfmpe)_2$ upon u.v. irradiation at room temperature under 1 atm of D_2 gas. In contrast to its methylated analogue, $RuH_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane), $RuH_2(dfmpe)_2$ does not form products when subjected to u.v. irradiation in the presence of alkenes or arenes, or in the presence of carbon monoxide or triethylsilane. This surprising lack of reactivity is a direct consequence of the substitution of fluorine for hydrogen in this complex. Preliminary laser flash photolysis experiments indicate that the back-reaction of the coordinatively unsaturated complex formed under photochemical conditions with liberated hydrogen occurs too rapidly to allow reaction with any organic substrate.

The final section of this work deals with the synthesis of the new unsymmetrical bisphosphine ligand 2-(dimethylphosphino)ethyl(bis(trifluoromethyl)phosphine, $Me_2PCH_2CH_2P(CF_3)_2$, bife. Selective sulfurisation of $Me_2PCH_2CH_2PH_2$ to form $Me_2P(S)CH_2CH_2PH_2$ allowed subsequent chlorination of this compound using triphosgene to form $Me_2P(S)CH_2CH_2PCl_2$ in a yield of 70%. Application of the trifluoromethylation methodology developed in this work allowed the conversion of $Me_2P(S)CH_2CH_2PCl_2$ to $Me_2P(S)CH_2CH_2P(CF_3)_2$ in 20% yield. Desulfurisation of this compound using tri-*n*-butylphosphine gave the required ligand, bife, and data for this compound are reported.

ACKNOWLEDGEMENTS

This work was carried out under the supervision of Professor Les Field. I would like to thank Les for his help and guidance at many times throughout the course of this work.

Thanks must also go to the members of the L.D.F. group, past and present who have provided both help and friendship over the past four years.

Much of the work described in this work could not have been done without the help of the Professional and Technical staff at the University of Sydney. Thanks to Bruce, Rocco, Carlo, and Cliff (Organic Chemistry); Dr. Bill Bubb (NMR, Biochemistry); Dr. Jacques Nemorin and Dr. Ming Xie (NMR, Organic Chemistry); Dr. Irmi Buys, Dr. Trevor Hambley, Dr. Peter Turner (crystallography, Inorganic Chemistry); and Michael Smythe and Xiaou Mein (Mass spectrometry, Chemistry).

Finally, I would like to thank my parents and family for their love and support during the last four years, without which this work would not have been started, and Fiona for her love and support, without which this work would not have been completed.

ABBREVIATIONS

Ar	aryl
bife	2-(dimethylphosphino)ethyl(bis(trifluoromethyl)phosphine
br	broad (NMR)
COD	cyclooctadiene
COT	cyclooctatriene
Cp	C_5H_5
Cy	cyclohexyl
d	doublet (NMR)
DCM	dichloromethane
depe	1,2-bis(diethylphosphino)ethane
dfepe	1,2-bis(bis(pentafluoroethyl)phosphino)ethane
dfmpe	1,2-bis(bis(trifluoromethyl)phosphino)ethane
dfppe	1,2-bis(bis(pentafluorophenyl)phosphino)ethane
dmpe	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
dprpe	1,2-bis(di(*n*-propyl)phosphino)ethane
Et	ethyl
i-Pr	isopropyl
m	multiplet (NMR)
Me	methyl
Np	naphthyl
Ph	phenyl
PP	diphosphine ligand
q	quartet (NMR)
qu	quintet (NMR)
R	alkyl
s	singlet
sep	septet (NMR)
THF	tetrahydrofuran
t	triplet (NMR)

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CHAPTER 1 : INTRODUCTION

1.1 The role of organometallic complexes in chemical reactions

Alkanes are one of the most abundant classes of organic compounds in the world today, and represent an enormous source of energy and raw materials. The high C-H and C-C bond energies of alkanes have so far seen this resource under-utilised, as any conventional process used to functionalise alkanes has itself required large amounts of energy and proved to be very costly. One of the high priorities of the chemical industry today is to discover and implement efficient and cost-effective ways of carrying out the functionalisation of alkyl bonds in alkanes and other organic hydrocarbons.

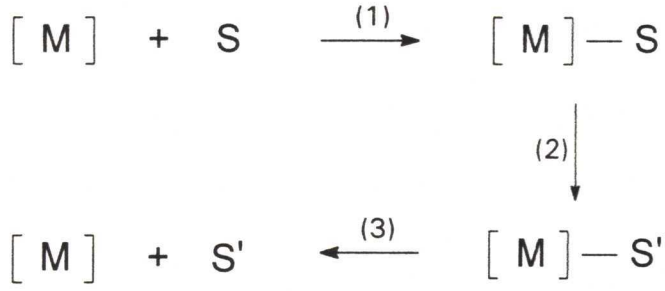
The use of organometallic complexes to facilitate the functionalisation of organic molecules has been an area of interest in organometallic chemistry for several decades. Coordination of a functional group to a metal has been shown to dramatically alter its reactivity, and to allow unconventional organic transformations to take place via highly reactive intermediates.[1] The specificity and selectivity which characterise the reactions of many organometallic reagents make them ideal candidates for carrying out the activation and functionalisation of the C-H and C-C bonds of hydrocarbons.

For an organometallic complex to effect the transformation of an organic substrate, three stages of reaction must occur (Scheme 1.1) :

1) Attachment of the substrate, S, to the organometallic complex, [M].

2) Transformation or functionalisation of the substrate, S, to produce the modified species, S', whilst the substrate, S, remains coordinated to the organometallic complex.

3) Release of the transformed substrate, S', from the coordination sphere of the complex, [M].



Scheme 1.1

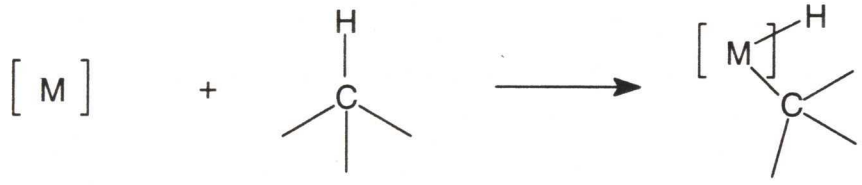
If the organometallic complex, [M], is regenerated in step (3) of the sequence shown in Scheme 1.1, the entire sequence may be catalytic. The catalytic behaviour of organometallic complexes can make such a procedure very cost-effective.

Many organic molecules, such as alcohols, amines, organic acids, aldehydes, ketones, alkenes and alkynes are electron-donors (either via lone-pairs or π-electrons), and so are relatively easy to bind to organometallic complexes. However, the lack of any obvious electron-rich features on the alkanes or alkyl groups makes coordination of this class of compounds to a metal complex more difficult. One way the coordination of alkanes to organometallic complexes has been achieved is through oxidative addition of highly reactive, electron-deficient organometallic species to the σ C-H bonds of the saturated hydrocarbon skeleton.

1.2 Oxidative addition of hydrocarbons

When an organometallic complex contains a transition metal which has access to less than eighteen electrons in its coordination shell, the metal is electron-deficient or *coordinatively unsaturated.* The metal can satisfy its electron deficiency by reaction with an available source of electrons, and in doing so regain a stable *coordinatively saturated* state. Some electron deficient complexes are sufficiently reactive that they will accept the electrons in the C-H bond of an organic molecule such as an alkane, arene or alkene. Reaction of the electron-deficient metal species with the C-H fragment results in a formal increase in the oxidation state of the metal by two, and the formation of an alkyl hydride metal species.

For example, a sixteen electron coordinatively unsaturated species, [M], might undergo an oxidative addition reaction with the C-H bond of an organic molecule to form the eighteen electron alkyl hydride species shown in Scheme 1.2.



Scheme 1.2

This reaction achieves the first aim of the sequence of reactions in Scheme 1.1, namely attachment of an organic fragment to a metal centre. If the two subsequent steps, reaction of the organic fragment and release of the modified organic substrate from the coordination sphere of the metal, can be carried out, then in principle a cycle can be formulated to functionalise organic molecules.

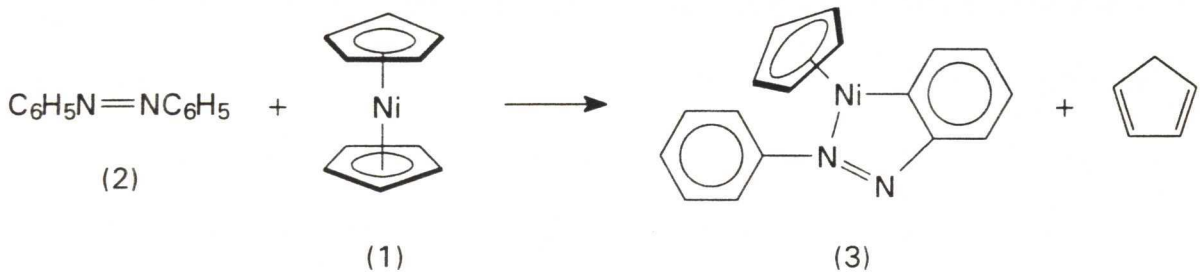
A related reaction of the coordinatively unsaturated, electron-deficient metal species, [M], is the oxidative addition with part of the organic group already bound to the metal, that is, an ancillary ligand making up the organometallic complex (Scheme 1.3).

Scheme 1.3

This reaction is often undesirable, as it represents reaction of the active species to form a complex that is usually incapable of further reaction, and thus results in a disruption of a catalytic cycle. In some cases where the reaction shown in Scheme 1.3 is reversible, the so-called cyclometallated product of intramolecular oxidative addition may effectively act as a reservoir for the coordinatively unsaturated species.

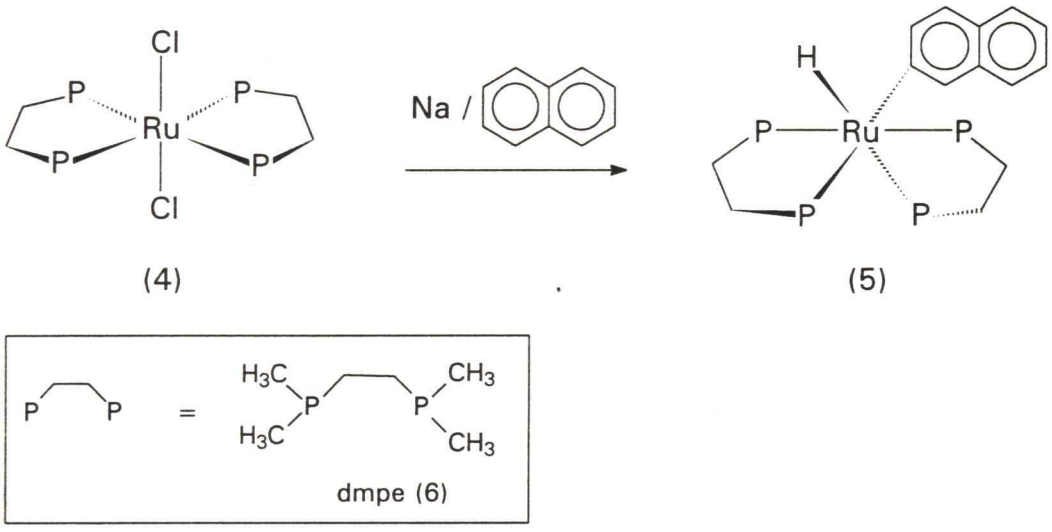
1.3 Oxidative addition reactions of organometallic complexes

Reports of organometallic complexes undergoing intermolecular oxidative addition reactions with the C-H bonds of organic hydrocarbons began in the 1960's. The first report of C-H activation was by Kleiman and Dubeck in 1963, who reacted dicyclopentadienylnickel (**1**) with azobenzene (**2**) at 135°C for 4 hours and formed a cyclometallated product (**3**) (Scheme 1.4).[2]



Scheme 1.4

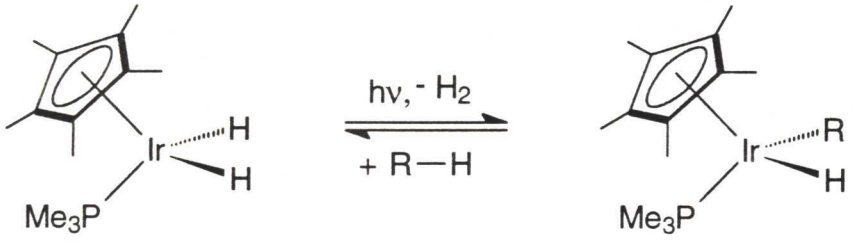
In 1965, Chatt and Davidson reported the reaction of *trans*-dichloro-bis[1,2-bis(dimethylphosphino)ethane]ruthenium (II), $RuCl_2(dmpe)_2$ **(4)** with sodium naphthalenide to form the naphthyl hydride complex **(5)** (Scheme 1.5).[3]



Scheme 1.5

These early reports of oxidative addition reactions of organometallic complexes with *aromatic* C-H bonds include both inter- and intramolecular reactions,[4] however the first oxidative addition reactions of organometallic complexes with *alkyl* C-H bonds were exclusively via intramolecular reactions.[5]

The first direct observation of intermolecular oxidative addition of a C-H bond in a saturated hydrocarbon to an organometallic complex was reported in 1982 by Bergman and Janowicz.[6] Photolysis of $Cp^*Ir(PMe_3)H_2$ (**7**) in alkane solvents resulted in the elimination of hydrogen gas, and the formation of alkyliridium hydride products (**8**) (Scheme 1.6).

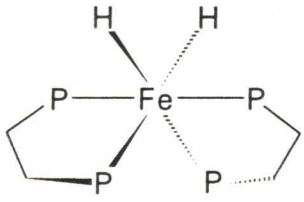


(7) (8)

Scheme 1.6

Since 1982, numerous reports of oxidative addition to alkanes (alkane activation) have emerged, involving organometallic complexes of Ir,[7] Rh,[8], Re,[9] Os,[10] lanthanides,[11] and actinides.[12] A study of the potential of bisphosphine complexes of iron for the activation of alkanes was reported in 1978 by Tolman, Ittel and co-workers.[13,14] In particular, the intermediates $Fe(dmpe)_2$ (**9**)[13] and $Fe(dppe)_2$ (**10**)[14] were described as being extremely electron deficient and reactive.

Field and co-workers have investigated the reaction of several iron bisphosphines with alkanes,[15,16] and have demonstrated the C-H activation of alkanes by dihydridobis(1,2-bis(dimethylphosphino)ethane) iron(II), $FeH_2(dmpe)_2$ (**11**). $FeH_2(dmpe)_2$ (**11**) is an eighteen electron iron complex which contains two bisphosphine dmpe ligands [dmpe = 1,2-bis(dimethylphosphino)ethane, (**6**)] and two hydride ligands.



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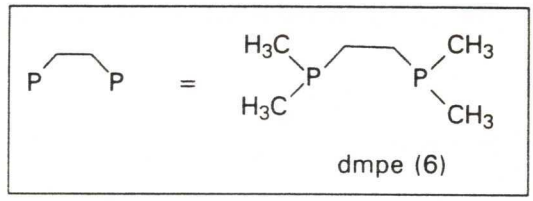
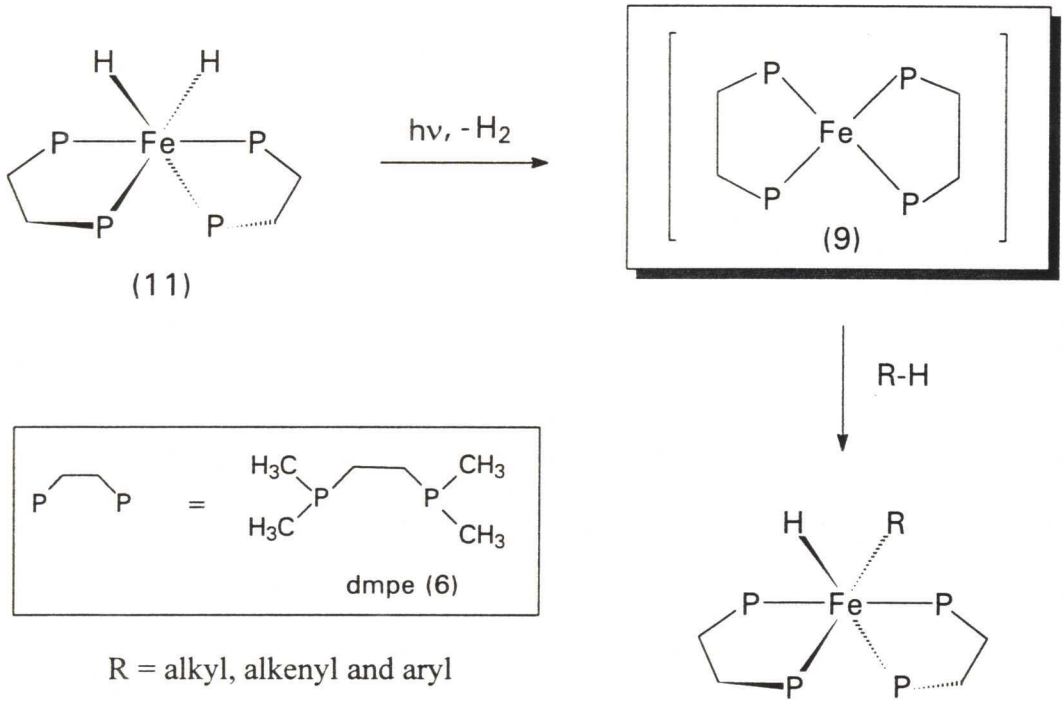


Upon irradiation with ultraviolet light, $FeH_2(dmpe)_2$ **(11)** eliminates dihydrogen and generates a sixteen electron, coordinatively unsaturated intermediate $Fe(dmpe)_2$ **(9)** (Scheme 1.7). $Fe(dmpe)_2$ **(9)** oxidatively adds to the C-H bonds of alkanes, alkenes and aromatic compounds, to form the corresponding iron alkyl and aryl hydrides (Scheme 1.7).[16,17]



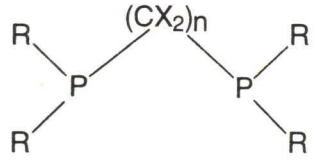
Scheme 1.7

$FeH_2(dmpe)_2$ **(11)** has been successfully used to activate the C-H bonds in a variety of hydrocarbon substrates.

1.4 Bisphosphines as ancillary ligands for organometallic complexes

Phosphines have traditionally been useful as spectator ligands in the synthesis of organometallic complexes capable of reacting with alkyl C-H bonds. The high donor strength of the alkyl phosphine provides some stabilisation of the high energy intermediates required to react with these unreactive substrates. In recent years, chelating aryl and alkyl bisphosphines have emerged as important and versatile ligands used in complexes used for C-H activation.

Bisphosphine ligands typically consist of two coordinating phosphorus atoms joined by a bridging group.

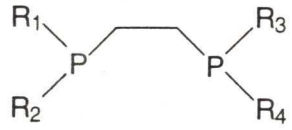


Bisphosphines offer several advantages over monodentate phosphines in the synthesis of organometallic complexes :

i) The chelation effect of bidentate phosphines typically results in stronger metal-ligand binding, enabling the formation of stronger, more stable complexes.

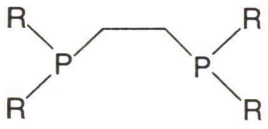
ii) The electronic and steric environment of the organometallic complex can be further tuned, or "fine-tuned", by varying the substituents on the phosphorus donor atoms, more so than that possible for simple phosphines. Each phosphorus atom can be substituted with a variety of groups, including alkyl groups, aryl groups, halogens and alkoxy groups.[18]

Bisphosphines may bear different substituents on the phosphorus atoms, allowing the steric and electronic properties of the bis-phosphine to be tuned by judicious choice of the substituents on the phosphorus donor groups.



iii) Bidentate ligands allow the possibility of decoordination of one phosphine donor atom (leaving the other phosphine donor atom still coordinated), to open up a site for reaction while retaining the basic integrity of the complex. Ligands containing mixed donor atoms can be synthesised, allowing a combination of strong and weak donors to be incorporated into the coordination sphere of the metal. The use of mixed donor ligands could allow tuning of the reactive metal fragment to a desired reaction or reagent.

Aryl and alkyl bisphosphines are extremely versatile and useful in the synthesis of organometallic complexes with a wide range of reactivities. The following ligands constitute only a small number of the ethylene-bridged bisphosphines that are known (Figure 1.1).[18]

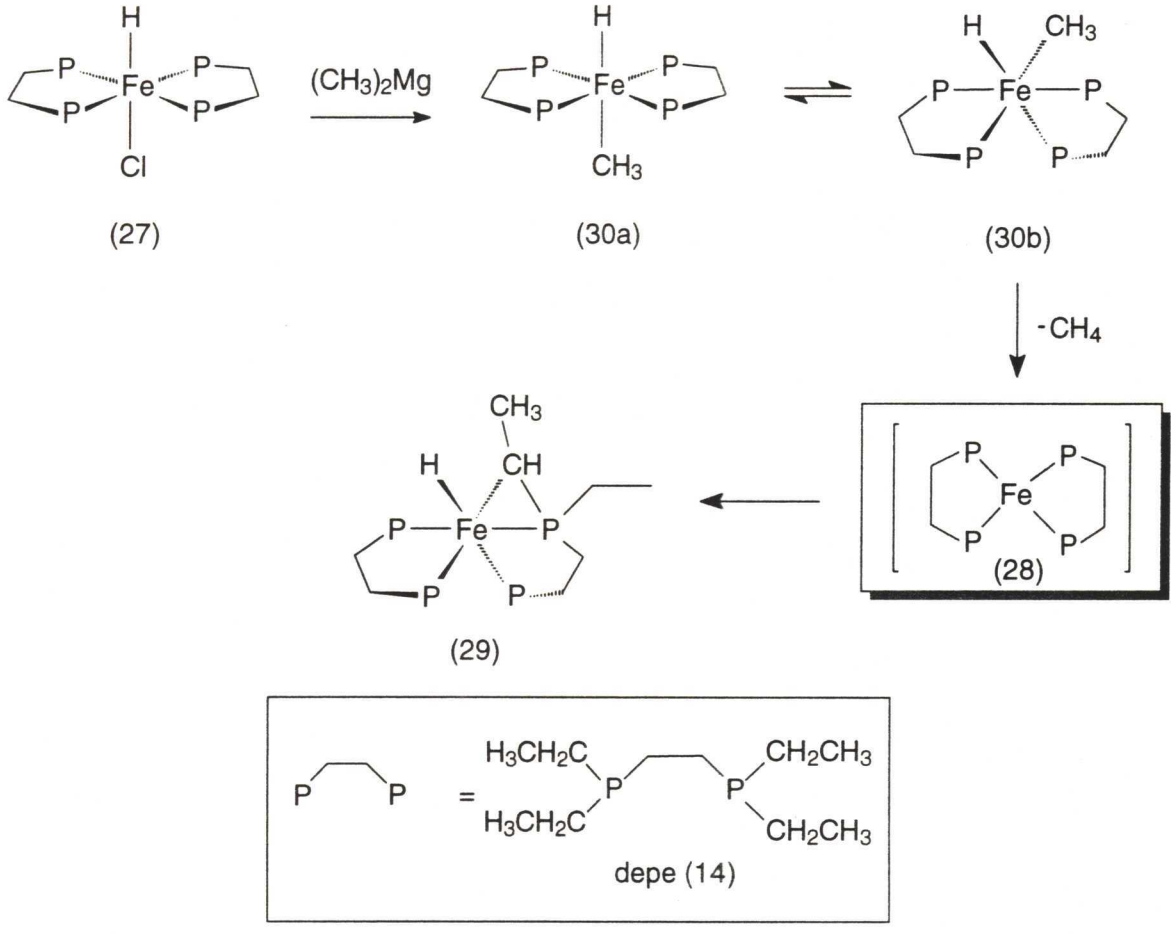


R = Cl, (**12**); F,[19] (**13**); Me, (**6**); Et, (**14**); *i*-Pr,[20] (**15**); Ph, (**16**); cyclo-C_6H_{11}, (**17**); C_6H_4OMe-*p*, (**18**); C_6H_4Me-*p*, (**19**); C_6H_4Me-*o*, (**20**); $C_6H_2Me_3$-2,4,6, (**21**); $C_6H_4NMe_2$-*p*, (**22**); C_6H_4Cl-*p*, (**23**); $C_6H_4CF_3$-*p*, (**24**); OMe, (**25**); OPh, (**26**).

Figure 1.1 : Known ethylene-bridged bisphosphines.

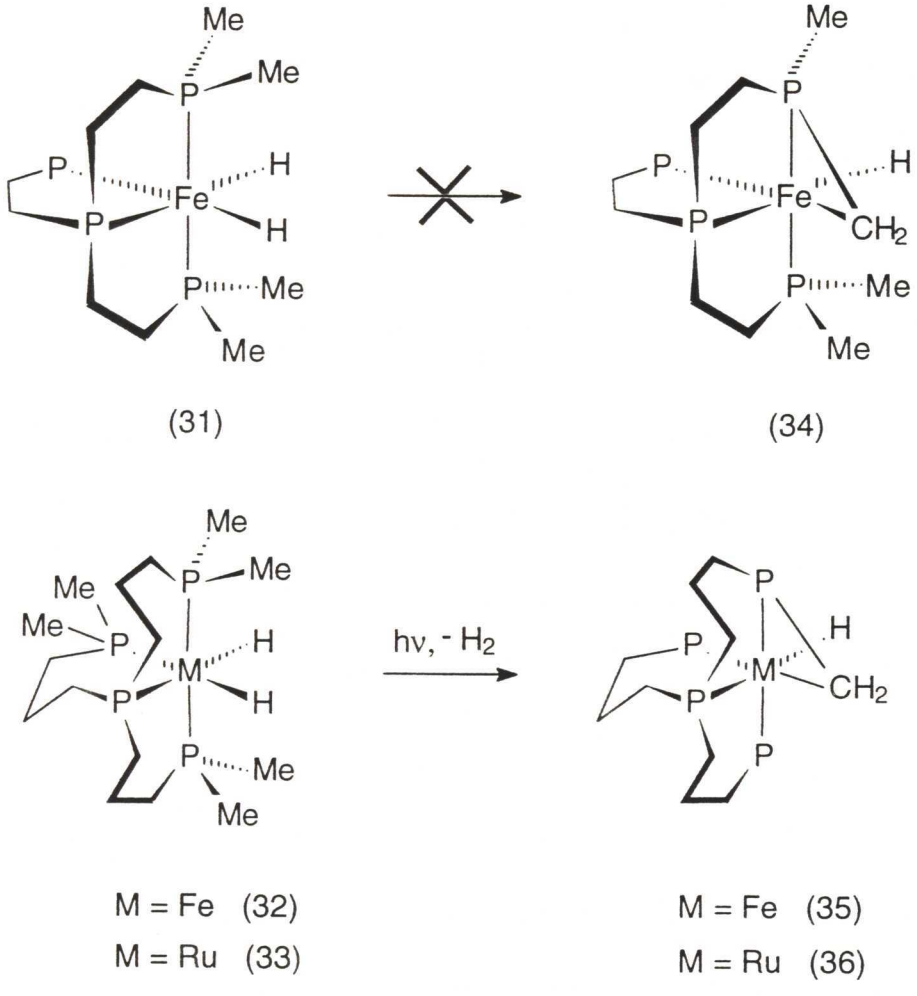
1.5 Competition between intra and intermolecular oxidative addition

A potential problem with the use of bisphosphines (and most other organic compounds containing C-H bonds) as ancillary ligands for organometallic complexes undergoing C-H activation reactions is that they contain C-H groups capable of undergoing oxidative addition to form a cyclometallated species. Such an intramolecular oxidative addition reaction has been observed in the reaction of $FeHCl(depe)_2$ (**27**) [depe = 1,2-bis(diethylphosphino)ethane, (**14**)] with excess dimethylmagnesium in THF or pentane, resulting in the formation of the coordinatively unsaturated species $Fe(depe)_2$ (**28**) via elimination of methane at temperatures above 240 K (Scheme 1.8).[15] The cyclometallated compound (**29**) (Scheme 1.8) arises from oxidative addition of the coordinatively unsaturated species $Fe(depe)_2$ (**28**) to a C-H bond in the methylene group of one of the depe ethyl substituents.



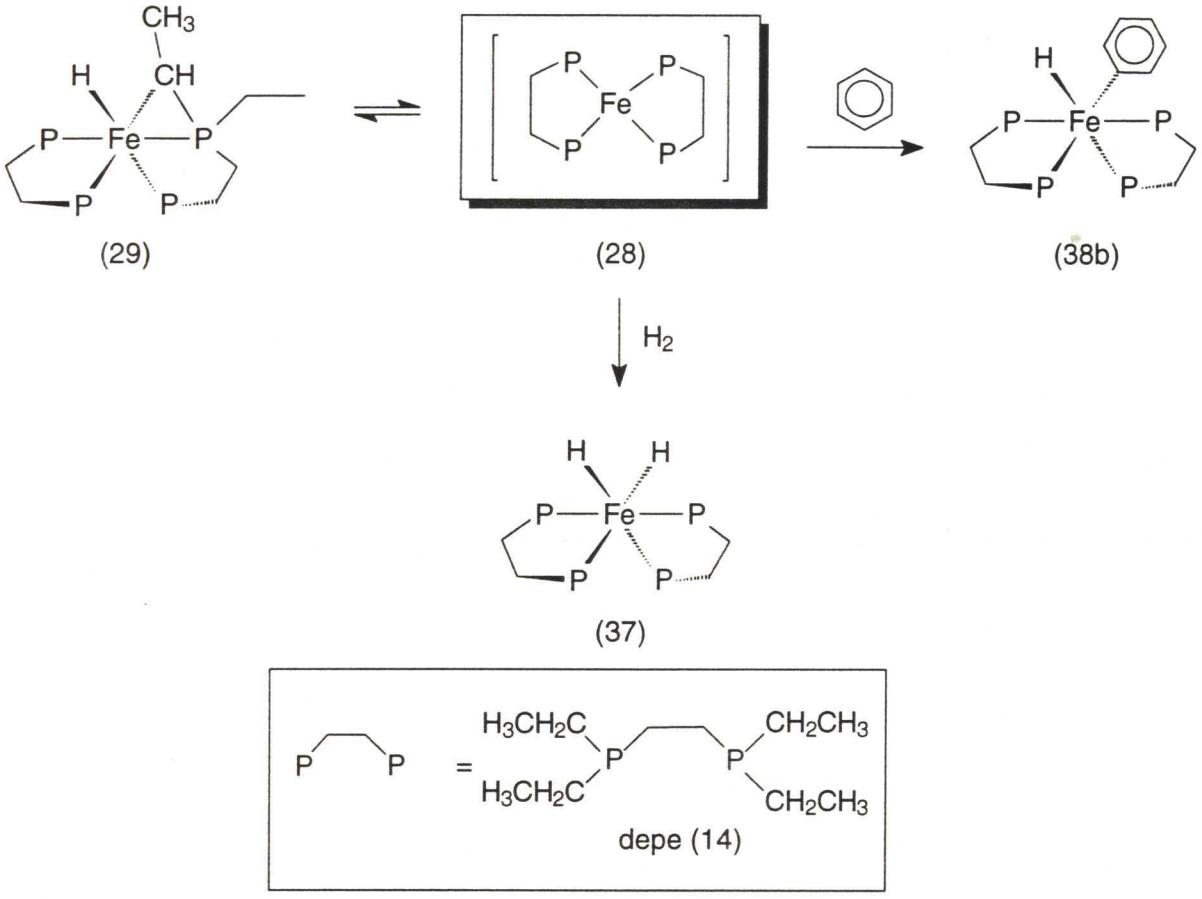
Scheme 1.8

Systems in which the alkyl groups are constrained away from the reactive metal centre may still exhibit competitive intramolecular cyclometallation reactions. Bampos, Smernik and Field have synthesised organometallic complexes of the form $MH_2(P\text{-}P_3)$ [M = Fe, $P\text{-}P_3 = P((CH_2)_nPMe_2)_3$, n = 2 (**31**); n=3 (**32**); M = Ru, n = 3, (**33**)], complexes which have methyl substituents on the tetradentate phosphine ligands constrained away from the metal centre by the bridging alkyl groups. (**32**) and (**33**) form the cyclometallated species (**35**) and (**36**) when irradiated with u.v. light in the presence of "inert" solvents such as THF or pentane (Scheme 1.9).[21] There is no evidence for the formation of the cyclometallated species (**34**) when (**31**) is irradiated in THF.[22]



Scheme 1.9

Formation of cyclometallated species such as **(34)**, **(35)** and **(36)** is not necessarily irreversible. Addition of hydrogen and benzene to the cyclometallated complex **(29)** formed from $Fe(depe)_2$ **(28)** generates the dihydride complex **(37)** and *cis*-phenyl hydride **(38b)** complexes respectively, indicating that the cyclometallation reaction is thermally reversible (Scheme 1.10).[15]



Scheme 1.10

Cyclometallation reactions do however compete with intermolecular C-H activation reactions and so limit the range of substrates which can be used. It is desirable to suppress cyclometallation reactions of organometallic complexes used for in C-H bond activation.

1.6 Metal complexes with fluorinated phosphine ligands

A class of ligands which has emerged recently in organometallic chemistry is the fluorinated phosphines. These ligands retain the skeletal carbon structure of their alkyl and aryl analogues, but are fully or partially substituted with fluorine where hydrogen is present in the alkyl analogues. Fluorophosphines potentially provide a class of ancillary ligands for organometallic complexes which are less likely to undergo intramolecular bond activation, due to the higher strength of the C-F bond compared to the C-H bond. As a consequence, complexes containing fluorinated ligands instead of hydrocarbon ligands are expected to have reduced intramolecular reactivity and hence promote intermolecular reactions.

The introduction of perfluoroalkyl groups into bisphosphines has a dramatic effect on the physical and chemical properties of the ligand and of complexes containing such ligands. These differences are a consequence of the differing atomic properties of hydrogen and fluorine, and can be discussed under the basic areas of electronic effects, steric effects, stability and physical properties.

1.6.1 Electronic effects of fluorophosphine ligands

Perfluorination or partial fluorination can dramatically alter the overall charge distribution within a molecule, as a result of the high electronegativity of the fluorine atom. Table 1.1 shows the relative electronegativity of the fluorine atom and some fluorinated groups compared to the electronegativity of other atoms and some non-fluorinated groups. The electronegativity of the fluorine atom is vastly different to that of hydrogen,[23] a difference that is magnified when replacing an alkyl group with a perfluoroalkyl group in a compound.

Table 1.1 : Pauling electronegativity[a] values, χ_P, of selected groups

Atom[b]	χ_P	Group	χ_P
H	2.2	CH_3	2.3
C	2.5	CH_3CH_2	2.3
O	3.5	$C(CH_3)_3$	2.3
P	2.8	CF_3	3.5
F	3.9	CF_3CF_2	3.4
Cl	3.0	CF_3CH_2	2.9
Br	2.6	OCH_3	2.7
I	2.5	OH	3.5

[a]Electronegativity values obtained from ref 65.

[b]Atomic electronegativities obtained from parameter "a" in ref 65, and converted to the Pauling scale using the formula $\chi_P = 0.336 (\chi_M - 0.615)$ where χ_M is the Mulliken electronegativity scale.

The electronegativity of the trifluoromethyl group has been calculated to be between 3.2 and 3.55, substantially higher than the electronegativity of a methyl group (2.3).[24,25] The electronic character of the coordinating phosphorus atoms in perfluoroalkylated phosphines is therefore expected to be altered substantially when perfluoroalkyl or partially fluorinated groups are attached.

The bonding of phosphine ligands to transition metals is usually considered in terms of two interdependent effects.

(i) Phosphines act as Lewis bases in donating the lone pair of electrons on the phosphorus atom to the metal centre. The primary effect of the introduction of

electron withdrawing groups onto a phosphine is to remove electron density from the phosphorus donor atoms, making them poorer σ-donors.[26] This effect weakens the bond between perfluorinated phosphines and transition metals.

(ii) Phosphines act as π-acceptor ligands. The phosphorus atom of a phosphine has empty *d*π orbitals and can participate in back-donation of electron density from filled metal *d*-orbitals, as illustrated in Figure 1.2.

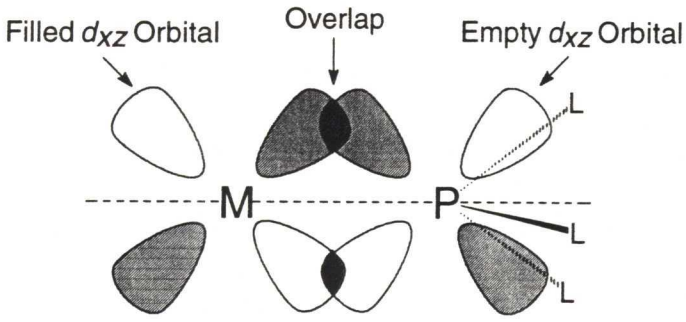


Figure 1.2 : Back-bonding from a filled metal *d* orbital to an empty phosphorus 3*d* orbital in the PX_3 ligand

The extent to which back-donation occurs depends on the electronegativity of the groups, L, attached to the phosphorus donor atom.[27] An increase in the electronegativity of the groups on a phosphine increases the extent of back-donation, increasing the strength of the metal-phosphorus bond. The presence of electronegative fluoroalkyl groups causes perfluoroalkylated ligands to be strong π-acceptors compared to non-fluorinated analogues, enabling increased back-donation from late transition metals, and improving the coordination ability of perfluorinated ligands to late transition metals.[26,28] Tris(trifluoromethyl)phosphine **(39)** is similar to carbon monoxide in its π-acceptor ability, and so perfluorinated bis-phosphines should have similar ligation properties to those of two *cis* carbonyl ligands.[29]

1.6.2 Steric effects of fluorophosphine ligands

The Van der Waal's radius of the fluorine atom is 1.50 Å, slightly larger than that of the hydrogen atom (1.20 Å), and thus substitution of fluorine for hydrogen in simple organic molecules causes no great distortion.[30] Similarly, the Van der Waal's radius of the trifluoromethyl group is 2.7 Å, again slightly larger than that of the methyl group at 2.0 Å.[31,32] This difference in Van der Waal's radii, however, becomes significant when three alkyl or perfluoroalkyl groups are bound to a phosphorus donor atom.

The importance of the steric properties of phosphine ligands was emphasised by Tolman in 1970.[33] Tolman introduced the concept of the *ligand cone angle*, θ, when it became clear that the ability of phosphorus ligands to compete for coordination positions on Ni(0) complexes could not be explained in terms of their electronic character alone.[33,34] The method for measuring θ is illustrated in Figure 1.3.

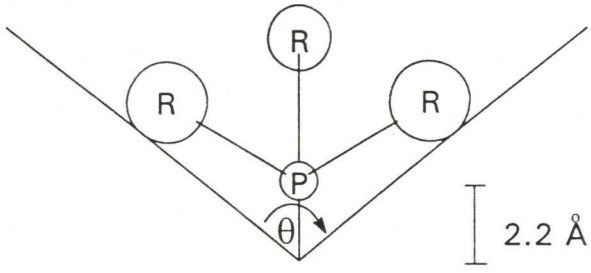


Figure 1.3 : Method for measuring the Tolman cone-angle of a phosphine, PR_3

Tolman estimated the cone-angle for numerous phosphine ligands, allowing the steric requirements of phosphines to be compared. An adaptation of this method was reported in 1977 by Tolman and co-workers to enable estimation of cone-angles of unsymmetrical phosphines of the form $PX_1X_2X_3$, and of chelating bisphosphines.[35] The cone-angles estimated by Tolman's method for selected phosphines are shown in Table 1.2.

Table 1.2 : Cone angles for selected phosphines

Ligand	Cone-Angle (θ)	Ligand	Cone-Angle (θ)
PH_3 **(40)**	87 ± 2	PF_3 **(46)**	104 ± 2
$P(CH_3)_3$ **(41)**	118 ± 4	$P(CF_3)_3$ **(39)**	137 ± 2
$P(CH_3)_2CF_3$ **(42)**	124 ± 2	$PCH_3(CF_3)_2$ **(47)**	131 ± 4[a]
$P(CH_2CH_3)_3$ **(43)**	132 ± 4	$P(CF_2CF_3)_3$ **(48)**	142[c]
$P(C_6H_5)_3$ **(44)**	145 ± 2	$P(C_6F_5)_3$ **(49)**	184 ± 2
$Me_2PCH_2CH_2PMe_2$ **(6)**	107 ± 2	$(CF_3)_2PCH_2CH_2P(CF_3)_2$ **(50)**	120 ± 2[a]
$Et_2PCH_2CH_2PEt_2$ **(14)**	115 ± 2	$(C_2F_5)_2PCH_2CH_2P(C_2F_5)_2$ **(51)**	123[b]
$Ph_2PCH_2CH_2PPh_2$ **(16)**	125 ± 2	$(C_6F_5)_2PCH_2CH_2P(C_6F_5)_2$ **(52)**	151 ± 2[a]

Cone angles obtained from Ref. 34; (a) denotes estimated for this work using formulae described in refs 34 and 35 for cone-angles of bisphosphines, and values for symmetrical phosphines from ref. 34; (b) obtained from ref 26; (c) obtained by calculation from value obtained from ref 26 for dfepe, using formulae in ref 34.

It can be seen from Table 1.2 that in all cases, phosphine ligands containing perfluoroalkyl groups have larger cone angles and impose greater steric demands on a metal centre than their alkylated analogues. Thus, a complex containing perfluorinated ligands may have a more crowded or less accessible reaction site, and as a consequence may have altered reactivity or selectivity, compared to a complex containing the analogous alkylated ligands.

The primary advantage of using perfluoroalkylated bis-phosphines over ligands such as carbon monoxide, given that their electronic properties are similar, is that their size and

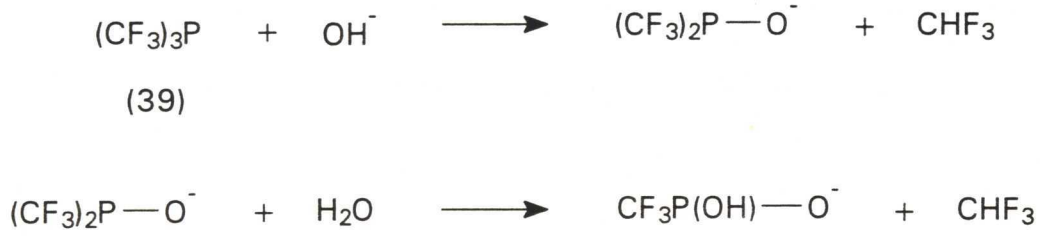
shape can be altered by varying the perfluoroalkyl groups attached to the phosphorus donor atom. In this way, the reactivity of complexes containing perfluoroalkyl or perfluoroaryl ligands can be tuned through choice of the ancillary ligands, a flexibility unavailable with ligands such as CO.

1.6.3 Stability of fluorophosphine ligands

The average C-F bond strength is 451-485 $kJ.mol^{-1}$, substantially stronger than the average C-H bond which has a dissociation energy of approximately 430 $kJ.mol^{-1}$.[23,36] As a result, fluorocarbons are generally more resistant to chemical attack and demonstrate high thermal stability. Ligands comprising fluoroalkyl groups are expected to be more robust than alkyl analogues, and more chemically inert. A coordinatively unsaturated metal fragment will be less likely to undergo intramolecular oxidative addition with a ligand substituent due to this higher C-F bond strength. Metal complexes with perfluorinated ligands are therefore expected to promote intermolecular oxidative addition reactions over intramolecular oxidative reactions (cyclometallation).

The high C-F bond strength does not, however, preclude perfluoroalkylgroups from reaction with the extremely reactive organometallic species which are often generated in alkane activation reactions. There are numerous examples of both intra and intermolecular activation of aromatic and alkenyl C-F bonds by transition metal complexes, and this is due to the susceptibility of π-frameworks of fluorinated alkenes and arenes to nucleophilic attack and the good leaving ability of fluoride.[30,37] In addition, reports have recently appeared concerning the activation of saturated fluorocarbons by organometallic complexes.[30,38]

The trifluoromethyl group is often considered to be chemically inert, but some reactions are known. Trifluoromethyl groups have been reported to be susceptible to hydrolysis (although the hydrolytic behaviour of a trifluoromethyl group is very dependent upon its position in a molecule), chlorination and reduction reactions.[31,39] The stability of the trifluoromethyl radical may result in an increased susceptibility of trifluoromethyl-containing groups (and hence perfluoroalkylated phosphines) to radical cleavage reactions, compared to their alkyl counterparts. In 1954, Bennett, Emeleus and Haszeldine reported the base-initiated hydrolysis of tris(trifluoromethyl)phosphine **(39)** to liberate fluoroform (Scheme 1.11).[40]



Scheme 1.11

Therefore, while the replacement of alkyl groups for fluoroalkyl groups may represent an increase in the stability of these groups, reactions at these sites are still possible.

1.6.4 Physical properties of fluorinated phosphines

The boiling point and solubility of perfluorinated and partially fluorinated organic compounds are generally unique. Polyfluorinated alkanes show dramatically reduced boiling points and higher vapour pressures than their alkyl analogues, even though their molecular weight is greater. For example, the boiling point of methyl bromide is 4°C, whereas the boiling point of trifluoromethyl bromide is -58°C.[41]

The solubility of perfluorinated compounds in organic solvents is variable, with perfluoroalkanes being immiscible with organic solvents, but perfluorinated aromatics and partially fluorinated compounds being more soluble in organic solvents than their alkyl counterparts. Fluorocarbons are emerging as useful solvents in the area of C-H activation, as they are less reactive than alkyl and aryl solvents.[10,42] The solubility of organometallic complexes in fluorinated solvents is sometimes very low, and can lead to difficulties in carrying out homogeneous reactions. The presence of highly lipophilic perfluoroalkyl groups, R_f, should enhance the solubility of complexes containing perfluoroalkylated ligands in inert, nonpolar solvents such as fluorocarbons.[29] These solubility properties are beginning to be exploited in the area of phase-transfer catalysis, examples being the recent application of the "Fluorous Biphase System" to homogeneous catalysis by Horvath and Rabai,[43,44] and the synthesis of perfluorinated crown ethers by Lin and co-workers.[45]

1.7 Fluorinated monophosphines

The first fluorinated phosphine to be synthesised was tris(trifluoromethyl)phosphine, $P(CF_3)_3$ (**39**), reported in 1953 by Emeleus and co-workers.[46] Tris(trifluoromethyl)phosphine (**39**) was synthesised by the reaction of white phosphorus (**54**) and trifluoromethyl iodide (**55**) at high temperature and elevated pressure.[46] As expected, tris(trifluoromethylphosphine) (**39**) has very different properties from its methylated counterpart, trimethylphosphine (**41**). Tris(trifluoromethyl)phosphine (**39**) does not react with elemental sulfur or carbon disulfide, even up to temperatures of 200°C, whereas trimethylphosphine (**41**) does so cleanly and rapidly at room temperature.[46] The trifluoromethyl group apparently acts like an electronegative halogen - phosphorus trichloride only reacts with sulfur at 140°C.[46]

In 1956, Haszeldine and West reported the synthesis of dimethyl(trifluoromethyl)-phosphine (**42**) by the reaction of trimethylphosphine (**41**) with trifluoromethyl iodide (**55**) (Scheme 1.12).[47]

$$\underset{(41)}{(CH_3)_3P} + \underset{(55)}{CF_3I} \longrightarrow \underset{(42)}{(CF_3)P(CH_3)_2} + \underset{(56)}{[(CH_3)_4P]^+ I^-}$$

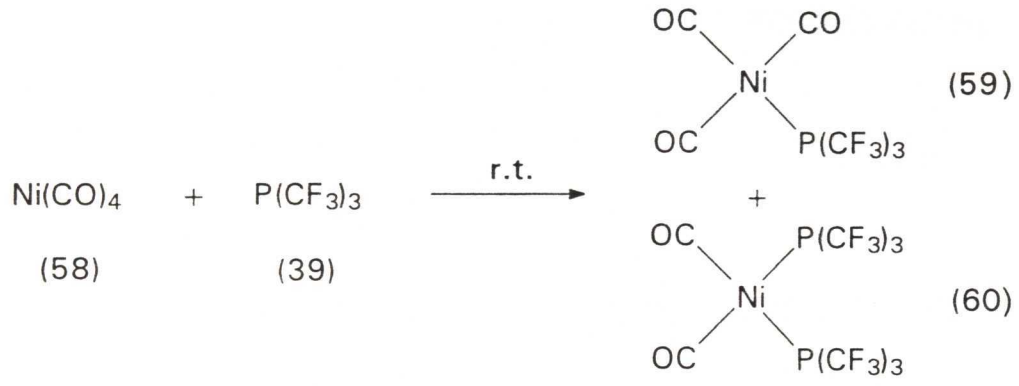
Scheme 1.12

Haszeldine and West also reported the synthesis of bis(trifluoromethyl)methyl-phosphine (**47**) by the reaction of tris(trifluoromethylphosphine) (**41**) with methyl iodide (**57**) at elevated temperatures (Scheme 1.13).[48]

$$\underset{(41)}{(CH_3)_3P} + \underset{(57)}{CH_3I} \xrightarrow{240^\circ C} \underset{(47)}{(CF_3)_2PCH_3} + \underset{(55)}{CF_3I}$$

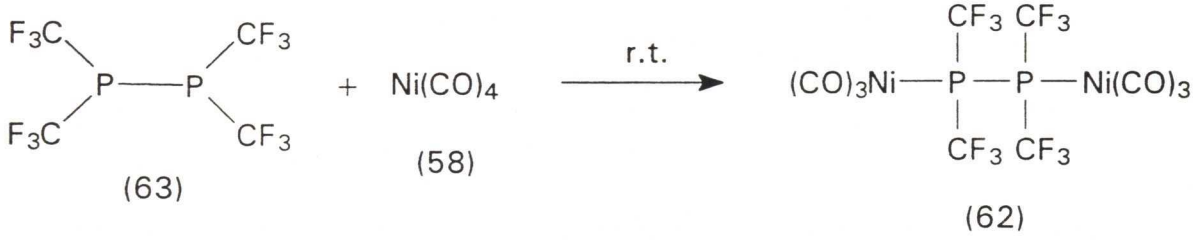
Scheme 1.13

Emeleus and Smith reacted tris(trifluoromethyl)phosphine (**39**) with nickel tetracarbonyl (**58**) in a sealed tube at room temperature and formed a mixture of the mono and bis nickel complexes (**59**) and (**60**) shown in Scheme 1.14.[49] This reaction demonstrates the coordination properties of fluoroalkylphosphines, as tris(trifluoromethyl)phosphine (**39**) binds more strongly to nickel than carbon monoxide.



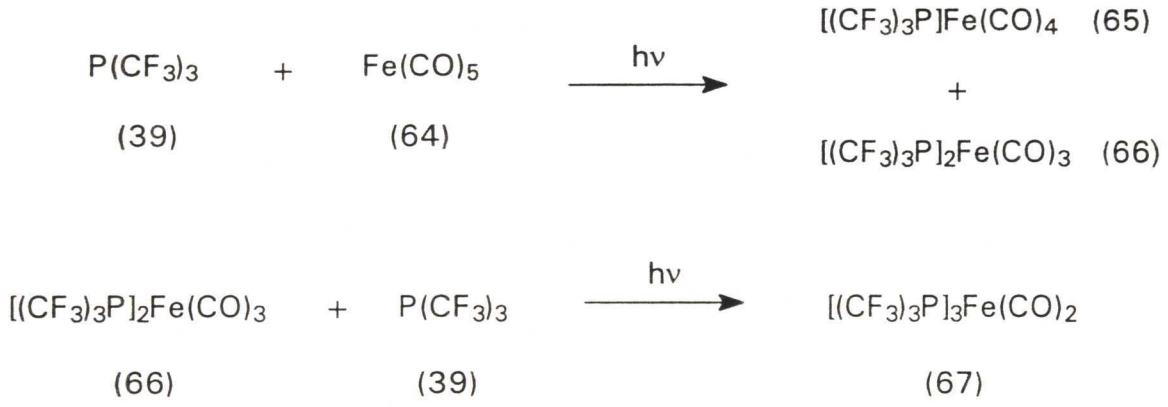
Scheme 1.14

A report by Burg and Mahler in 1958 also discusses the synthesis of $[(CF_3)_3P]_2Ni(CO)_2$ **(61)**, and also details the synthesis of **(62)** (Scheme 1.15), formed by the reaction of tetrakis(trifluoromethyl)diphosphine **(63)** with $Ni(CO)_4$ **(58)** at room temperature.[50]



Scheme 1.15

The displacement of carbon monoxide from iron pentacarbonyl **(64)** by tris(trifluoromethyl)phosphine **(39)** was reported by Burg in 1986 to form a mixture of iron carbonyl complexes **(65)**, **(66)** and **(67)**, containing one, two and three tris(trifluoromethyl)phosphine groups (Scheme 1.16).[51]

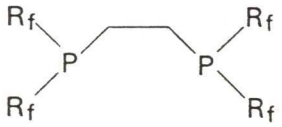


Scheme 1.16

These tris(trifluoromethyl)phosphine iron complexes were reported to be extremely volatile, and were isolated and characterised only by use of advanced high-vacuum techniques.

1.8 Synthesis and properties of fluorinated bis-phosphines

A class of ligands which is only beginning to be developed following the widespread application of alkylated bisphosphines in organometallic chemistry is that of perfluorinated bis-phosphines. Perfluorinated bisphosphines **(50)**, **(51)** and **(52)** retain the ethylene-bridged bis-phosphine structure of the aryl or alkyl bisphosphines discussed previously, but have perfluoroalkyl or perfluoroaryl groups bonded to the phosphorus donor atoms.



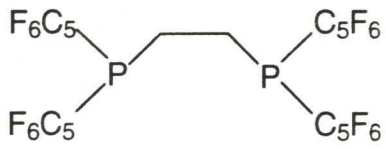
$R_f = C_6F_5$, **PP** = 1,2-bis(bis(pentafluorophenyl)phosphino)ethane, dfppe **(52)**

$R_f = CF_2CF_3$, **PP** = 1,2-bis(bis(pentafluoroethyl)phosphino)ethane, dfepe **(51)**

$R_f = CF_3$, **PP** = 1,2-bis(bis(trifluoromethyl)phosphino)ethane, dfmpe **(50)**

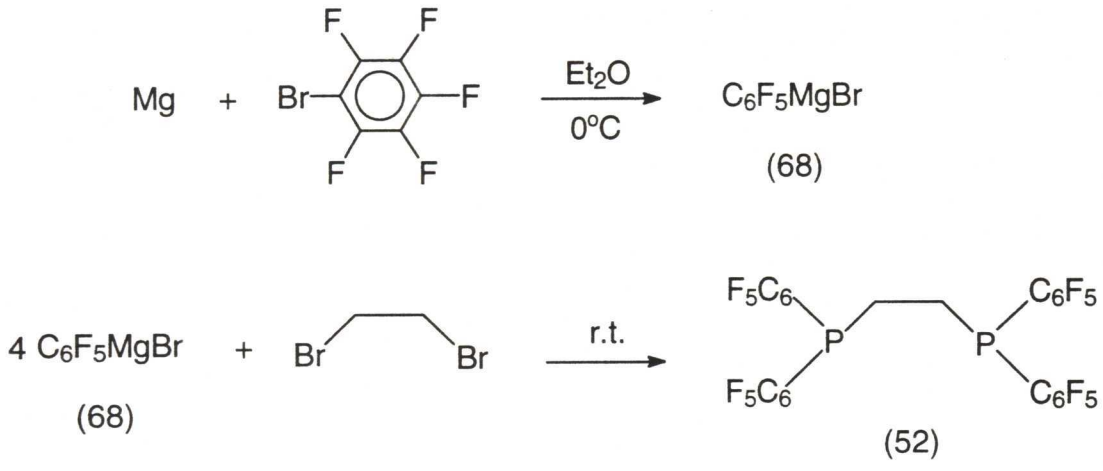
Perfluoroalkylated bis-phosphines provide a series of chemically robust, soluble ligands with very different properties to the alkyl or aryl bis-phosphines that have been used extensively in the area of alkane activation. While the synthetic difficulties in the preparation of these ligands have limited their widespread application, some work has been carried out on each of the ligands in this series.

1.8.1 1,2-Bis(bis(pentafluorophenyl)phosphino)ethane, dfppe (52)



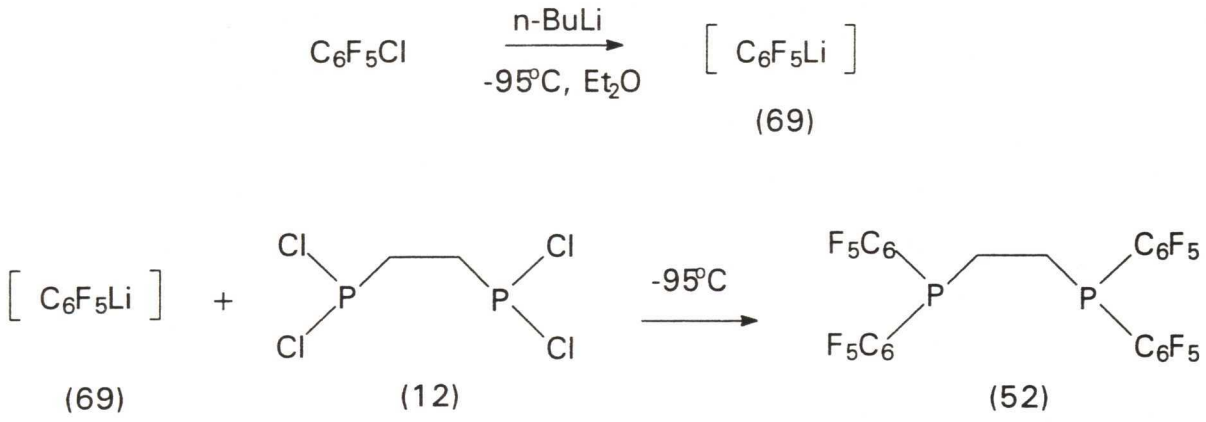
dfppe, (52)

1,2-Bis(bis(pentafluorophenyl)phosphino)ethane (**52**) was first synthesised by Cook and Morse in 1982, by room temperature addition of 1,2-dibromoethane to pentafluorophenylmagnesium bromide (**68**) (Scheme 1.17).[52]



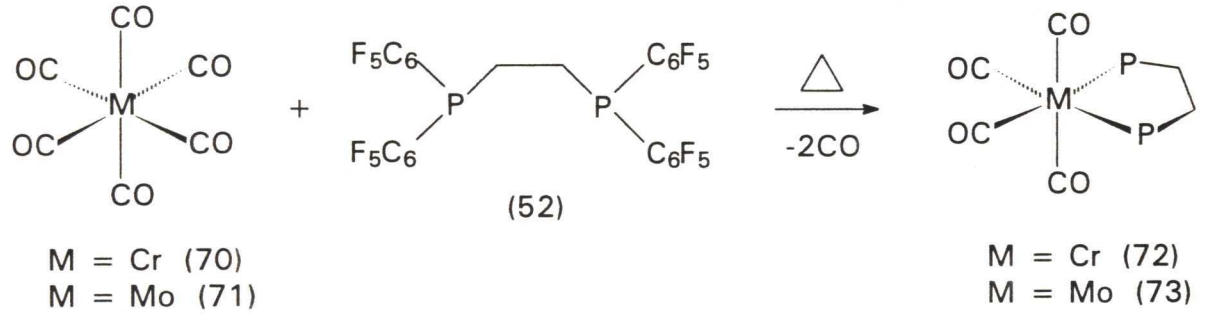
Scheme 1.17

Dfppe, **(52)** was also synthesised by Cook and Morse by generation of pentafluorophenyllithium **(69)** at low temperature and subsequent nucleophilic substitution of 1,2-bis(dichlorophosphino)ethane **(12)** (Scheme 1.18).[52] Typical yields of 30-35% for both of these reactions were reported.



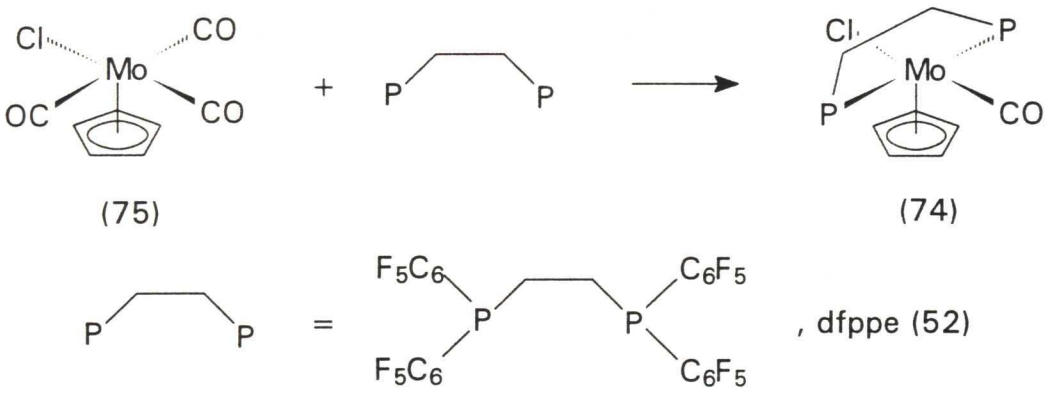
Scheme 1.18

Several organometallic complexes containing dfppe **(52)** have been synthesised. In 1989, Roddick and Ernst reported the thermal substitution of two carbonyl ligands on $M(CO)_6$ (M = Cr, **(70)**; M = Mo, **(71)**) by dfppe **(52)** to form the metal tetracarbonyl complexes $(dfppe)M(CO)_4$ (M = Cr, **(72)**; M = Mo, **(73)**) (Scheme 1.19).[26]



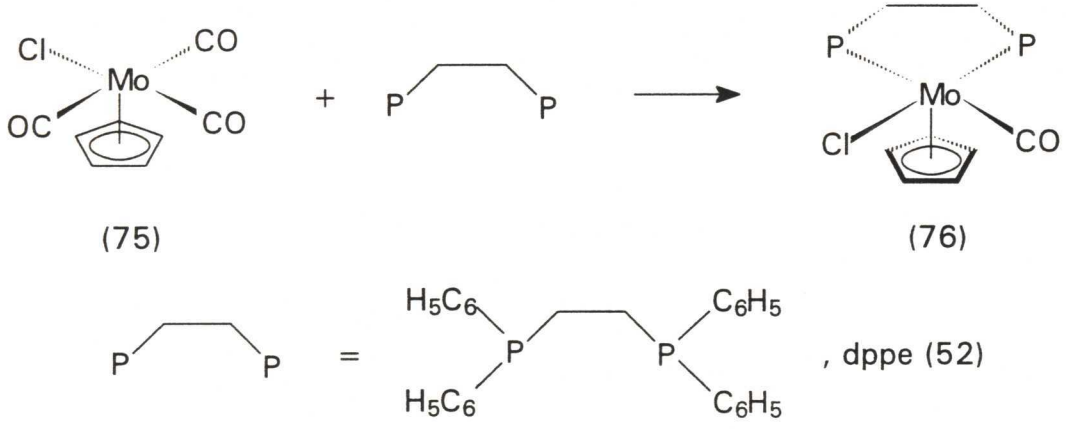
Scheme 1.19

Roddick and Ernst subsequently described the synthesis of *trans*-(η^5-C_5H_5)Mo(dfppe)(CO)Cl **(74)** by reaction of dfppe **(52)** with (η^5-C_5H_5)Mo(CO)$_3$Cl **(75)** (Scheme 1.20).[53]



Scheme 1.20

It is interesting to note that the non-fluorinated parent molecule, CpMo(dppe)(CO)Cl **(76)** adopts the alternative stereochemistry in which the carbonyl and chloride groups are not *trans*, but *cis* (Scheme 1.21).[54]



Scheme 1.21

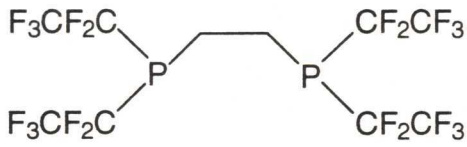
The synthesis of (dfppe)Pt(Ph)$_2$ (**77**) and facile reductive elimination of biphenyl from (dfppe)Pt(Ph)$_2$ (**77**) was reported in 1992 by Roddick and co-workers.[55] Thermolysis of (dfppe)Pt(Ph)$_2$ (**77**) in aromatic solvents in the presence of one equivalent of dfppe (**52**) produces the bis-chelate (dfppe)$_2$Pt (**78**) cleanly in 82% isolated yield (Scheme 1.22).[55]

$$\underset{(77)}{(dfppe)Pt(Ph)_2} + \underset{(52)}{dfppe} \xrightarrow[toluene]{\triangle} \underset{(78)}{(dfppe)_2Pt} + C_{12}H_{10}$$

Scheme 1.22

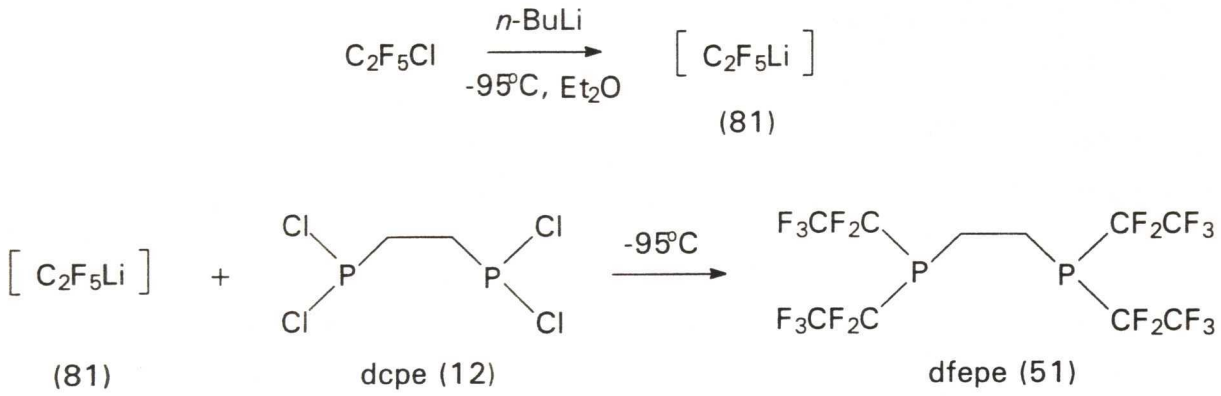
Unfortunately, reductive elimination from analogous alkylated diphosphine complexes such as (dppe)Pt(Ph)$_2$ (**79**) and (dmpe)Pt(Ph)$_2$ (**80**) has not been reported, as a comparison between the properties and reactivity of these complexes could provide useful information about the effects of fluorine substitution on the reactivity of complexes.

1.8.2 1,2-Bis(bis(pentafluoroethyl)phosphino)ethane, dfepe (51)



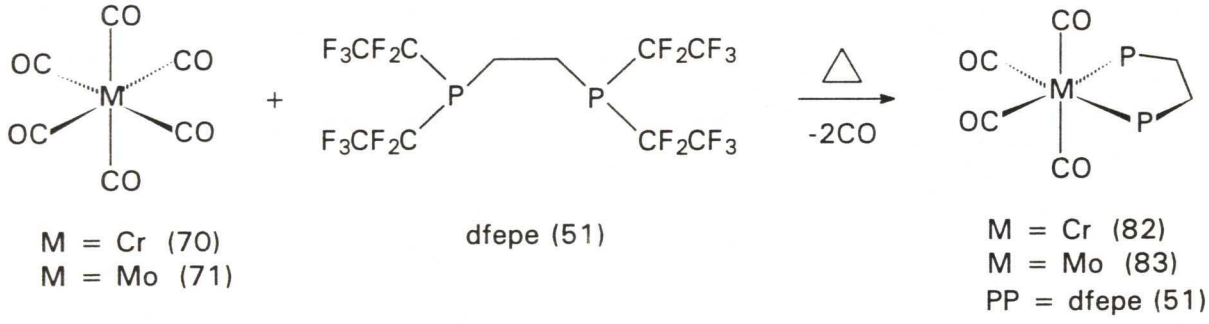
dfepe, (51)

The first preparation of 1,2-bis(bis(pentafluoroethyl)phosphino)ethane, dfepe (**51**), was reported in 1989 by Ernst and Roddick.[26] Dfepe (**51**) was prepared by a two step, one pot procedure, involving generation of pentafluoroethyllithium (**81**) via low temperature halogen-metal exchange, followed by low temperature addition of 1,2-bis(dichlorophosphino)ethane (**12**) (Scheme 1.23). Dfepe (**51**) was isolated upon workup as an odourless, colourless liquid in 68% yield.



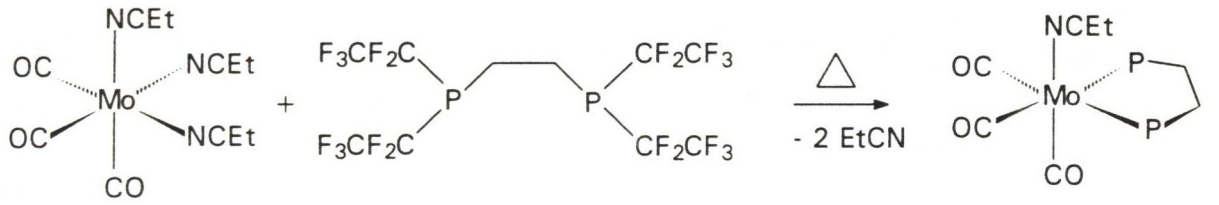
Scheme 1.23

Several complexes containing dfepe **(51)** have been reported. Roddick and Ernst describe the thermal substitution of $Cr(CO)_6$ **(70)** and $Mo(CO)_6$ **(71)** by dfepe **(51)** to prepare the corresponding metal tetracarbonyl complexes (dfepe)$M(CO)_4$ (M = Cr, **(82)**; M = Mo, **(83)**) (Scheme 1.24).[26]



Scheme 1.24

Roddick and Ernst also describe the synthesis of *fac*-Mo(dfepe)(NCEt)$(CO)_3$ **(84)** by reaction of *fac*-Mo$(EtCN)_3(CO)_3$ **(85)** with dfepe **(51)** in refluxing hexane (Scheme 1.25).[26]

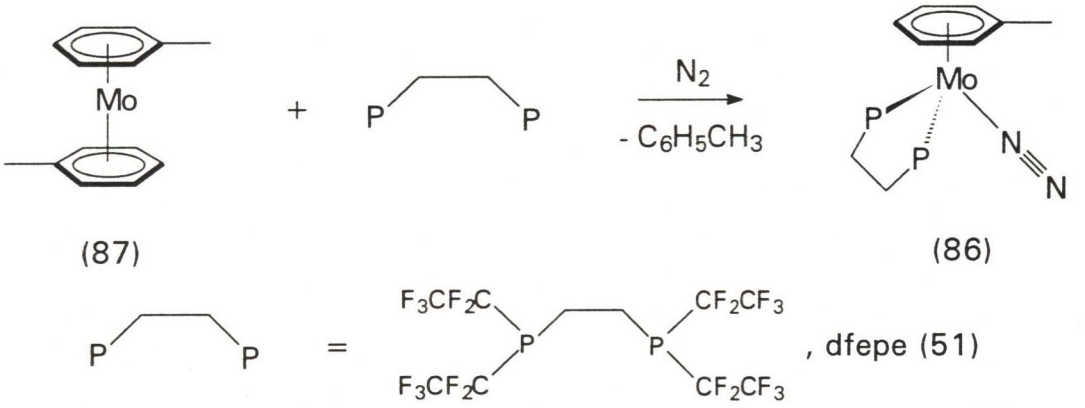


(85) (51) (84)

PP = dfepe (51)

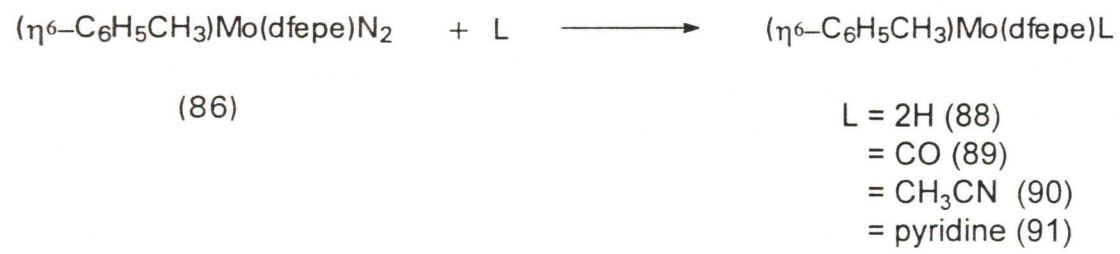
Scheme 1.25

A more detailed investigation of molybdenum complexes containing dfepe **(51)** was reported by Roddick and Ernst in 1990.[28] The (η^6-arene)Mo(dfepe)N_2 complex **(86)** was prepared by the treatment of $(\eta^6\text{-}C_6H_5CH_3)_2Mo$ **(87)** with an excess of dfepe **(51)** at -78 °C in ether or THF (Scheme 1.26).



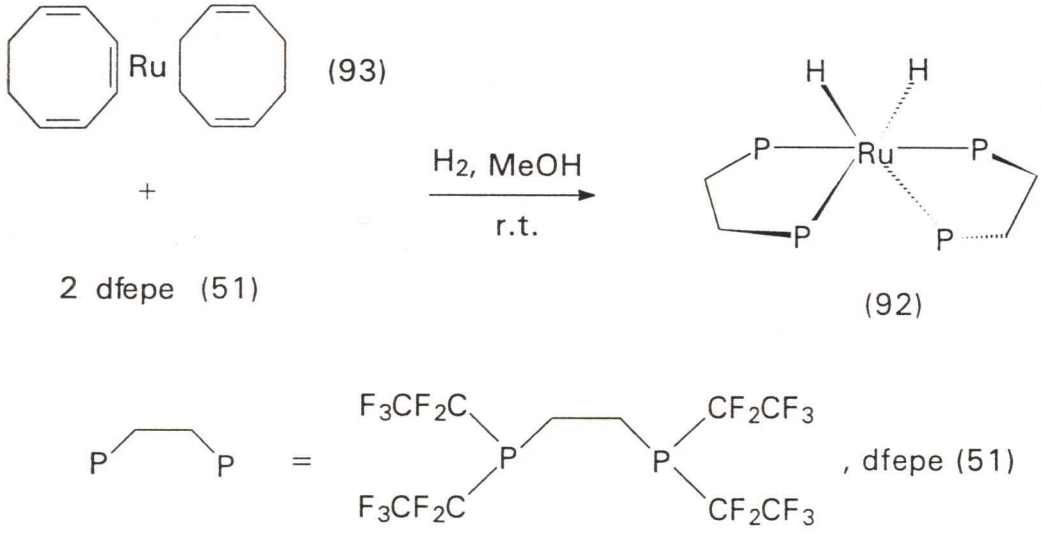
Scheme 1.26

Displacement of the N_2 ligand in **(86)** by a variety of 2-electron donors formed the series of stable complexes **(88) - (91)** (Scheme 1.27).[28]



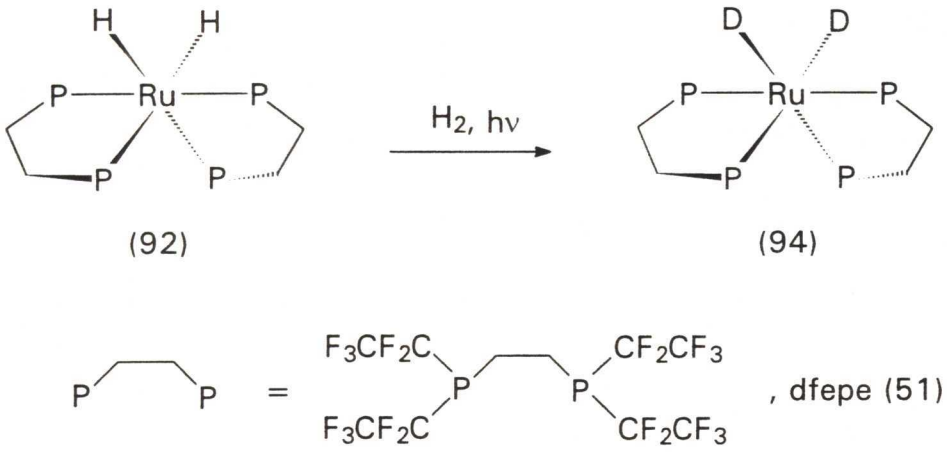
Scheme 1.27

Roddick *et al.* synthesised the *cis*-dihydride ruthenium complex $RuH_2(dfepe)_2$ **(92)** by reaction of (η^4-Cyclo-octa-1,5-diene)(η^6-cyclo-octa-1,3,5-triene)ruthenium (0), Ru(COD)(COT) **(93)** with 2 equivalents of dfepe **(51)** under 1 atmosphere of hydrogen gas at room temperature (Scheme 1.28).[56]



Scheme 1.28

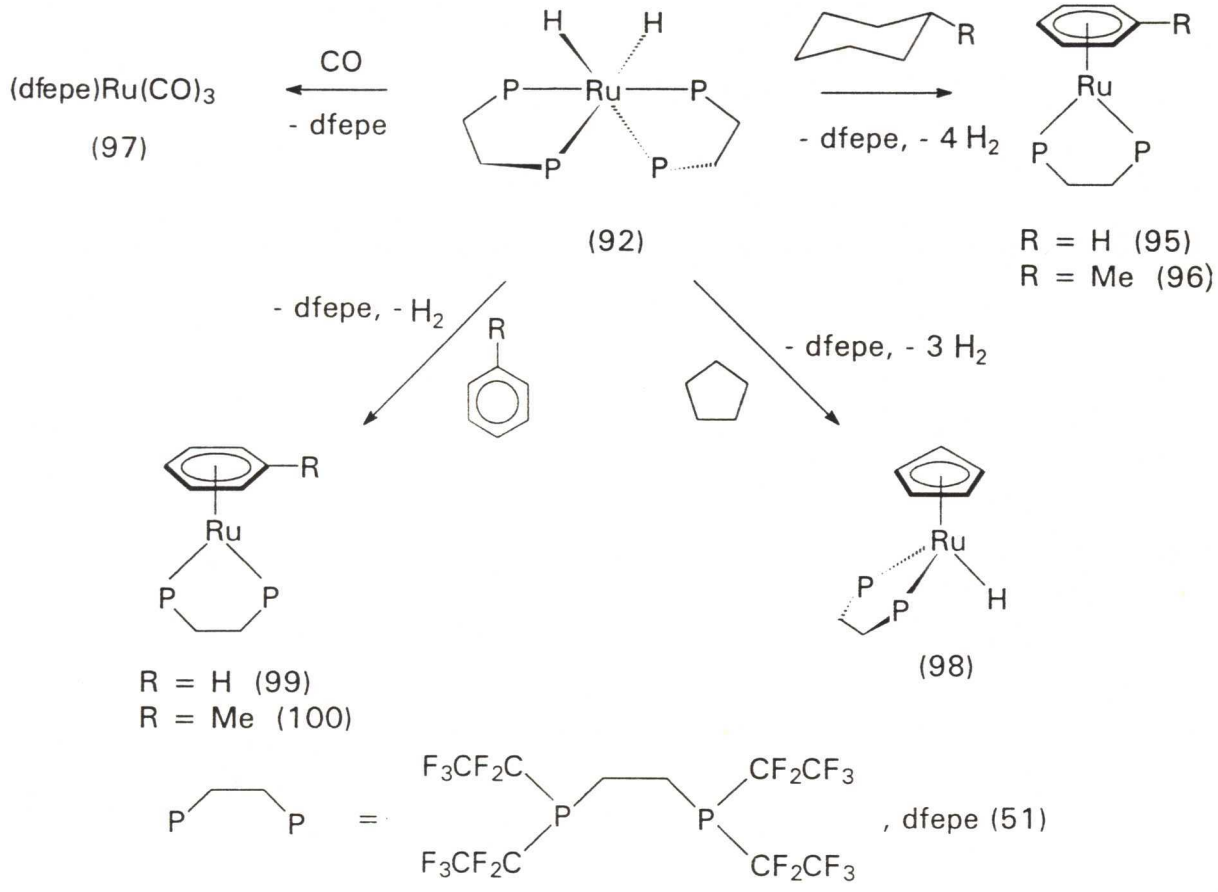
$RuH_2(dfepe)_2$ **(93)** is an air-stable, white crystalline solid which was reported to undergo photochemical exchange of hydrogen gas for deuterium gas (Scheme 1.29).[56]



(92) (94)

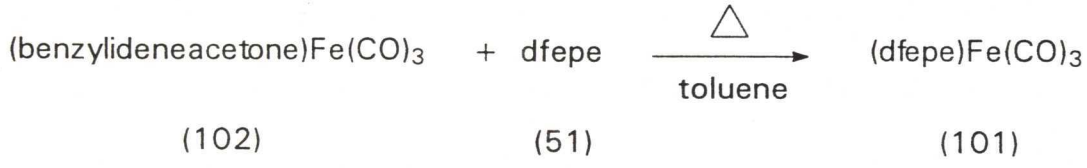
Scheme 1.29

$RuH_2(dfepe)_2$ **(92)** was also reported to undergo thermal substitution reactions with arenes to form products **(95)** and **(96)** with the general structure (η^6-arene)Ru(dfepe), and with carbon monoxide to form $(dfepe)Ru(CO)_3$ **(97)**, both arising from loss of one dfepe ligand. Thermolysis of $RuH_2(dfepe)_2$ **(92)** in neat cyclopentane, cyclohexane and methylcyclohexane at 180°C yields the corresponding polyene complexes (η^5-C_5H_5)Ru(dfepe)H, **(98)**, (η^6-C_6H_6)Ru(dfepe)H **(99)** and (η^6-$C_6H_5CH_3$)Ru(dfepe)H **(100)**, arising from thermal dehydrogenation of the corresponding cycloalkane (Scheme 1.30).



Scheme 1.30

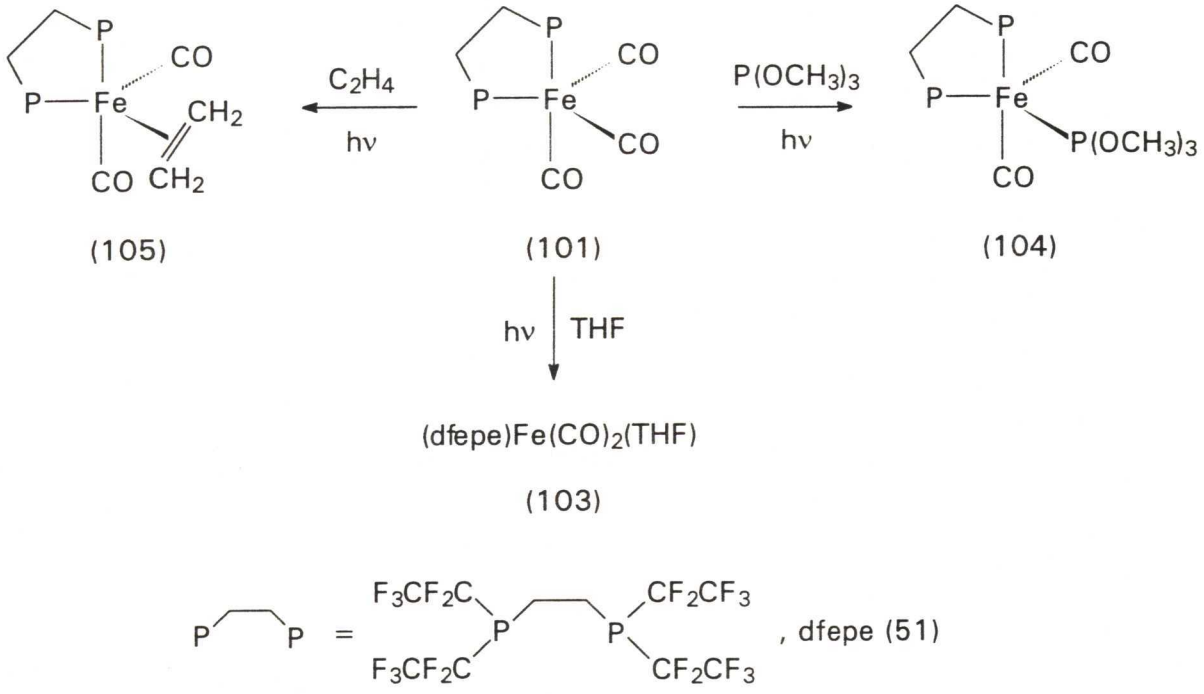
In 1992, Brookhart *et al.* reported the synthesis of $Fe(dfepe)(CO)_3$ **(101)** in 59% yield by the displacement of benzylideneacetone (bda) from $(bda)Fe(CO)_3$ **(102)** in toluene at 110°C (Scheme 1.31).[29]



Scheme 1.31

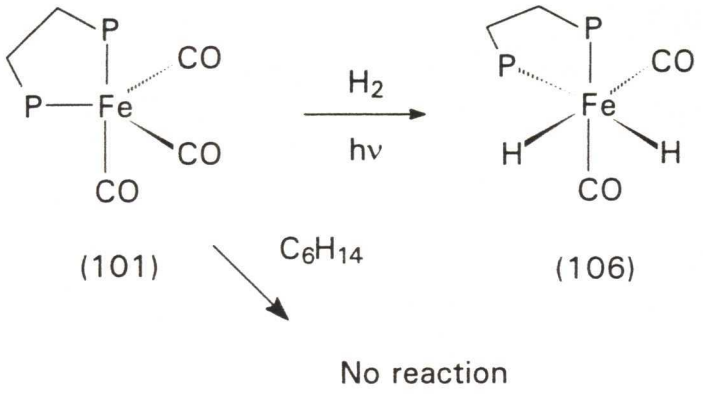
The photochemistry of **(101)** in the presence of a number of organic substrates was

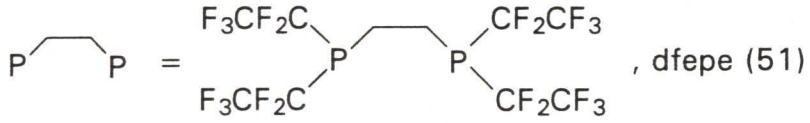
explored. Low temperature photolysis of $Fe(dfepe)(CO)_3$ **(101)** in THF and trimethylphosphite gave $Fe(dfepe)(CO)_2(THF)$ **(103)** and $Fe(dfepe)(CO)_2(P(OCH_3)_3)$ **(104)** respectively, while photolysis of $Fe(dfepe)(CO)_3$ **(101)** in the presence of ethylene gave the corresponding ethylene complex $Fe(dfepe)(CO)_2(C_2H_4)$ **(105)** as a crystalline solid in 70% yield (Scheme 1.32).



Scheme 1.32

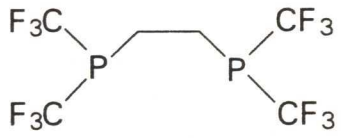
Photolysis of $Fe(dfepe)(CO)_3$ **(101)** in the presence of acetylene, butadiene and other unsaturated ketones were also reported, and found to form η^4-complexes. Of particular interest is the oxidative addition reactions carried out by $Fe(dfepe)(CO)_3$ **(101)**. Photolysis of $Fe(dfepe)(CO)_3$ **(101)** under a purge of hydrogen gas in diethyl ether produces the dihydride **(106)**, via oxidative addition of dihydrogen (Scheme 1.33). However, no oxidative addition products were observed when $Fe(dfepe)(CO)_3$ **(101)** was photolysed in the presence of hexane.





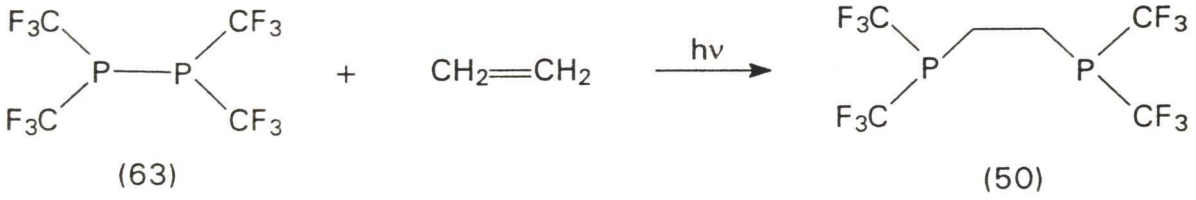
Scheme 1.33

1.8.3 1,2-Bis(bis(trifluoromethyl)phosphino)ethane, dfmpe (50)



dfmpe **(50)**

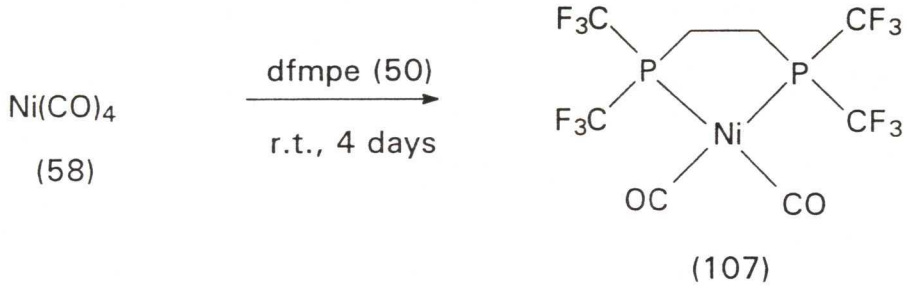
The synthesis of dfmpe **(50)** was first reported by Burg and Grant by the photochemical reaction of ethylene and tetrakis(trifluoromethyl)diphosphine **(63)**.[57] Tetrakis-(trifluoromethyl)diphosphine **(63)** was synthesised using the method developed by Haszeldine and co-workers in 1956 (Scheme 1.34).[46] This photochemical synthesis was applied to dfmpe **(50)** and several related ligands in 1971 by Haszeldine and co-workers.[58]



(63) (50)

Scheme 1.34

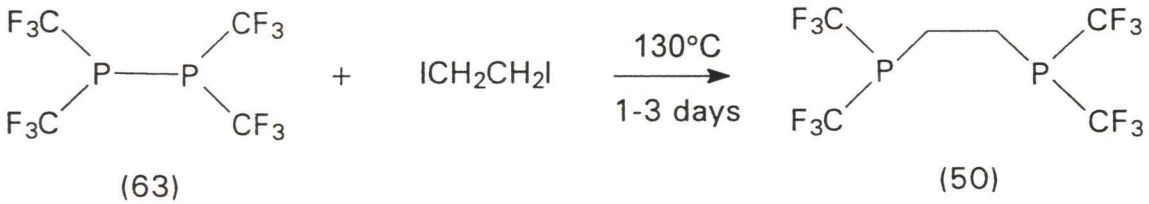
The first complex of dfmpe **(50)** was reported in 1963 by Burg and Street, who reacted dfmpe **(50)** with nickeltetracarbonyl, $Ni(CO)_4$ **(58)** to form the mono-phosphine complex $Ni(CO)_2$(dfmpe) **(107)**, shown in Scheme 1.35.[59,60]



(107)

Scheme 1.35

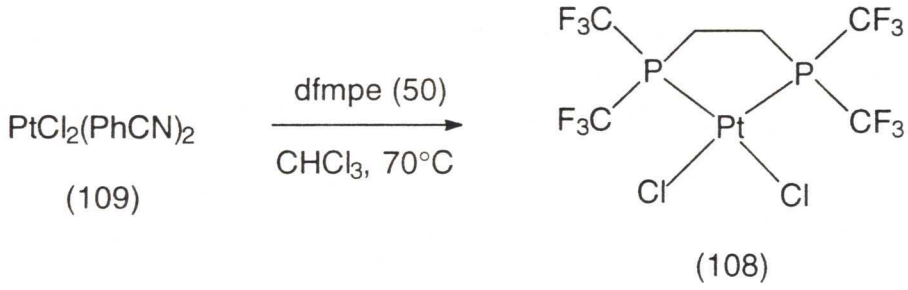
Cavell *et al* synthesised dfmpe **(50)** by a similar method to that outlined in Scheme 1.34, by reacting (tetrakistrifluoromethyl)diphosphine **(63)** with 1,2-diodoethane in a sealed tube at 130°C for several days (Scheme 1.36).[61]



(63) (50)

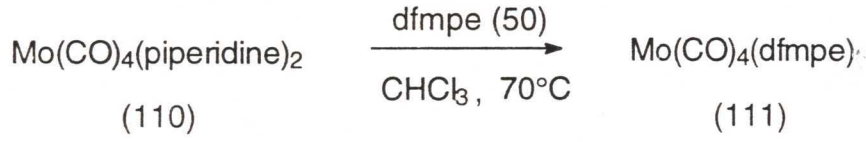
Scheme 1.36

Cavell *et al* synthesised and characterised the platinum complex **(108)**, by reacting dfmpe **(50)** with dichlorodibenzonitrileplatinum (II) **(109)** (Scheme 1.37).[61]



Scheme 1.37

The coordination chemistry of dfmpe **(50)** with molybdenum has also been investigated. The reaction of dfmpe **(50)** with *cis*-[$Mo(CO)_4$(piperidine)$_2$] **(110)** in refluxing chloroform produced the mono-phosphine molybdenum tetracarbonyl complex **(111)** in poor yield (Scheme 1.38).[61]



Scheme 1.38

1.9 Summary of application of fluorinated bisphosphines in organometallic chemistry

The synthesis and reactions of fluorinated bisphosphines discussed so far show the potential utility of fluorinated bisphosphines as ancillary ligands in organometallic complexes. The difficulties encountered in the synthesis of fluorinated bisphosphines has been a real

limitation to a full investigation of the properties of complexes containing fluorinated bisphosphine ligands.

Fluorinated bisphosphines have properties which differ significantly from their alkyl counterparts in terms of steric requirements, electronic nature, physical properties and chemical properties. As a consequence, complexes containing fluorinated bisphosphines are similarly expected to exhibit unique properties, however the few reports directly comparing alkyl and fluoroalkyl analogues makes a definitive comparison difficult. An improvement in the access to these compounds by the development of synthetic routes to fluorinated bisphosphines would facilitate such a comparison.

The paucity of reports describing the properties of complexes of dfmpe **(50)** reflects the difficulty encountered in synthesising this compound, not the potential dfmpe **(50)** shows as an ancillary ligand in organometallic chemistry. The robust nature of the trifluoromethyl groups, in conjunction with their low steric demand indicate that 1,2-bis(bis(trifluoromethyl)-phosphino)ethane, dfmpe **(50)**, is a potentially useful ligand in the field of organometallic chemistry. The comparatively high number of references discussing properties and reactions of complexes of dfepe **(51)** suggests the potential of dfmpe **(50)** in this area has not been attained due purely to difficulties in its synthesis. Furthermore, properties of dfmpe **(50)** such as its lipophilic nature (resulting from the high number of fluorine atoms surrounding its skeleton) may prove to afford complexes containing it and other highly fluorinated ligands advantages not available to alkyl analogues such as 1,2-bis(dimethylphosphino)ethane, dmpe **(6)**. A synthesis that allows the production of gram quantities of this compound using standard laboratory equipment and techniques is required to fully investigate the C-H activation properties of organometallic complexes of dfmpe **(50)**.

1.10 Aims of this work

The aims of this work are :

1) To develop a convenient, one-step synthetic method for the introduction of trifluoromethyl groups onto phosphines, and to apply this method to the synthesis of 1,2-bis(bis(trifluoromethyl)phosphino)ethane, dfmpe **(50)**. Such a synthetic method must be able to be carried out under normal laboratory conditions using standard equipment, to enable a thorough investigation of the properties of dfmpe to be carried out.

2) To carry out a detailed investigation of the coordination properties of dfmpe **(50)** with iron and ruthenium, and to devise synthetic schemes for the synthesis of the iron and ruthenium dihydride complexes, $FeH_2(dfmpe)_2$ **(112)** and $RuH_2(dfmpe)_2$ **(113)**.

3) To investigate the reactions of $FeH_2(dfmpe)_2$ **(112)** and $RuH_2(dfmpe)_2$ **(113)** in the presence of alkanes, alkenes and arenes, in order to assess the potential of **(112)** and **(113)** for the activation of C-H bonds in organic substrates. A comparison of the properties of these dfmpe-containing organometallic complexes and those of organometallic complexes containing the methyl analogue, dmpe **(6)** will also be made.

5) To apply the trifluoromethylation methodology developed to the synthesis of asymmetrical phosphines containing one or more trifluoromethyl groups. Also to extend the method developed for the trifluoromethylation of phosphines into the devising of a general procedure for the introduction of a bis(trifluoromethyl)phosphino group into a more elaborate ligand.

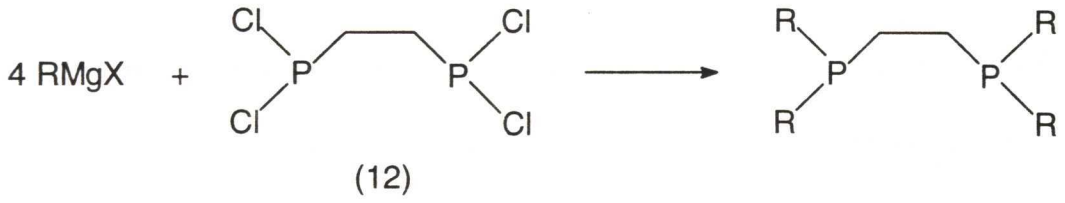
CHAPTER 2 : SYNTHESIS OF DFMPE

2.1 Introduction : Synthesis of trifluoromethylated phosphines

To investigate the C-H activation properties of organometallic complexes containing dfmpe (**50**), a convenient synthetic procedure was required to form the phosphorus-trifluoromethyl bond.

2.1.1 Trifluoromethyl Grignard and trifluoromethyllithium reagents

Ethylene bridged alkyl and aryl bis-phosphines are usually synthesised by direct nucleophilic substitution of an alkyl Grignard or alkyllithium reagent onto 1,2-bis(dichloro-phosphino)ethane (**12**) (Scheme 2.1).[18]



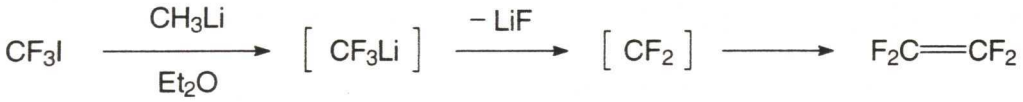
(12)

R = Me, Et, *i*-Pr, Ph; X = Cl, Br, I

Scheme 2.1

Alkyl Grignard and alkyllithium reagents have been the subject of extensive study and discussion, and are stable and relatively simple to prepare. In contrast, the thermal instability of perfluoroalkyllithium and perfluoroalkyl Grignard reagents make the application of alkyl synthetic methods to the synthesis of perfluoroalkylated bisphosphines very difficult.[62] While it has proved possible to apply this approach to the synthesis of pentafluoroethyllithium,[26,63] higher perfluoroalkyllithium reagents[64] and pentafluorophenyllithium,[18] it is well documented that attempts to generate trifluoromethyllithium are generally unsuccessful.[62]

The problem encountered is the facile elimination of lithium fluoride from trifluoromethyllithium to form difluorocarbene, which dimerises to form ultimately tetrafluoroethylene (Scheme 2.2).[62,65]



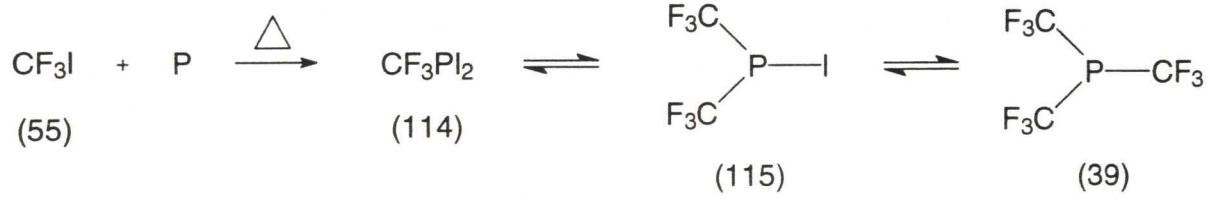
Scheme 2.2

Problems of irreproducibility are encountered when attempting to prepare trifluoromethylated Grignard reagents such as trifluoromethylmagnesium iodide.[66] While there are several reports of the synthesis and use of higher perfluoroalkyl Grignard reagents,[66,67] these are invariably accompanied by reports of the difficulty of carrying out the synthesis of the trifluoromethylated Grignard analogue. Factors such as reaction initiation, temperature, solvent and the dilution of trifluoromethyl iodide in the reaction mixture all affect the formation and stability of trifluoromethylmagnesium iodide.[66] As for the preparation of trifluoromethyllithium, the preparation of trifluoromethylmagnesium iodide is often accompanied by the formation of fluoroform, CF_3H, and tetrafluoroethylene, the latter obtained in polymeric form.[66] The trifluoromethyl Grignard has, however been prepared from CF_3I[66] and CF_3Br[68] at low temperature in the presence of a trapping agent, and some trifluoromethyl adducts have been isolated, albeit in low yield. The trifluoromethyl Grignard can be formed and captured, however the difficulties associated with its synthesis preclude its practical utility in organic synthesis.[69]

An alternative approach must be developed to give a synthetically viable route to trifluoromethylated phosphines.

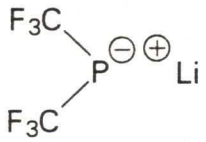
2.1.2 Previous syntheses of trifluoromethylated phosphines

The first literature report of the synthesis of a simple trifluoromethylated phosphine is that of tris(trifluoromethyl)phosphine (**39**), reported in 1953 by Bennett, Emeleus and Haszeldine.[46] Tris(trifluoromethyl)phosphine (**39**) was synthesised by the reaction of white phosphorus and trifluoromethyl iodide (**55**) at high pressure and high temperature. This reaction produces an equilibrium mixture of mono-, bis- and tris(trifluoromethylated) phosphines (**114**), (**115**) and (**39**) which must be separated by careful high-vacuum distillation to isolate tris(trifluoromethyl)phosphine (**39**) (Scheme 2.3).

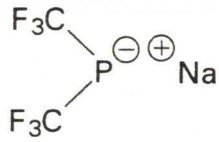


Scheme 2.3

The reaction shown in Scheme 2.3 is the only literature preparation for molecules containing the trifluoromethylphosphine moiety.[61,70,71] Compounds such as $(CF_3)_2P\text{-}PH_2$,[72] $(CH_3)_3Si\text{-}P(CF_3)_3$,[73] and $Me_3SnP(CF_3)_3$[74,75,76] have been reported, and all use the basic strategy of Bennett, Emeleus and Haszeldine to form the P-CF_3 bond. Syntheses of trifluoromethylphosphines reported as recently as 1988 have not improved on this method for the introduction of the trifluoromethyl group onto phosphorus. Minkwitz and Liedtke[77] were able to prepare and store alkali-metal bis(trifluoromethyl)phosphides (**116**) and (**117**) for short periods of time. Reagents such as (**116**) and (**117**) would be useful in preparing a variety of trifluoromethylated phosphines.

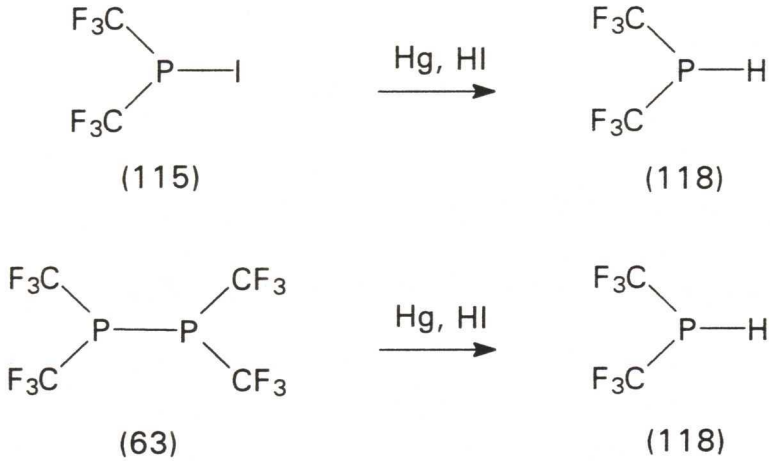


(116)



(117)

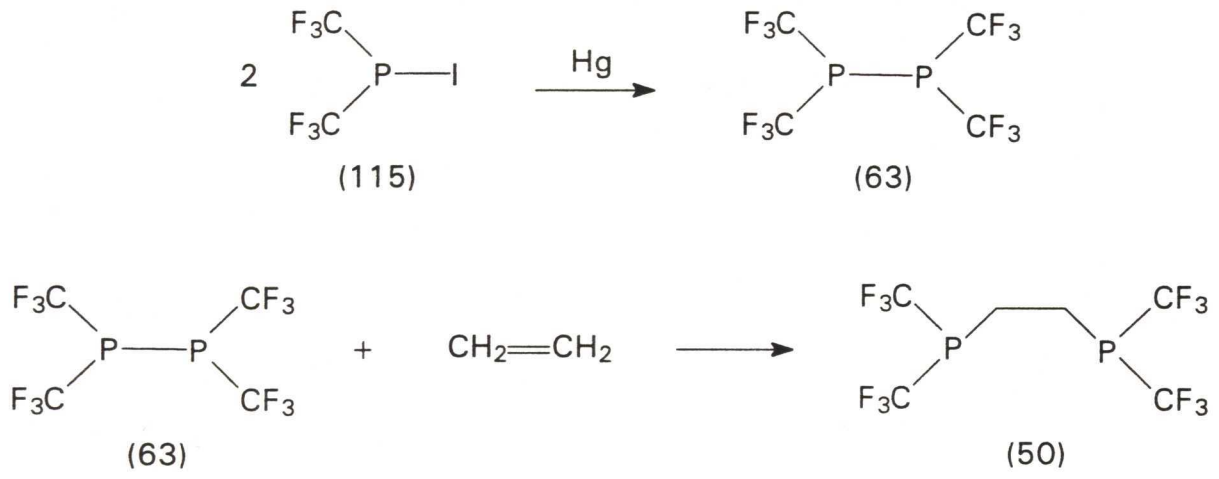
The synthesis of **(116)** and **(117)**, however, involved the preparation of bis(trifluoromethyl)phosphine **(118)** by reduction of bis(trifluoromethyl)phosphine iodide **(115)** or tetrakis(trifluoromethyl)diphosphine **(63)** using hydrogen iodide and mercury (Scheme 2.4).[78] Bis(trifluoromethyl)phosphine iodide **(115)** and tetrakis(trifluoromethyl)diphosphine **(63)** have been prepared by the reaction between white phosphorus and trifluoromethyliodide **(55)**, the low-yielding, technically difficult reaction developed by Emeleus and co-workers in 1953.



Scheme 2.4

The first synthesis of dfmpe **(50)** by Burg and Grant used the reaction of Bennett, Emeleus and Haszeldine to synthesise bis(trifluoromethyl)phosphine iodide **(115)**.[57] Bis(trifluoromethyl)phosphine iodide **(115)** was separated from the reaction mixture by high

vacuum distillation, and was stirred with mercury for 48 h to form tetrakis(trifluoromethyl)-diphosphine **(63)**. Typical yields reported by Bennett and co-workers for the overall synthesis of tetrakis(trifluoromethyl)diphosphine **(63)** were between 15% and 25%. Photochemical reaction between ethylene and tetrakis(trifluoromethyl)diphosphine **(63)** afforded 1,2-bis(bis(trifluoromethyl)phosphino)ethane, dfmpe **(50)** (Scheme 2.5).

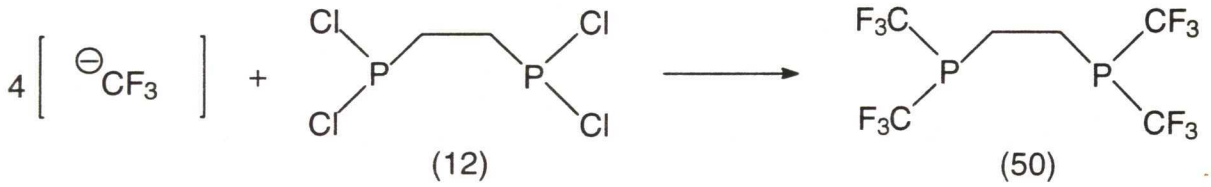


Scheme 2.5

This synthesis of dfmpe **(50)** is by no means ideal as it is low-yielding, requires the difficult separation of the required product from several other by-products, and is a multi-step process involving intermediates which are difficult to handle. A synthesis of dfmpe **(50)** carried out as recently as 1988 by Cavell and co-workers were able to improve on the final step of this reaction sequence, with the thermal reaction of 1,2-diiodoethane and tetrakis(trifluoromethyl)diphosphine **(63)** affording a 55% yield of dfmpe **(50)** with respect to 1,2-diiodoethane.[61] However, the method used to synthesise the key tetrakis(trifluoromethyl)diphosphine intermediate **(63)** was still that used in 1953 by Bennett, Emeleus and Haszeldine.

2.1.3 Alternative strategies for the synthesis of trifluoromethylated phosphines

Clearly what is required is a trifluoromethylating reagent that has the versatility of the analogous alkylating reagents used to synthesise alkyl bisphosphines, to enable the introduction of a trifluoromethyl group effectively by nucleophilic substitution. This reagent would effectively be a "trifluoromethyl anion equivalent", one capable of delivering the trifluoromethyl group to a phosphorus atom in the analogous way that a Grignard reagent effectively delivers a methyl anion equivalent to a chlorophosphine (Scheme 2.6).



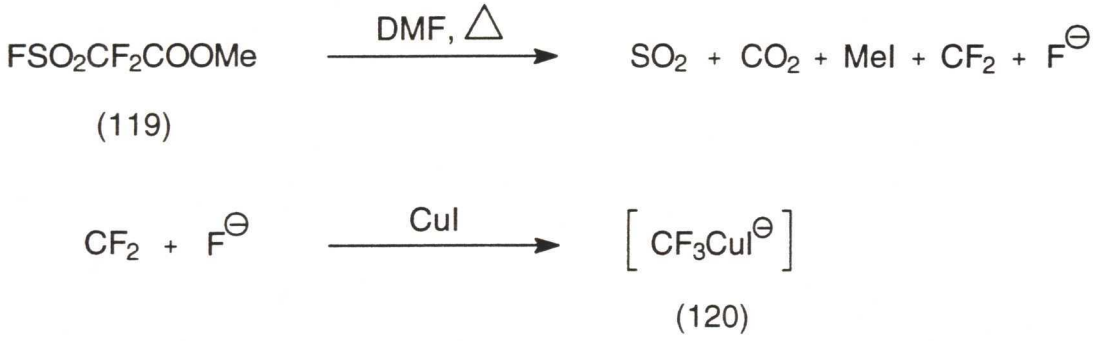
Scheme 2.6

2.2 Reactions of trifluoromethylating reagents and phosphines

In recent years, the biological application of fluorinated and trifluoromethylated compounds has driven the development of methods for the trifluoromethylation of many classes of organic compounds.[31,79] As a result, there have been numerous reports of trifluoromethyl anion equivalents capable of effecting trifluoromethylation of organic compounds. The application of some of these reagents to the synthesis of trifluoromethylated phosphines was examined.

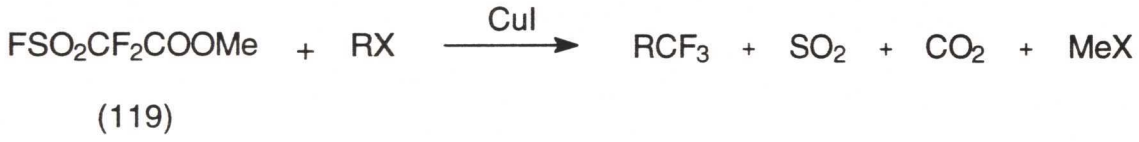
2.2.1 Methyl fluorosulphonyldifluoroacetate, FSO_2CF_2COOMe

Methyl fluorosulphonyldifluoroacetate **(119)** is a commercially available trifluoromethylating reagent, first reported in 1989 by Chen and Wu.[80] **(119)** decomposes at moderate temperatures in *N,N*-dimethylformamide to eliminate sulfur dioxide and carbon dioxide, and form difluorocarbene and fluoride. In the presence of copper(I) iodide, the combination of difluorocarbene and fluoride produces trifluoromethyl copper iodide (Scheme 2.7), which can act as a trifluoromethyl anion equivalent in the presence of alkyl halides.



Scheme 2.7

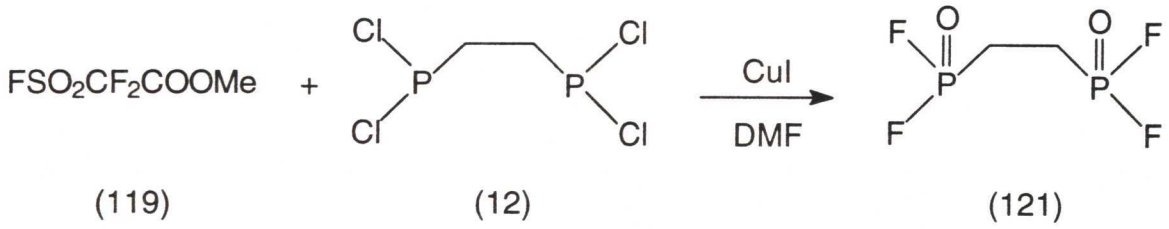
Methyl fluorosulphonyldifluoroacetate **(119)** has been reported to trifluoromethylate aryl and alkenyl halides in high yields (Scheme 2.8).[80]



Scheme 2.8 : R = Ph, CH_2Ph, CH_2=$CHCH_2$, naphthyl, $CH_2CON(Et)_2$; X = Br or I.

The reaction of methyl fluorosulphonyldifluoroacetate (**119**) with 1,2-bis(dichlorophosphino)ethane, dcpe (**12**), under these reaction conditions was examined, to see if trifluoromethylated phosphines could be formed.

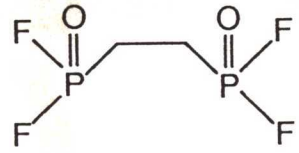
A mixture of methyl fluorosulphonyldifluoroacetate (**119**), dcpe (**12**) and a catalytic amount of copper(I) iodide was heated at 70°C in *N,N*-dimethylformamide for 1h. ^{31}P NMR analysis of the crude reaction mixture showed that although all dcpe (**12**) was consumed, no trifluoromethylated phosphines were formed. The sole product formed was 1,2-bis(difluorophosphino)ethane dioxide, $F_2P(O)CH_2CH_2P(O)F_2$ (**121**), arising from oxidation of the chlorophosphine (**12**) and fluoride exchange for chloride under the reaction conditions (Scheme 2.9).



(119) (12) (121)

Scheme 2.9

The $^{31}P\{^1H\}$ NMR spectrum of $F_2P(O)CH_2CH_2P(O)F_2$ (**121**) has been reported previously, and the ^{31}P chemical shift obtained experimentally for this compound (δ 24.5 ppm) agrees with the ^{31}P chemical shift reported in the literature (^{31}P NMR (CD_3CN) 20.2 ppm).[81] Simulation of the second-order spectrum of (**121**) (including reports of coupling constants) has also been carried out.[81] The experimental $^{31}P\{^1H\}$ NMR spectrum of (**121**) obtained is shown in Figure 2.1. A full listing of the literature values and signs of coupling constants used to simulate this spectrum is given in Appendix A2.



(121)

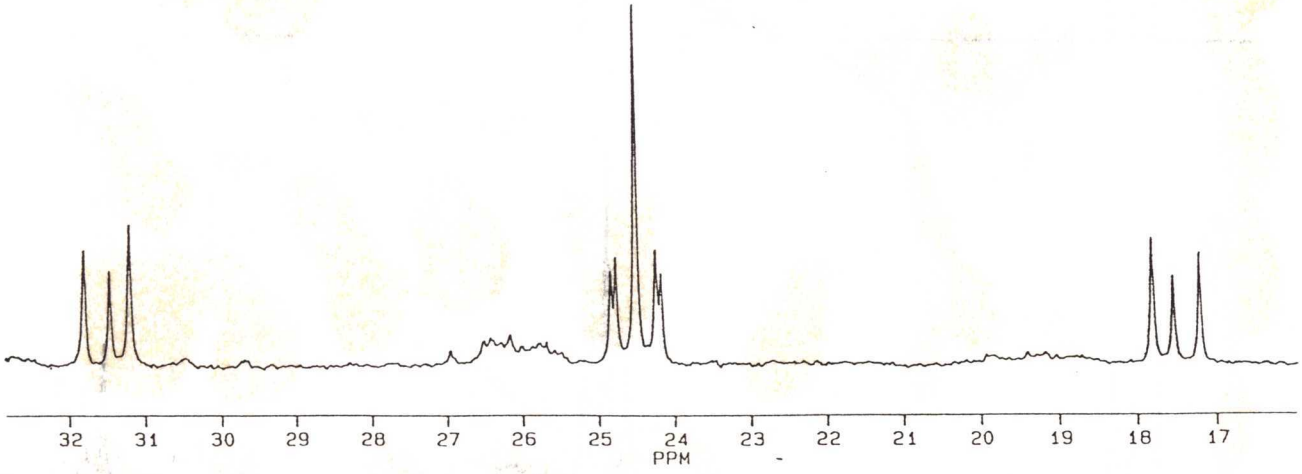
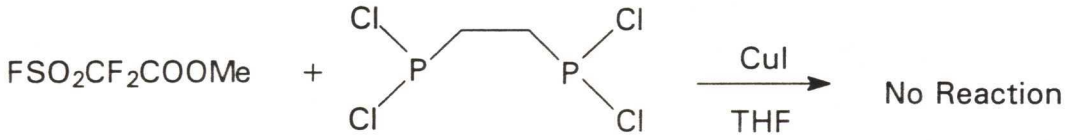


Figure 2.1 : Experimental $^{31}P\{^{1}H\}$ NMR spectrum of $F_2P(O)CH_2CH_2P(O)F_2$ **(121)**

When the reaction of dcpe **(12)** and methyl fluorosulphonyldifluoroacetate **(119)** was carried out without copper iodide , the tetrafluorophosphine dioxide **(121)** was not formed, and the starting material **(12)** decomposed to form a complex mixture of products. Copper iodide participates directly in the formation of $F_2P(O)CH_2CH_2P(O)F_2$ **(121)**.

It is known that disubstituted formamides react with phosphorus oxychloride, the Vilsmeier reaction used to formylate aromatic rings.[82] It is possible that dcpe **(12)** reacts with DMF, a reaction which may compete with and suppress the desired trifluoromethylation reaction.

The reaction of methyl fluorosulphonyldifluoroacetate **(119)** with dcpe **(12)** in THF in the presence of copper iodide was investigated, as dcpe **(12)** is known to be stable in THF. When this reaction was carried out in an identical procedure to that described above, no reaction was observed, even after extended reaction times (Scheme 2.10).

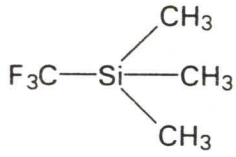


(119) (12)

Scheme 2.10

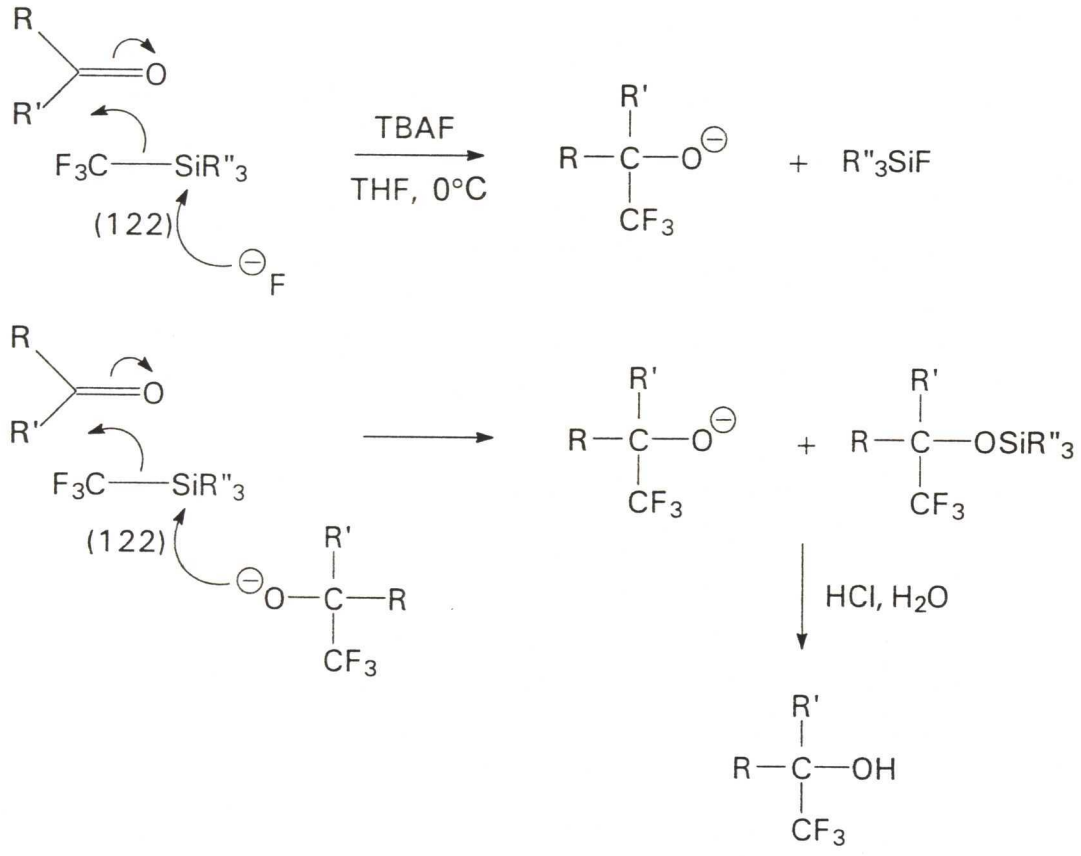
DMF is necessary for FSO_2CF_2COOMe **(119)** to effect the trifluoromethylation of organic halides. The instability of dcpe **(12)** in DMF makes methyl fluorosulphonyldifluoroacetate **(119)** unsuitable as a reagent for the synthesis of dfmpe **(50)** by substitution of dcpe **(12)**. Although methyl fluorosulphonyldifluoroacetate **(119)** has proved to be a useful reagent for the trifluoromethylation of organic halides, it is clearly not useful for the synthesis of trifluoromethylated phosphines.

2.2.2 (Trifluoromethyl)trimethylsilane, (CF_3TMS)



(Trifluoromethyl)trimethylsilane **(122)**

The synthesis of (trifluoromethyl)trimethylsilane **(122)** was first reported in 1984 by Ruppert and co-workers.[83] In 1989, Prakash, Krishnamurti and Olah reported a modification of the synthesis of (trifluoromethyl)trimethylsilane **(122)** and used this reagent to carry out efficient trifluoromethylation of aldehydes and ketones by a fluoride-initiated catalytic process (Scheme 2.11).[84]



Scheme 2.11

A further report describes the extension of this procedure to a wider range of substrates including esters, lactones and acid chlorides, again resulting in yields between 60% and 90%.[85] In this reaction, CF_3TMS **(122)** acts as a trifluoromethyl anion equivalent for carbonyl compounds where the oxygen atom is able to bond to the silicon atom of CF_3TMS **(122)**, and results in the efficient transfer of the trifluoromethyl group to the carbon atom of the carbonyl group. CF_3TMS **(122)** is a colourless, volatile liquid which is stable for long periods of time at room temperature, and so is a convenient trifluoromethylating reagent for carbonyl-containing compounds.

Reactions were carried out between (trifluoromethyl)trimethylsilane **(122)** and chloro-phosphines and chloro-phosphine oxides in an attempt to trifluoromethylate these phosphorus-containing compounds.

(Trifluoromethyl)trimethylsilane **(122)** was synthesised by the low temperature addition of hexaethylphosphorus triamide (hepa) **(53)** to a solution of trifluoromethyl bromide **(123)** and trimethylsilyl chloride **(124)** in benzonitrile (Scheme 2.12), the procedure reported by Prakash and co-workers in 1989.[84]

$$\underset{(124)}{(CH_3)_3SiCl} + \underset{(123)}{CF_3Br} + \underset{(53)}{P(NEt_2)_3} \xrightarrow[-60°C]{PhCN} \underset{(122)}{(CH_3)_3SiCF_3}$$

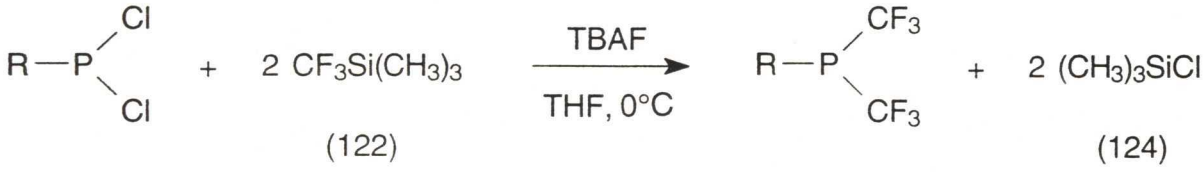
Scheme 2.12

An excess of trifluoromethyl bromide **(123)** was condensed into a solution of trimethylsilyl chloride **(124)** in benzonitrile at liquid nitrogen temperature. The reaction

mixture was allowed to warm to -60°C, and a solution of 4 equivalents of hexaethylphosphorus triamide (**53**) in benzonitrile was added slowly at -60°C. The mixture was allowed to warm to room temperature, and (trifluoromethyl)trimethylsilane (**122**) was isolated by distillation under vacuum. The product was found to be >95% pure by ^{1}H NMR spectroscopy, with NMR spectra and physical properties identical to that reported in the literature.[84]

2.2.2.1 Reaction of dichlorophenylphosphine with (trifluoromethyl)trimethylsilane

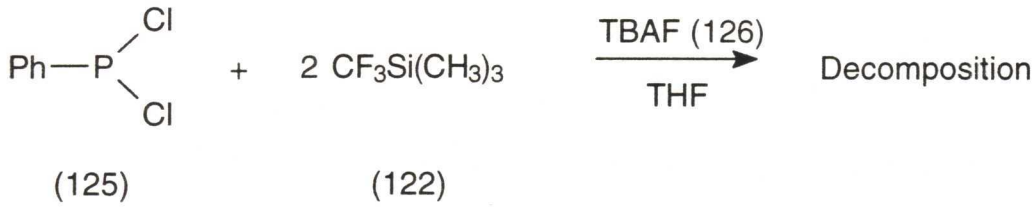
The reaction of (trifluoromethyl)trimethylsilane (**122**) with R-PCl_2 was attempted to determine whether the effective substitution of the trifluoromethyl group for chloride could be induced by (**122**) (Scheme 2.13).



Scheme 2.13

(Trifluoromethyl)trimethylsilane (**122**) was added to dichlorophenylphosphine (**125**) in THF solution at 0°C in the presence of tetra-*n*-butylammonium fluoride (TBAF) (**126**) under a variety of reaction conditions, and the reactions were monitored by ^{31}P NMR spectroscopy. No trifluoromethylated phosphines were detected, and the only products observed arose from decomposition of dichlorophenylphosphine (**125**) by water present in the tetra-*n*-butylammonium fluoride (**126**) (Scheme 2.14). Commercially available tetra-*n*-

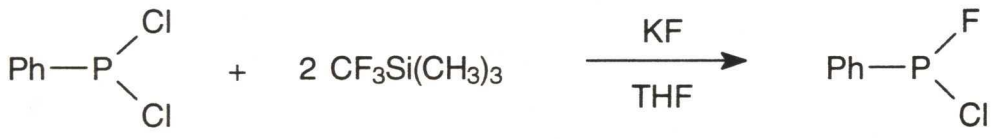
butylammonium fluoride (**126**) contains 3 moles of water for every mole of compound. Attempts to dry tetra-*n*-butylammonium fluoride (**126**) to avoid side reactions induced by water led only to its decomposition, consistent with literature reports.[86]



(125) (122)

Scheme 2.14

A fluorinating agent which could be dried was used in this reaction to avoid the decomposition of dichlorophenylphosphine (**125**) by water. (Trifluoromethyl)trimethylsilane (**122**) was added to dichlorophenylphosphine (**125**) in THF solution at 0°C in the presence of dry potassium fluoride, and the reaction mixture was monitored by ^{31}P NMR spectroscopy. No trifluoromethylated phosphines were observed, however after prolonged reaction times, a small resonance was apparent in the ^{31}P NMR spectrum at δ 30.5 ppm, exhibiting a doublet coupling of 1000 Hz (typical of the size of $^{1}J_{P\text{-}F}$ coupling constants). It appears that substitution of fluorine for chlorine occurs under the reaction conditions, to form chlorofluorophenylphosphine (**127**) (Scheme 2.15).



(125) (122) (127)

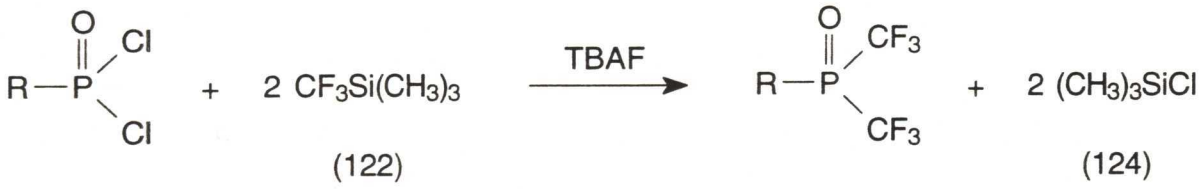
Scheme 2.15

There is only one reference in the literature which reports $^{31}P\{^{1}H\}$ NMR data for chlorofluorophenylphosphine (**127**), and this gives a $^{1}J_{F\text{-}P}$ value only.[87] The $^{1}J_{F\text{-}P}$ coupling constant reported in the literature (1050 Hz) is consistent with that observed for (**127**) in this reaction (1000 Hz).

An identical ^{31}P NMR spectrum was obtained when dichlorophenylphosphine (**125**) was reacted with potassium fluoride in THF, indicating that (trifluoromethyl)trimethylsilane (**122**) is not necessary for this reaction. The volatility of CF_3TMS (**122**) precluded the use of higher temperatures in this and subsequent reactions using this reagent.

2.2.2.2 Reaction of dichlorophenylphosphine oxide with (trifluoromethyl)trimethylsilane

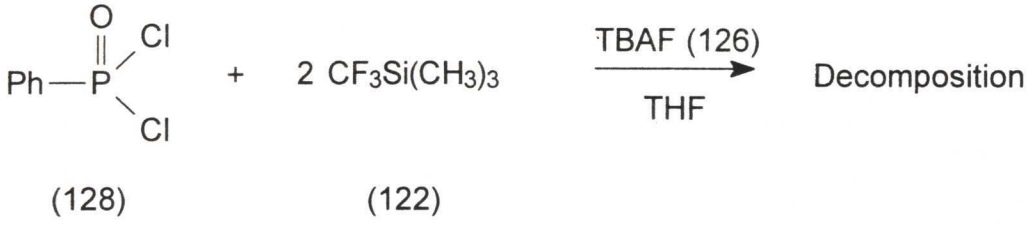
The reaction of (trifluoromethyl)trimethylsilane (**122**) with $R\text{-}P(O)Cl_2$ was attempted to determine whether the effective substitution of the trifluoromethyl group for chloride could be induced by this reagent, and to examine whether the phosphorus-oxygen bond facilitates this reaction in preference to the dichlorophosphine (**125**) examined already (Scheme 2.16).



Scheme 2.16

(Trifluoromethyl)trimethylsilane (**122**) was added to dichlorophenylphosphine oxide (**128**) in THF solution at 0°C in the presence of tetra-*n*-butylammonium fluoride (TBAF) (**126**) under a variety of reaction conditions, and the reaction was monitored by ^{31}P NMR

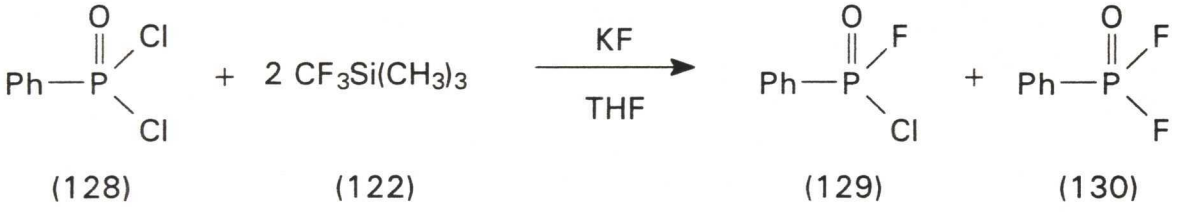
spectroscopy. No trifluoromethylated phosphines were detected, and the only products observed arose from decomposition of dichlorophenylphosphine oxide **(128)** by water present in the tetra-*n*-butylammonium fluoride **(126)** (Scheme 2.17). Again, attempts to dry **(126)** to avoid this decomposition lead only to its decomposition, consistent with literature reports.[86]



(128) (122)

Scheme 2.17

A fluorinating agent which could be dried was used in this reaction to avoid the decomposition of dichlorophenylphosphine oxide **(128)** by water. Dichlorophenylphosphine oxide **(128)** was reacted with CF_3TMS **(122)** under identical conditions as above, but in the presence of potassium fluoride. Again no trifluoromethylated phosphines were observed, however after a short time at room temperature, ^{31}P NMR analysis showed the formation of two products, exhibiting peaks at δ 11.4 ppm (triplet, $^1J_{P\text{-}F}$ = 1100 Hz) and δ 13.5 ppm (doublet, $^1J_{P\text{-}F}$ = 985 Hz) (Figure 2.2). These products are assigned as chlorofluorophenylphosphine oxide **(129)** and difluorophenylphosphine oxide **(130)**, again arising from substitution of fluoride for chloride on phosphorus (Scheme 2.18).



(128) (122) (129) (130)

Scheme 2.18

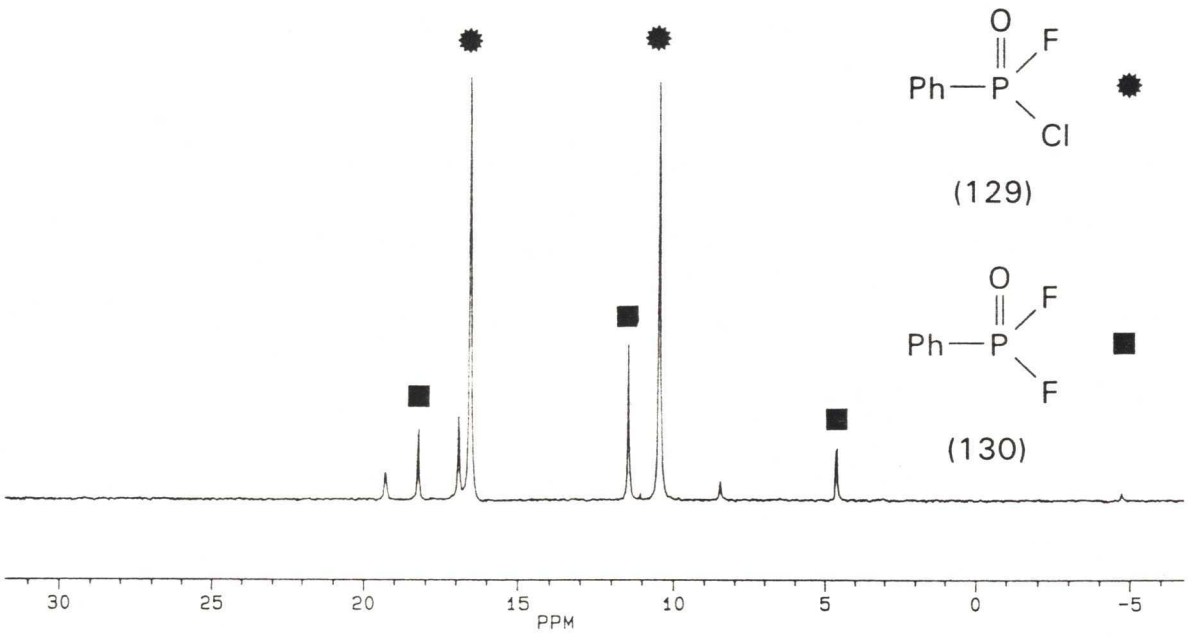


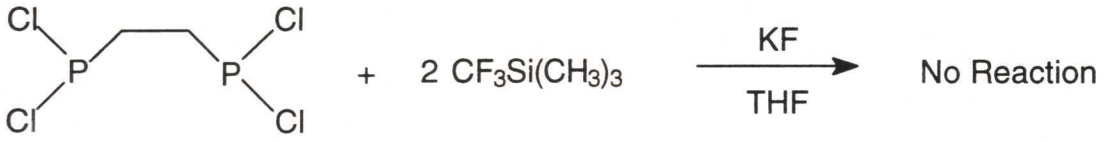
Figure 2.2 : $^{31}P\{^{1}H\}$ NMR spectrum of a mixture of chlorofluorophenylphosphine **(129)** and difluorophenylphosphine **(130)** in THF at room temperature.

The $^{31}P\{^{1}H\}$ NMR spectrum of difluorophenylphosphine oxide **(130)** is reported in the literature as a triplet ($^{1}J_{P\text{-}F}$ = 1105 Hz) at δ 11.5 ppm,[88] very similar to the experimental spectrum obtained for **(130)** in this work (δ 11.4 ($^{1}J_{P\text{-}F}$ = 1100 Hz) ppm). The only $^{31}P\{^{1}H\}$ NMR data reported for chlorofluorophenylphosphine oxide **(129)** (δ 30.4 ppm, $^{1}J_{P\text{-}F}$ = 1140 Hz)[88] does not agree well with the experimental data obtained for this compound in this work (δ 13.5 ($^{1}J_{P\text{-}F}$ = 985 Hz) ppm.

After an extended period of time at room temperature, the ^{31}P NMR spectrum of this reaction mixture showed the formation of a single trifluoromethyl group attached to phosphorus, at δ 8.2 ppm. Substitution of a second trifluoromethyl group was never observed, and it is not yet clear how this reaction proceeds. Due to the time required for the formation of a mono(trifluoromethyl) phosphine, and the fact that further reaction did not occur, no further investigation of this reaction was undertaken.

2.2.2.3 Reaction of dcpe with (trifluoromethyl)trimethylsilane

The reaction of (trifluoromethyl)trimethylsilane (**122**) and dcpe (**12**) was carried out in the presence of a catalytic amount of potassium fluoride in THF. Analysis of the reaction mixture by ^{31}P NMR spectroscopy after a prolonged reaction time showed that dcpe (**12**) was the predominant phosphorus-containing compound present (Scheme 2.19). No resonances arising from trifluoromethylation or fluoride substitution of dcpe (**12**) were observed.



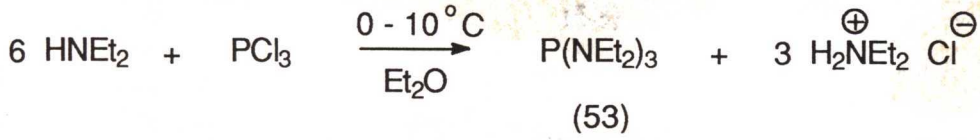
(12) (122)

Scheme 2.19

Although (trifluoromethyl)trimethylsilane (**122**) is a useful reagent for carrying out trifluoromethylation of carbonyl compounds, (**122**) was not found to be a useful reagent for the synthesis of trifluoromethylated phosphines.

2.2.3 Trifluoromethyl bromide and hexaethylphosphorus triamide, hepa

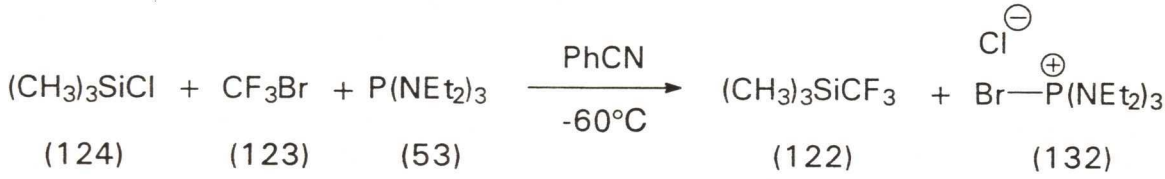
Hexaethylphosphorus triamide, hepa (**53**), is commercially available, but may be prepared by the method of Mark,[89] a modification of the original method reported by Stuebe and Lankelma (Scheme 2.20).[90]



Scheme 2.20

Phosphorus triamides are known to be extremely nucleophilic compounds which are reported to undergo a vast number of reactions where the driving force is the oxidation of the phosphorus atom from III to V.[91]

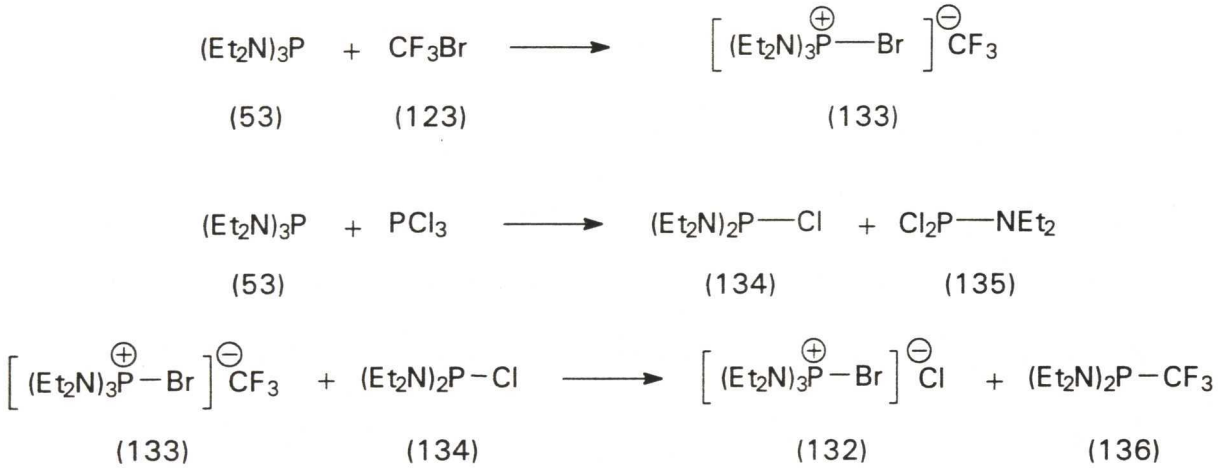
Hexaethylphosphorus triamide, hepa **(53)**, is used in the synthesis of (trifluoromethyl)-trimethylsilane **(122)** to transfer the trifluoromethyl group from trifluoromethyl bromide **(123)** to trimethylsilyl chloride **(124)** (Section 2.2.2).[83] One product of this reaction is the dihalogenated hepa species **(132)**, the oxidised form of hepa **(53)** (Scheme 2.21). The driving force for this transformation is the change in oxidation state of the hepa phosphorus atom from III to V.



Scheme 2.21

The mechanism of this transformation is not discussed in the literature, but it is clear that hepa **(53)** is acting as a powerful reagent where potential for oxidation can be used to drive otherwise difficult transformations. The combination of trifluoromethyl bromide **(123)** and hepa **(53)** is effectively a trifluoromethyl anion equivalent.

In 1983, Ruppert and co-workers reported the reaction of hepa **(53)** with trifluoromethyl bromide **(123)** and formed the phosphonium salt **(133)** shown in Scheme 2.22.[92] Hepa **(53)** also disproportionates with phosphorus trichloride to form bis(diethylamino)chlorophosphine **(134)** and dichlorodiethylaminophosphine **(135)**. The phosphorus-chlorine bond in **(134)** is then attacked by the phosphonium salt **(133)**, and results in the trifluoromethylated phosphine $(Et_2N)_2P\text{-}CF_3$ **(136)** (Scheme 2.22).[92]



Scheme 2.22

This reaction reported by Ruppert demonstrates that hepa **(53)** has the capability to effect the transfer of a trifluoromethyl group to a chlorophosphine, as well as to a chlorosilane. The reaction of hepa **(53)** with chlorophosphines was examined to test the versatility of this reagent for the synthesis of trifluoromethylated phosphines.

2.3 The preparation of 1,2-bis(bis(trifluoromethyl)phosphino)ethane, dfmpe

2.3.1 The synthesis of dfmpe

The combination of reagents used to prepare (trifluoromethyl)trimethylsilane **(122)** (Section 2.2.2) was employed in an attempt to effect trifluoromethylation of 1,2-bis(dichlorophosphino)ethane **(12)** to synthesise dfmpe **(50)**.[93] An excess of hepa **(53)** was added dropwise to a mixture of 1,2-bis(dichlorophosphino)ethane **(12)** and excess trifluoromethyl bromide **(123)** in dichloromethane at -78°C. As hepa **(53)** was added, the solution became clear and upon the completion of addition of hepa **(53)**, a pale yellow colour was observed. ^{31}P NMR analysis of the reaction mixture at 200K, 30 minutes after addition of hepa **(53)** showed that excess hepa **(53)**, the oxidised hepa-derivative **(132)** (hepaX_2, X = Br, Cl) and dfmpe **(50)** were the main phosphorus-containing compounds present in solution (Figure 2.3(a)).

If a portion of the reaction mixture was allowed to warm to room temperature, a deep orange colour became apparent and a gas was evolved. ^{31}P NMR analysis at 200K of a portion of the reaction mixture warmed to room temperature for 5 minutes showed some decomposition of dfmpe **(50)** (Figure 2.3(b). A ^{31}P NMR spectrum at 200K of the same sample after it had been warmed to room temperature for 30 minutes showed significant decomposition of both excess hepa **(53)** and dfmpe **(50)** (Figure 2.3(c)).

Almost complete decomposition of dfmpe **(50)** was observed after a portion of the reaction mixture was warmed to room temperature and allowed to stand for 1 hour. ^{1}H NMR analysis showed the formation of a significant amount of fluoroform, CF_3H, in these samples and in any dfmpe reaction mixture which was allowed to warm to room temperature.

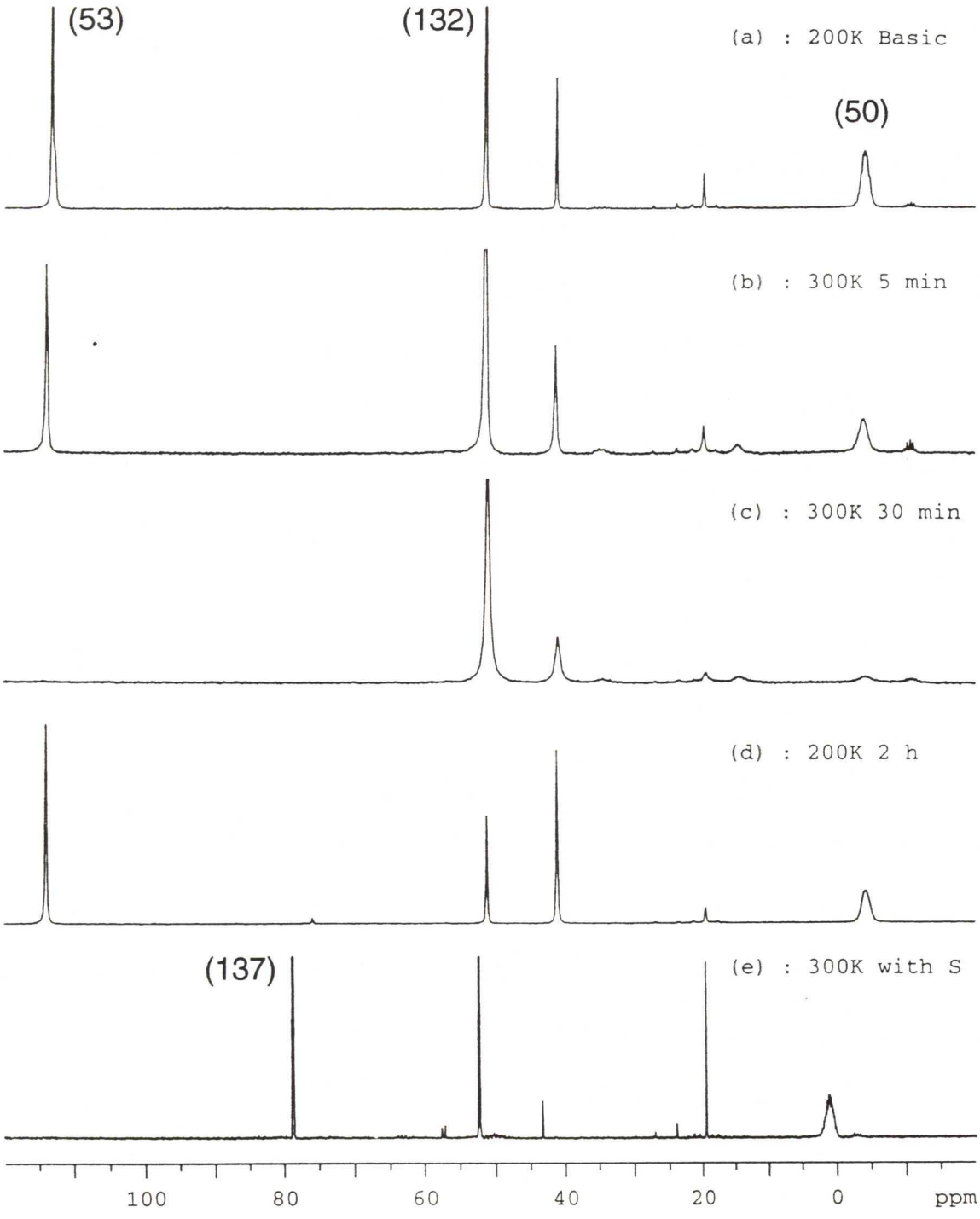


Figure 2.3 : (a) $^{31}P\{^{1}H\}$ NMR spectrum of reaction mixture of dfmpe synthesis at 200K, 30 min after completion of reaction

(b) $^{31}P\{^{1}H\}$ NMR spectrum of reaction mixture of dfmpe synthesis at 200K, after warming sample to room temperature for 5 min.

(c) $^{31}P\{^{1}H\}$ NMR spectrum of reaction mixture of dfmpe synthesis at 200K, after warming sample to room temperature for 30 min.

(d) $^{31}P\{^{1}H\}$ NMR spectrum of reaction mixture of dfmpe synthesis at 200K, 2 h after completion of reaction.

(e) $^{31}P\{^{1}H\}$ NMR spectrum of reaction mixture of dfmpe synthesis at 300K, after warming reaction mixture to room temperature in the presence of sulfur powder.

The liberation of fluoroform suggests that the observed decomposition of dfmpe (**50**) is occurring by a process involving single electron transfer. Fluoroform was also observed by Bennett, Emeleus and Haszeldine in the decomposition of tris(trifluoromethyl)phosphine (**39**) under basic conditions, however no further mechanistic information is given.[40]

Excess hepa (**53**) was required in the reaction to ensure that full substitution of the tetrachlorophosphine (**12**) occurred to form dfmpe (**50**). The instability of dfmpe (**50**) in the presence of excess hepa (**53**) at room temperature required that excess (**53**) had to be removed before the reaction mixture was allowed to warm to room temperature.

2.3.2 Removal of excess hepa from dfmpe reaction mixture

Excess hepa (**53**) could be successfully removed from the reaction mixture by reaction with elemental sulfur. Hexaethylphosphorothioic triamide (**137**) forms readily as a result of the facile oxidation potential of hepa (**53**).[90] A portion of the reaction mixture was allowed to warm to room temperature in the presence of excess sulfur powder. Analysis of this sample of the reaction mixture by ^{31}P NMR spectroscopy at room temperature showed that excess hepa (**53**) was converted cleanly to hexaethylphosphorothioic triamide (**137**) (δ 78.1 ppm), which was prepared independently by addition of sulfur powder to hepa (**53**) at room temperature. Furthermore, the $^{31}P\{^{1}H\}$ NMR spectrum of this sample of the reaction mixture showed that little decomposition of dfmpe (**50**) had occurred, and that dfmpe (**50**) was still the only trifluoromethylated phosphorus-containing product in the reaction mixture (Figure 2.3(e). ^{1}H NMR analysis of this sample showed no formation of fluoroform. The colour of the reaction mixture also remained pale yellow in contrast to the dark orange colour of the reaction mixture warmed to room temperature in the presence of excess hepa (**53**).

2.3.3 Separation and isolation of dfmpe

The dramatic influence of the trifluoromethyl group on the physical properties of organic compounds was discussed in Section 1.6.4, and is also apparent in the physical properties of dfmpe **(50)**. While dmpe **(6)** (b. p. 26°C at 1 mmHg)[94] is separable from solvents such as ether by removal of the solvent under vacuum, dfmpe **(50)** co-distils with dichloromethane under high vacuum at room temperature. The volatile nature of dfmpe **(50)** allows its separation from the non-volatile by-products of the dfmpe synthesis, namely hexaethylphosphorothioic triamide **(137)** and the oxidised hepa-derivative **(132)** (hepaX_2, X = Br, Cl). Subjecting the reaction mixture containing hexaethylphosphorothioic triamide **(137)**, the oxidised hepa-derivative **(132)** (hepaX_2, X = Br, Cl) and dfmpe **(50)** to high vacuum and condensing all volatiles obtained in a trap at liquid nitrogen temperature produced a solution consisting exclusively of a mixture of dichloromethane and dfmpe **(50)**.

Dfmpe **(50)** was easily obtained as a solution in dichloromethane, and the product yield was estimated by integration against an internal standard in the ^{19}F NMR spectrum ($CF_3COONHPh$) and ^{1}H NMR and ^{31}P NMR spectra ($PhP(O)(OCH_3)_2$). The yield of the reaction was estimated at 20%, and dfmpe **(50)** was used in most subsequent reactions as a solution in dichloromethane. This yield is surprisingly low, considering the clean conversion of dcpe **(12)** to dfmpe **(50)** indicated by a $^{31}P\{^{1}H\}$ NMR spectrum of the crude reaction mixture (Figure 2.3(a)). This low yield reflects the difficulty in removing dfmpe **(50)** from the extremely viscous reaction mixture which remains once the dichloromethane is removed under vacuum, not in synthesising dfmpe **(50)** by this method.

Several methods for isolating dfmpe **(50)** from the reaction mixture were attempted. Chromatographic techniques were employed in an effort to separate dfmpe **(50)** from the viscous hepa by-products formed in the reaction. A small amount of the reaction mixture was flushed through a plug of flash silica, and eluted with dichloromethane. The oxidised hepa-derivative **(132)** was completely removed by this process, however the hepa-sulfide **(137)** was eluted along with dfmpe **(50)**. Dfmpe **(50)** and hepa-sulfide **(137)** could be separated by careful chromatography of the reaction mixture. This technique was successful on a small scale but was much more difficult to apply to the entire reaction mixture, a typical reaction mixture containing approximately 34 g of hepa-derived products. In addition, the volatile nature of dfmpe **(50)** meant that removal of solvent used in the chromatography process was not possible, so this separation technique was not pursued further.

A variety of other separation techniques were attempted in order to isolate dfmpe **(50)**. Column chromatography through alumina using a variety of solvents, addition of a solid support (celite) to adsorb the viscous reaction mixture and allow more efficient removal of the volatile components from the mixture, addition of counterions (KPF_6) to precipitate out the oxidised hepa-derivative **(132)** (hepaX_2, X = Cl, Br), hydrolysis of the hepa-derivative **(132)** by addition of methanol, ethanol and water at various pHs, and extraction of the reaction mixture with solvents such as ether and toluene, were all attempted. None of these techniques enabled the isolation of dfmpe **(50)** from the by-products of its synthesis.

The best method found for the separation of dfmpe **(50)** from by-products formed in its synthesis was to Kugelrohr the crude reaction mixture under high vacuum for several hours at room temperature.

The NMR spectra of dfmpe **(50)** are shown in Figure 2.4. Although dfmpe **(50)** is a relatively simple and symmetrical molecule, its NMR spectra are complicated by the fact that it contains several NMR-active nuclei and the molecular symmetry dictates that the ^{19}F nuclei are magnetically non-equivalent, the ^{31}P nuclei are magnetically non-equivalent and the ^{1}H nuclei are magnetically non-equivalent. The $^{31}P\{^{1}H\}$ NMR spectrum (Figure 2.4(a)) appears as a symmetrical fluorine-coupled multiplet at δ 0.2 ppm; the ^{19}F NMR spectrum (Figure 2.4(b)) is a symmetrical multiplet dominated by two intense lines centred at δ -51.5 ppm and the ^{1}H NMR spectrum (Figure 2.4(c)) is a deceptively simple 3-line multiplet centred at δ 2.29 ppm, typical of the "filled-in" doublet[95] frequently encountered in the spectra of $X_2PCH_2CH_2PX_2$ species. The $^{13}C\{^{1}H, ^{31}P\}$ NMR spectrum consists of two resonances δ 14.9 ($-CH_2-$) and δ 128.4 ppm with a carbon-fluorine coupling of 325 Hz.

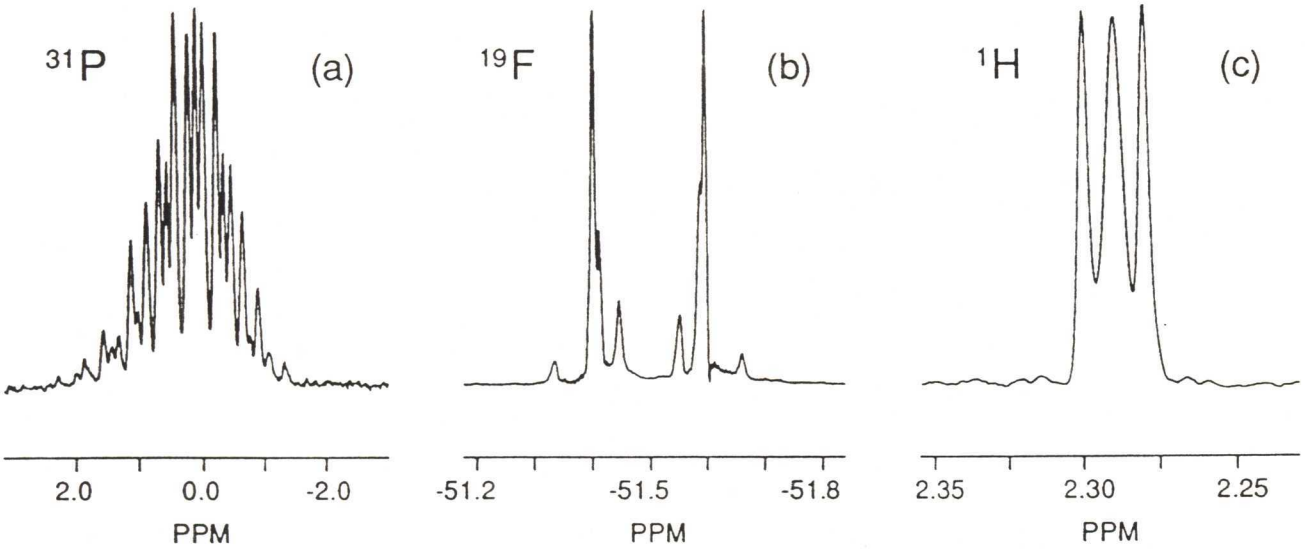


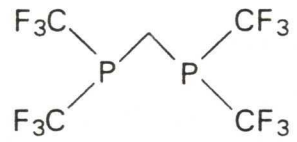
Figure 2.4 : (a) $^{31}P\{^{1}H\}$ NMR spectrum of dfmpe **(50)** (CH_2Cl_2 solvent, 25°C)
(b) ^{19}F NMR spectrum of dfmpe **(50)** ($CDCl_3$ solvent, 25°C);
(c) ^{1}H NMR spectrum of dfmpe **(50)** (CH_2Cl_2 solvent, 25°C).

The spectroscopic data obtained for dfmpe (**50**) are consistent with that previously described in the literature.[58,61]

The appearance of a second product was often observed in the dichloromethane solutions of dfmpe (**50**) obtained by vacuum transfer. This product was assigned as 1,2-bis(bis(trifluoromethyl)phosphino)methane, $(CF_3)_2PCH_2P(CF_3)_2$ (**138**) using spectroscopic techniques. $(CF_3)_2PCH_2P(CF_3)_2$ (**138**) was observed if the dichloromethane used as reaction solvent was not distilled immediately prior to use, and was also observed if the crude dfmpe reaction mixture was left at room temperature for an extended period of time. $(CF_3)_2PCH_2P(CF_3)_2$ (**138**) was also observed if the dfmpe reaction mixture was heated while vacuum transfer was taking place.

$(CF_3)_2PCH_2(CF_3)_2$ (**138**) has a similar structure to dfmpe (**50**), but has a methylene bridge joining the two bis(trifluoromethyl)phosphino groups. The symmetry of this compound results in $(CF_3)_2PCH_2P(CF_3)_2$ (**138**) having NMR spectra similar in chemical shift and appearance to those exhibited by dfmpe (**50**). The NMR spectra of (**138**) are shown in Figure 2.5.

$(CF_3)_2PCH_2P(CF_3)_2$ (**138**) exhibits a $^{31}P\{^1H\}$ NMR spectrum consisting of a fluorine-coupled multiplet at δ -7.0 ppm. The ^1H NMR spectrum of (**138**) shows a sharp phosphorus-coupled triplet at δ 2.62 ppm ($^2J_{P\text{-}H}$ = 2.5 Hz), while the ^{19}F NMR spectrum exhibits a second order multiplet similar in complexity to that of dfmpe (**50**), at δ -52.1 ppm. The NMR data obtained for (**138**) is identical to previous literature reports of $(CF_3)_2PCH_2P(CF_3)_2$ (**138**).[61]



(138)

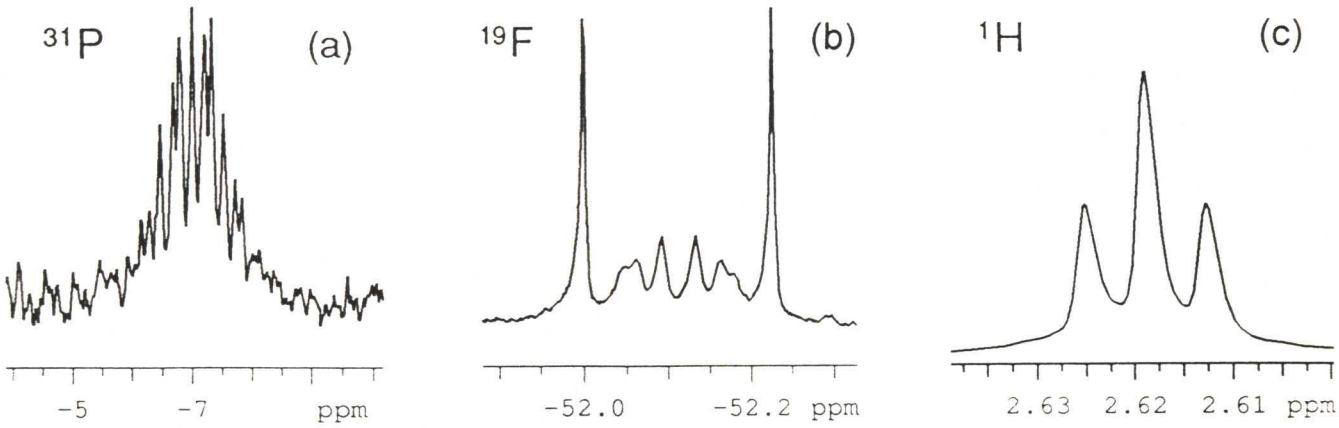


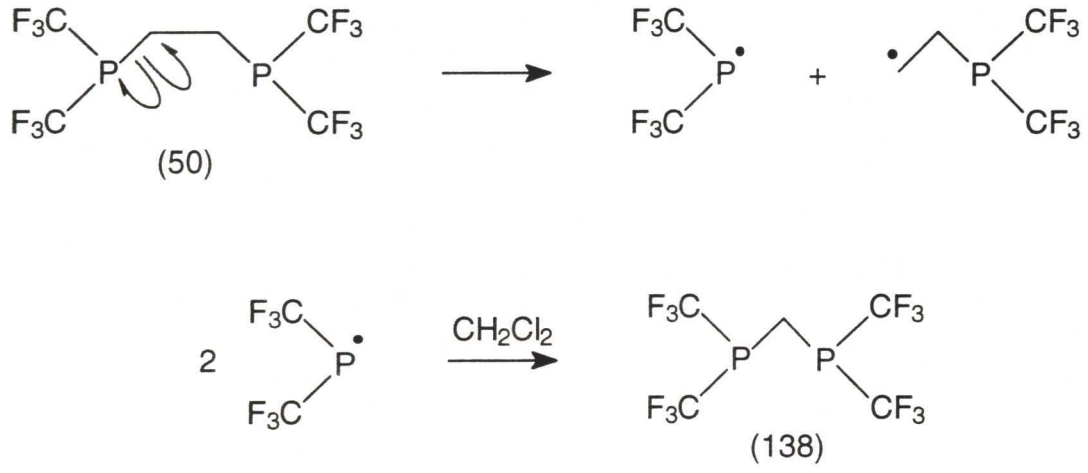
Figure 2.4 : (a) $^{31}P\{^{1}H\}$ NMR spectrum of $(CF_3)_2PCH_2P(CF_3)_2$ **(138)** (CH_2Cl_2 solvent, 25°C)

(b) ^{19}F NMR spectrum of $(CF_3)_2PCH_2P(CF_3)_2$ **(138)** (CH_2Cl_2 solvent, 25°C);

(c) ^{1}H NMR spectrum of $(CF_3)_2PCH_2P(CF_3)_2$ **(138)** (CH_2Cl_2 solvent, 25°C).

The mechanism by which **(138)** is formed is by no means obvious. The compound is apparently formed both during the course of the reaction, if the solvent has not been dried thoroughly, and in the reaction mixture if left untreated. Solutions of dichloromethane containing dfmpe **(50)** only, obtained through vacuum distillation of the reaction mixture are stable and show no formation of **(138)**, even after several months of storage at room temperature.

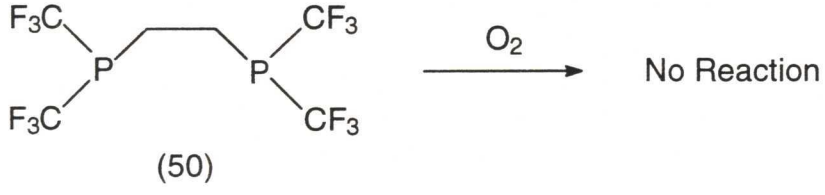
$(CF_3)_2PCH_2P(CF_3)_2$ **(138)** may be formed as a consequence of the radical decomposition of dfmpe **(50)** to form alkyl and fluoroalkyl phosphinyl radicals, $[(CF_3)_2P]^{\bullet}$. Such phosphinyl radicals are expected to be substantially stabilised by the presence of the electron-withdrawing trifluoromethyl groups bound to phosphorus. Reaction of bis(trifluoromethyl)phosphinyl radicals with dichloromethane in a series of single electron processes may result in the formation of $(CF_3)_2PCH_2P(CF_3)_2$ **(138)** (Scheme 2.23).



Scheme 2.23

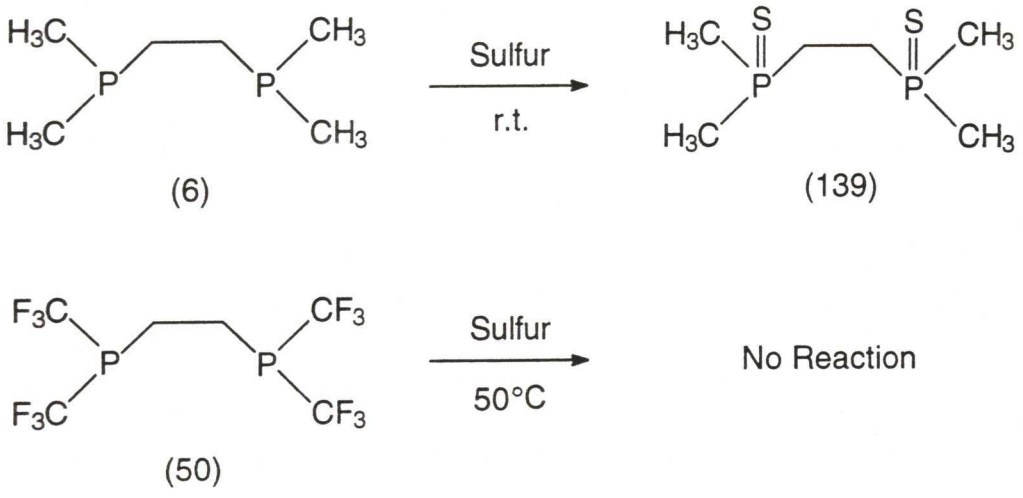
2.3.4 Properties of dfmpe

Dfmpe **(50)** is stable in dichloromethane solution for indefinite periods in the presence of air, unlike dmpe **(6)** which oxidises readily in the presence of air (Scheme 2.24).[94]



Scheme 2.24

Attempts to form a sulfurised derivative of dfmpe by reaction of dfmpe (**50**) with sulfur powder, even at elevated temperatures and in the presence of aluminium trichloride as an initiator gave no trace of the dfmpe mono- or di-sulfide. This is again in contrast to the reaction of dmpe (**6**) with elemental sulfur, which forms dmpe disulfide (**139**) rapidly and cleanly at room temperature (Scheme 2.25).[94]



Scheme 2.25

Dfmpe (**50**) is a very volatile compound, and although it can be separated from mixtures and solvents by gas chromatography, it is difficult to purify by distillation as it readily co-distils with solvents such as dichloromethane.

2.3.5 Variations of the synthesis of dfmpe

In an attempt to improve the yield of dfmpe (**50**) and the ease with which dfmpe (**50**) could be separated from the reaction mixture, the reaction conditions were varied. Changes made included use of different solvents and variations in the relative proportions of reagents used.

2.3.5.1 Variations in solvent in dfmpe synthesis

The synthesis of dfmpe (**50**) was attempted using several different solvents including benzonitrile, tetrahydrofuran, dichloromethane, toluene and *m*-toluonitrile. While in all cases, ^{31}P NMR analysis of the crude reaction mixtures showed dfmpe (**50**) as the primary trifluoromethylated phosphorus-containing product, dichloromethane and tetrahydrofuran were found to be the solvents of choice.

The high melting point of benzonitrile (approximately 60°C higher than the boiling point of trifluoromethyl bromide (**123**)) did not permit a homogeneous reaction mixture until close to room temperature. Prakash and co-workers used benzonitrile to synthesise CF_3TMS (**122**) (Section 2.2.2) and its high boiling point does not appear to affect the efficiency of the reaction. However, in the synthesis of dfmpe (**50**) in which four sites must be trifluoromethylated, an excess of trifluoromethyl bromide (**123**) in solution is considered essential. A solvent which has a melting point below the boiling point of trifluoromethyl bromide (**123**) (-58°C) is desirable for this reaction.

When the synthesis of dfmpe (**50**) was attempted using toluene as solvent, two immiscible layers were formed. Analysis of both layers by ^{31}P NMR revealed the presence of several phosphorus-containing by-products, which were not observed when dichloromethane was employed as the reaction solvent.

Dichloromethane was the solvent of choice for the synthesis of dfmpe (**50**) as it promoted clean reaction, had a low freezing point ensuring a homogeneous reaction mixture, and enabled convenient isolation of dfmpe (**50**) by vacuum distillation.

2.3.5.2 Variations in ratio of reagents in dfmpe synthesis

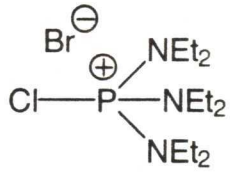
The synthesis of dfmpe (**50**) was attempted using the stoichiometric amount of hepa (**53**) required to effect conversion of dcpe (**12**) to dfmpe (**50**), that is, four equivalents of hepa (**53**) with respect to dcpe (**12**).

When four equivalents of hepa (**53**) were added to one equivalent of dcpe (**12**) and four equivalents of trifluoromethyl bromide (**123**) in dichloromethane, ^{31}P NMR analysis of the crude reaction mixture showed the formation of a mixture of trifluoromethylated products. When the amount of hepa (**53**) and trifluoromethyl bromide (**123**) was increased to eight equivalents, dfmpe (**50**) was the sole trifluoromethylated product observed. An excess of both hepa (**53**) and trifluoromethyl bromide (**123**) is required to complete full trifluoromethylation of the four sites on 1,2-bis(dichlorophosphino)ethane (**12**).

2.3.6 Reaction mechanism of dfmpe synthesis

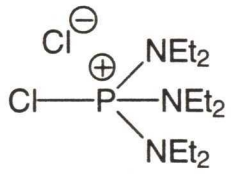
The mechanism of reaction of hexaethylphosphorus triamide (**53**) and trifluoromethyl bromide (**123**) with phosphorus halides is essentially unknown, however there are certain facts about the synthesis which have mechanistic implications.

1) In the course of the synthesis of dfmpe (**50**), hepa (**53**) is converted to an oxidised hepa-derivative (**132**) which exhibits a resonance in the ^{31}P NMR spectrum at δ 52 ppm. This species is common to the synthesis of (trifluoromethyl)trimethylsilane (**122**), and was assigned by Prakash and co-workers as the chloro-bromo-hepa compound (**132**).

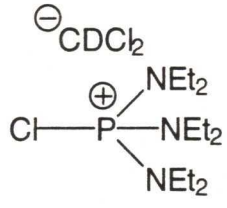


(132)

Hepa (**53**) was found to be unstable in chloroform solution, decomposing to products which exhibit resonances in the ^{31}P NMR spectrum at a similar chemical shift to the di-halogenated hepa-derivative (**132**) shown above. A series of ^{31}P NMR spectra was run at 30 min intervals on a sample of hepa (**53**) in $CDCl_3$ at room temperature, using an automatic program on the AMX400 NMR spectrometer (Appendix A1). After 90 min, complete reaction of hepa (**53**) had occurred to form two products, the major product (**140**) exhibiting a singlet in the ^{31}P NMR spectrum at δ 51.5 ppm, and the minor product (**141**) exhibiting a singlet in the ^{31}P NMR spectrum at δ 50.5 ppm. ^{1}H NMR and ^{13}C NMR data of the major product are consistent with its assignment as the dichloro-hepa compound (**140**). The minor product (**141**) has very similar spectral properties to (**140**), and clearly is a hepa-derivative also. It is tentatively assigned the structure shown below, however it is yet to be conclusively identified.



(140)



(141)

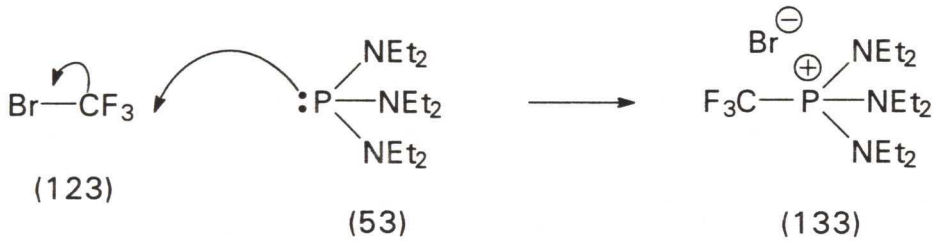
Hepa (**53**) was found to be much more stable in dichloromethane solution. A ^{31}P NMR spectrum of a solution of hepa (**53**) in dichloromethane-d_2 was run every 30 min at room temperature, using the same automatic program as described above (Appendix A1).

After 20 h, only slight decomposition of hepa **(53)** had occurred to the hepa-derivative **(140)**, exhibiting a resonance in the $^{31}P\{^{1}H\}$ NMR spectrum at δ 51.5 ppm.

2) Reaction of hepa **(53)** with dcpe **(12)** in the absence of trifluoromethyl bromide **(123)** was carried out under identical conditions to those used in the synthesis of dfmpe **(50)**. Analysis of the crude reaction mixture by $^{31}P\{^{1}H\}$ NMR showed complete conversion of dcpe **(12)** to a complex mixture of phosphorus-containing products. Similarly, the reaction of hepa **(53)** with trifluoromethyl bromide **(123)** (in the absence of dcpe **(12)**) under identical conditions resulted in complete reaction of hepa **(53)** to form several phosphorus-containing products.

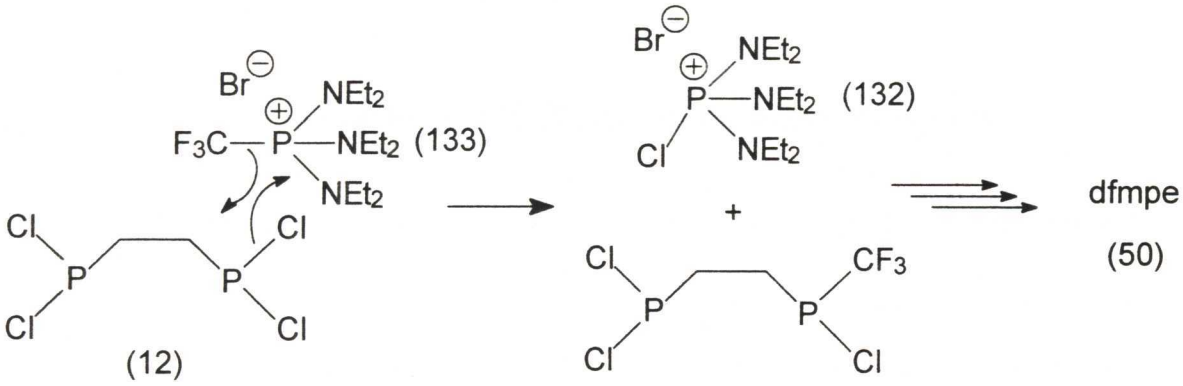
Hepa **(53)** reacts independently with each of the components present in the synthesis of dfmpe **(50)**. It is clear that this combination of reagents represents a finely balanced reaction system, involving all three reagents in a mechanistic process which has yet to be determined.

Ruppert and co-workers postulated a mechanism for the reaction between hepa **(53)** and trifluoromethyl bromide **(123)**, the first step of which involved the formation of the reactive phosphonium salt **(133)** (Scheme 2.26).[92]



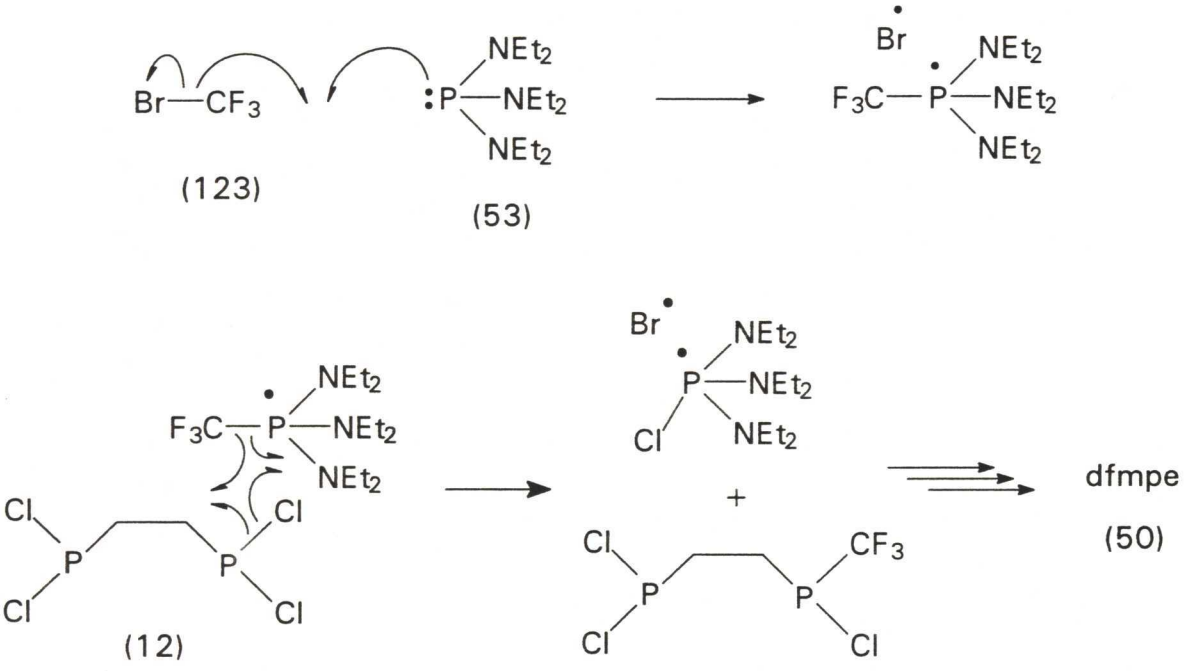
Scheme 2.26

The phosphonium salt **(133)**, which is the active trifluoromethylating reagent, then reacts via a cyclic mechanism to transfer the trifluoromethyl group to the chloro-phosphine **(12)** while accepting a chloride ion from **(12)**. Repetition of this process results in the synthesis of dfmpe **(50)** (Scheme 2.27).



Scheme 2.27

An equivalent mechanism involving radical processes, which achieves the same result as the ionic mechanism described above, can also be postulated.



Scheme 2.28

There is as yet no direct evidence to implicate either of these mechanisms. The known instability of the trifluoromethyl anion, and the known stability of the trifluoromethyl radical may suggest that a radical mechanism be favoured, however the low temperature at which this reaction occurs may be sufficient to allow formation of unstable intermediates. Further speculation on the mechanism of this transformation requires more direct evidence.

2.4 Summary of the synthesis of trifluoromethylated phosphines

In summary, while FSO_2CF_2COOMe **(119)** and $TMSCF_3$ **(122)** are useful reagents in the trifluoromethylation of general organic compounds, **(119)** and **(122)** were found to be unsuitable for the synthesis of trifluoromethylated phosphines. The synthesis of trifluoromethylated phosphines was effected by the low temperature addition of hepa **(53)** to a mixture of trifluoromethyl bromide **(123)** and the appropriate chlorophosphine. 1,2-Bis(bis(trifluoromethyl)phosphino)ethane **(50)** was synthesised by the reaction of dcpe **(12)** with hepa and trifluoromethyl bromide at low temperature. Removal of excess hepa **(53)** from the reaction mixture by addition of sulfur powder at low temperature significantly improved the yield of this procedure. Difficulties were encountered in the separation of dfmpe **(50)** from the by-products of its synthesis, however dfmpe **(50)** was obtained as a dichloromethane solution in 20% yield by vacuum transfer of all volatile material from the reaction mixture.

The physical properties of dfmpe **(50)** were found to be very different to those of its methylated analogue, dmpe **(6)**. Dfmpe **(50)** is stable for long periods in the presence of air, fails to react with sulfur under mildly vigorous conditions, and has drastically greater volatility than that of dmpe **(6)**. This volatility facilitates the separation of dfmpe **(50)** from the by-products formed in its synthesis.

The mechanism of the reaction for the synthesis of trifluoromethylated phosphines is as yet unknown. Plausible ionic and radical mechanisms have been proposed, but in the absence of direct supporting evidence, neither proposal can be favoured.

This synthesis of dfmpe **(50)** represents a very significant improvement in the ease of synthesis and hence the availability of this ligand. Gram quantities are readily accessible via a simple synthesis using standard laboratory techniques. A study of the properties of dfmpe **(50)** as an ancillary ligand for organometallic complexes is now possible. Extension of this method of synthesis of trifluoromethylated phosphines to more sophisticated ligands may also be possible.

CHAPTER 3 : REACTIONS OF DFMPE

WITH METAL COMPLEXES

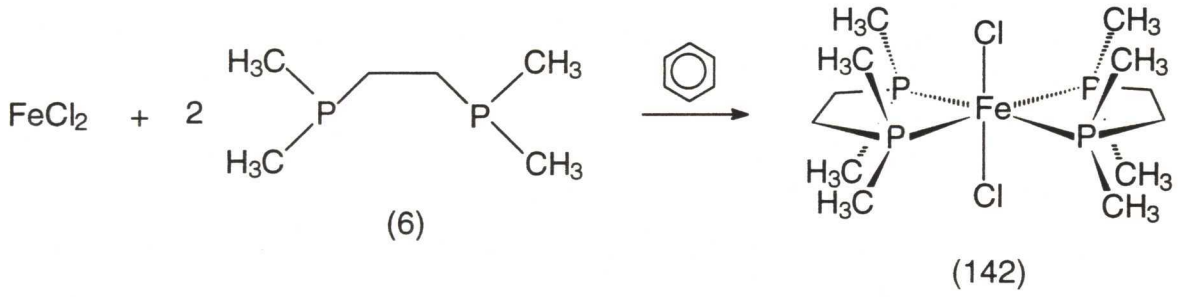
3.1 Introduction

The improved synthesis of dfmpe (**50**) described in Chapter 2 enables a study of the coordination properties of this ligand, as well as an assessment of its potential as an ancillary ligand for organometallic complexes with the potential to carry out C-H activation.

The C-H activation potential of complexes containing the methylated analogue of dfmpe (**50**), dmpe (**6**), has been extensively studied, and dmpe (**6**) has emerged as one of the most important phosphine ligands in the field of C-H activation. Dmpe (**6**) forms organometallic complexes with iron and ruthenium which have demonstrated the capability to undergo oxidative addition to the C-H bonds of organic substrates.

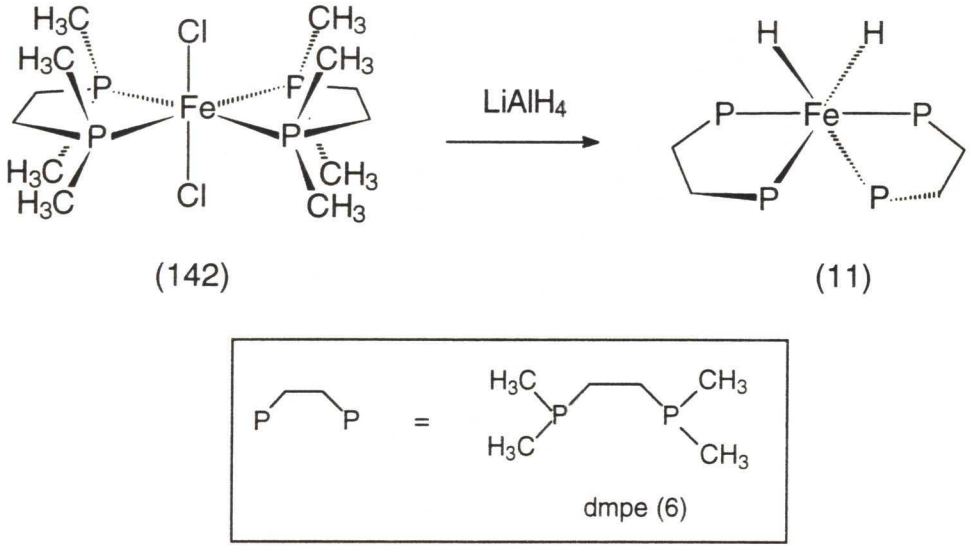
3.1.1 C-H activation reactions of iron complexes containing dmpe

An excess of dmpe (**6**) reacts readily with anhydrous iron dichloride at room temperature to form *trans*-dichloro-bis(1,2-bis(dimethylphosphino)ethane) iron (II), $FeCl_2(dmpe)_2$ (**142**), an octahedral iron complex which is unstable in the presence of oxygen (Scheme 3.1).[96]



Scheme 3.1

$FeCl_2(dmpe)_2$ **(142)** can be reduced by lithium aluminium hydride to form *cis*-dihydrido-bis(1,2-bis(dimethylphosphino)ethane) iron(II), $FeH_2(dmpe)_2$ **(11)**, first synthesised by Gerlach, Peet and Muetterties in 1973 (Scheme 3.2).[97]



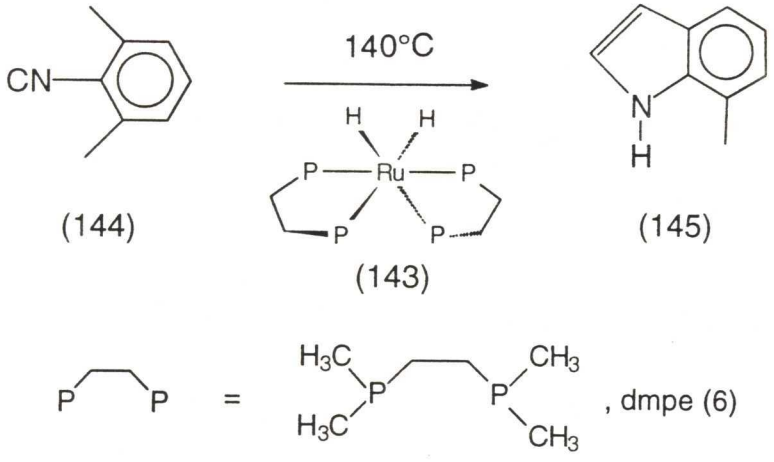
Scheme 3.2

Cis-dihydrido-bis(1,2-bis(dimethylphosphino)ethane) iron (II), $FeH_2(dmpe)_2$ **(11)**, undergoes photochemical elimination of dihydrogen to generate a reactive intermediate which undergoes C-H activation with alkanes, alkenes and arenes.[17] The first aim was to synthesise the analogous iron complex, *cis*-dihydrido-bis(1,2-bis(bis(trifluoromethyl)phosphino)ethane) iron(II), $FeH_2(dfmpe)_2$ **(112)**, and to investigate its photochemical reactivity in the presence of organic substrates.

3.1.2 C-H activation reactions of ruthenium complexes containing dmpe

$RuH_2(dmpe)_2$ **(143)** was first reported in 1965,[3] and was more fully characterised by Tolman and co-workers who synthesised this complex by the thermal reaction of

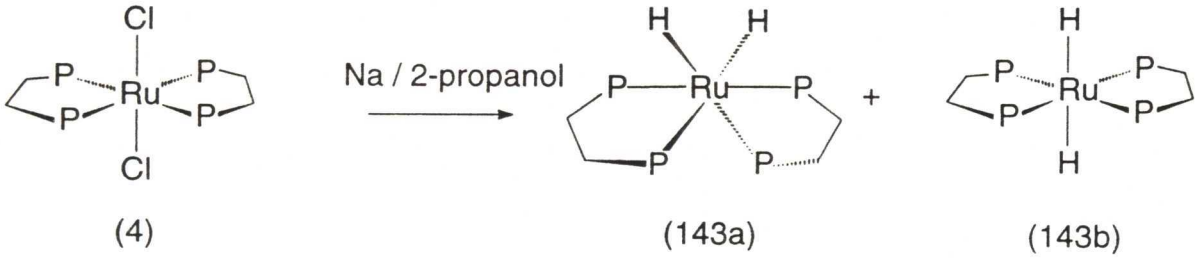
$Ru(dmpe)_2(C_{10}H_7)H$ (**5**) with H_2.[13a] $RuH_2(dmpe)_2$ (**143**) was used by Jones and Kosar to carry out the catalytic conversion of 2,6-xylyl isocyanide (**144**) into 7-methylindole (**145**), via thermal elimination of H_2 and generation of the coordinatively unsaturated intermediate, $Ru(dmpe)_2$ (**146**) (Scheme 3.3).[98]



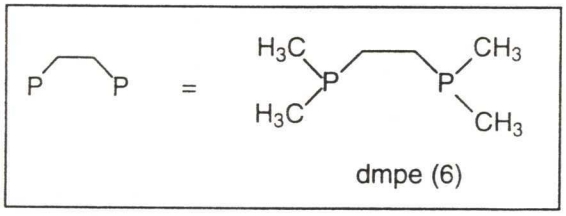
Scheme 3.3

A further report by Bergamini *et al.* showed that the loss of hydrogen from $RuH_2(dmpe)_2$ (**143**) to form the 16-electron species $Ru(dmpe)_2$ (**146**) is a concerted process.[99]

In 1988, Field and Yau reported the synthesis of $RuH_2(dmpe)_2$ (**143**) as a mixture of *cis* and *trans* isomers by reduction of *trans*-dichloro-bis(1,2-bis(dimethylphosphino)-ethane) ruthenium(II), $RuCl_2(dmpe)_2$ (**4**) using sodium metal in 2-propanol (Scheme 3.4).[100]



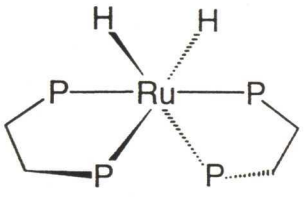
(4) (143a) (143b)



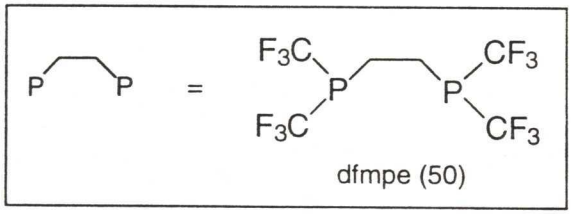
Scheme 3.4

Field and Yau also showed that the photochemically produced intermediate, $Ru(dmpe)_2$ (**146**), undergoes C-H activation with alkenes and arenes, albeit more slowly than the reaction of $Fe(dmpe)_2$ (**9**) with alkenes and arenes, however no intermolecular C-H activation was ever observed arising from the photolysis of $RuH_2(dmpe)_2$ (**143**) in the presence of alkanes.[101]

The C-H reactions carried out by $RuH_2(dmpe)_2$ (**143**) suggest that the analogous ruthenium complex containing the trifluoromethylated analog of dmpe, $RuH_2(dfmpe)_2$ (**113**), may also achieve C-H activation of organic substrates. Synthesis of dihydrido-bis(1,2-bis(bis(trifluoromethyl)phosphino)ethane) ruthenium(II), $RuH_2(dfmpe)_2$ (**113**), was attempted, and an investigation of its photochemical reactivity in the presence of organic substrates was undertaken.



(113)



3.2 Attempted formation of iron complexes containing dfmpe

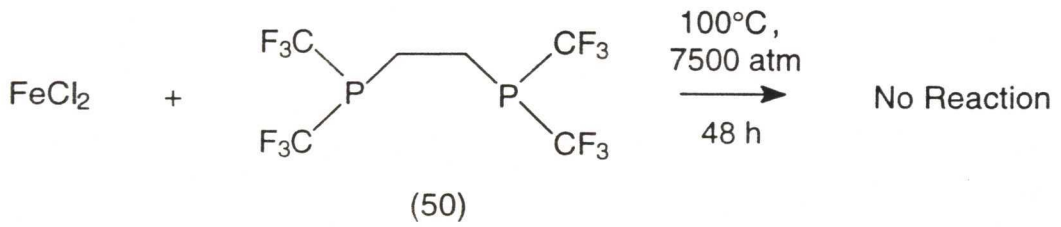
The synthesis of metal complexes may be approached in several ways. One approach that has proved successful is the displacement of one or more ligands from an existing complex by other ligands. Numerous iron complexes which contain suitably labile ligands are available which may be used to form iron complexes by substitution.

Despite numerous attempts, dfmpe **(50)** has not yet been successfully coordinated to iron. The following section describes the attempts made to coordinate dfmpe **(50)** to iron towards the synthesis of $FeH_2(dfmpe)_2$ **(112)**, by displacement of labile ligands from a series of precursor iron complexes.

3.2.1 Reaction of dfmpe with anhydrous iron(II) chloride

The first attempt to synthesise $FeH_2(dfmpe)_2$ **(112)** involved the reaction of dfmpe **(50)** with anhydrous iron dichloride, the iron precursor which has been used to synthesise $FeCl_2(dmpe)_2$ **(142)** and subsequently $FeH_2(dmpe)_2$ **(11)**.

Anhydrous iron dichloride was added to a solution of 2 equivalents of dfmpe **(50)** in dichloromethane and stirred for 24 h. Subsequent analysis of the reaction mixture by ^{19}F NMR spectroscopy showed that dfmpe **(50)** was the only fluorine-containing product present. Even when the reaction mixture was heated at 50°C for 12 h, and subsequently subjected to high pressure (7500 atm) at room temperature for 24h, ^{19}F NMR analysis of the reaction mixture again showed no formation of products. The reaction mixture was heated to 100°C at 7500 atm for a further 48h, but again no products were observed by ^{19}F NMR (Scheme 3.5). Dfmpe **(50)** was recovered unchanged from the reaction mixture.



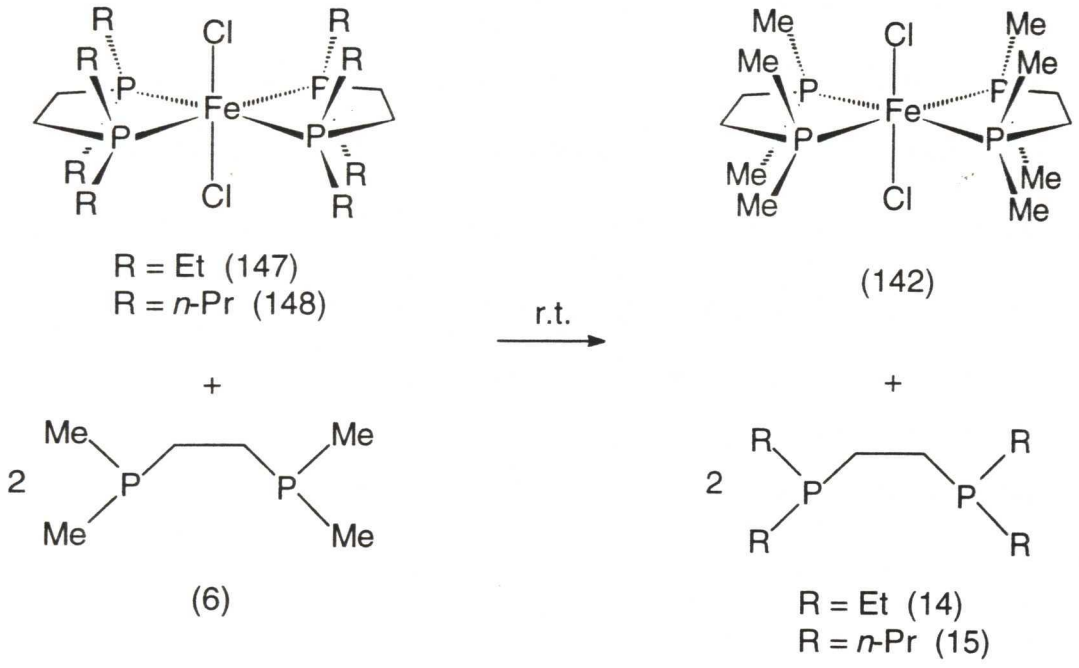
(50)

Scheme 3.5

3.2.2 Reaction of dfmpe with $FeCl_2(depe)_2$ and $FeCl_2(dprpe)_2$

Trans-dichloro-bis(1,2-bis(diethylphosphino)ethane) iron (II), $FeCl_2(depe)_2$ **(147)**, was synthesised by the method of Chatt and Hayter,[96] and *trans*-dichloro-bis(1,2-bis(di-*n*-propyl-phosphino)ethane) iron (II), $FeCl_2(dprpe)_2$ **(148)**, was synthesised by the method of Baker and Field.[20]

Both $FeCl_2(depe)_2$ **(147)** and $FeCl_2(dprpe)_2$ **(148)** are octahedral iron complexes which contain two bisphosphine ligands with bulky substituents on phosphorus. Steric crowding around the iron centre in both of these complexes is greater than in the analogous $FeCl_2(dmpe)_2$ **(142)** complex due to the bulkier bisphosphine ligands. This steric crowding makes the ligands in $FeCl_2(depe)_2$ **(147)** and $FeCl_2(dprpe)_2$ **(148)** vulnerable to displacement by less-sterically demanding ligands.[20] For example, it has been shown by Field and co-workers that when dmpe **(6)** is added to a solution of $FeCl_2(depe)_2$ **(147)** at room temperature, displacement of depe **(14)** bound to the iron centre by dmpe **(6)** rapidly occurs at room temperature, resulting in the formation of $FeCl_2(dmpe)_2$ **(142)** as the exclusive product (Scheme 3.5).[20] Similarly, the reaction of $FeCl_2(dprpe)_2$ **(148)** with two equivalents of dmpe **(6)** at room temperature again leads to quantitative formation of $FeCl_2(dmpe)_2$ **(142)** (Scheme 3.6).[20]



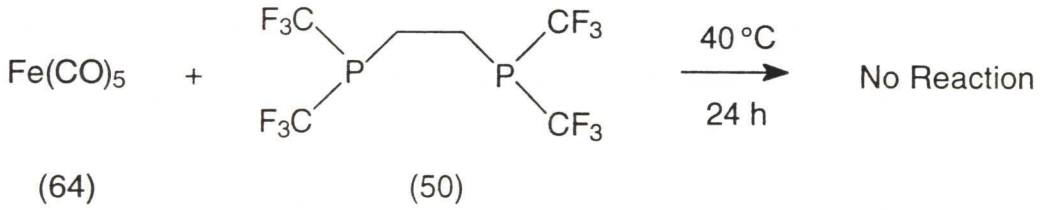
Scheme 3.6

Reactions of dfmpe (**50**) in dichloromethane were carried out with both $FeCl_2(depe)_2$ (**147**) and $FeCl_2(dprpe)_2$ (**148**), and the reactions were monitored by ^{31}P NMR and ^{19}F NMR spectroscopy. No displacement of depe (**14**) or dprpe (**15**) by dfmpe (**50**) was observed by ^{31}P NMR spectroscopy, while a ^{19}F NMR spectrum of both reaction mixtures showed dfmpe (**50**) as the only fluorinated species present. Even after several days of reaction at room temperature, there was no indication of displacement of depe (**14**) or dprpe (**15**) by dfmpe (**50**) in either of these reactions. Dfmpe (**50**) was again recovered unchanged by vacuum-transfer of all volatile material from the reaction vessel.

3.2.3 Reaction of dfmpe with $Fe(CO)_5$

Iron pentacarbonyl (**64**) is a commercially available iron precursor which has been used extensively to synthesise phosphine-containing iron complexes by displacement of carbon monoxide.[51]

A solution of dfmpe (**50**) in dichloromethane was added to a solution of iron pentacarbonyl (**64**) in toluene and stirred at room temperature for 24 h. Analysis of the resulting solution by ^{31}P NMR showed dfmpe (**50**) as the only fluorine-containing product. The mixture was heated at 40°C for 24 h, however ^{31}P NMR analysis again showed no trace of complexed dfmpe, and only free dfmpe (**50**) remaining (Scheme 3.7).



(64) (50)

Scheme 3.7

In summary, the affinity of dfmpe (**50**) for iron was found to be much lower than that of dmpe (**6**), to the extent that no iron complex containing dfmpe (**50**) was ever isolated (or even observed). The electron-withdrawing properties of the trifluoromethyl groups may be causing poor σ-donor properties of the phosphorus atoms in dfmpe (**50**), and a first row transition metal such as iron may not be able to back-donate electrons in order to bind dfmpe (**50**) strongly.

Substitution reactions with dfmpe (**50**) were complicated by the fact that (**50**) could only conveniently be used as a solution in dichloromethane, and so vigorous reaction conditions could not be employed. It is interesting to note that only one iron complex of dfepe (**51**) has been reported, by Brookhart and co-workers in 1992.[29] Fe(dfepe)$(CO)_3$ (**101**) was synthesised by refluxing a mixture of dfepe (**51**) with (benzylideneacetone)$Fe(CO)_3$ (**102**) in toluene (i.e at temperatures of approximately 110°C). If vigorous conditions are necessary to form analogous dfmpe complexes of iron, the difficulty encountered in separating

dfmpe (**50**) from dichloromethane is a limitation, and alternative solvents need to be employed in order to achieve more vigorous conditions.

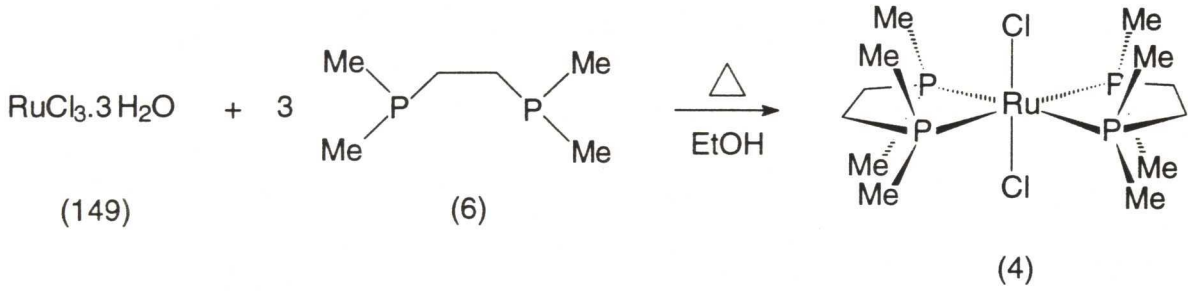
Reactions with dfmpe (**50**) are simplified by the fact that unreacted dfmpe (**50**) can be easily recovered from unsuccessful reactions by vacuum transfer of all volatile material from the reaction mixture.

3.3 Formation of ruthenium complexes containing dfmpe

The synthesis of $RuH_2(dfmpe)_2$ (**113**) was attempted by the addition of dfmpe (**50**) to appropriate ruthenium complexes containing vacant coordination sites or by substitution of ruthenium complexes containing labile ligands.

3.3.1 Reaction of dfmpe with $RuCl_3.3H_2O$

The synthesis of $RuH_2(dmpe)_2$ (**143**) has been achieved by the reaction of ruthenium trichloride trihydrate (**149**) with three equivalents of dmpe (**6**) to form $RuCl_2(dmpe)_2$ (**4**) (Scheme 3.8).[100]



(149) (6) (4)

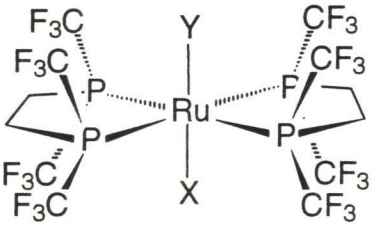
Scheme 3.8

The reaction of ruthenium trichloride trihydrate (**149**) with dfmpe (**50**) was investigated as a possible route to the analogous *trans*-dichloro-bis(1,2-bis(bis(trifluoromethyl)phosphino)-ethane) ruthenium (II), $RuCl_2(dfmpe)_2$ (**150**).

A solution of dfmpe (**50**) in dichloromethane was added to a solution of $RuCl_3.3H_2O$ (**149**) in ethanol, and the reaction mixture was refluxed for 1 h. During this time, the colour of the reaction mixture lightened from dark brown to yellow. Analysis of the crude reaction mixture by ^{19}F NMR and ^{31}P NMR spectroscopy showed the complete consumption of dfmpe (**50**), accompanied by the formation of a number of products. Column chromatography using ethyl acetate as eluant afforded a bright yellow solid. Analysis of this solid by NMR spectroscopy and mass spectroscopy showed that the solid was composed of two products. Attempts to separate the components of this mixture using column chromatography, high vacuum sublimation and recrystallisation from a variety of solvents were unsuccessful.

The major product (**151**) of this mixture (comprising approximately 80%, estimated by ^{31}P NMR and ^{19}F NMR spectroscopy) exhibits a ^{31}P NMR spectrum consisting of a single fluorine-coupled resonance at δ 118.6 ppm, and appears in the ^{19}F NMR spectrum as two phosphorus-coupled doublets at δ -50.3 ppm and δ -53.3 ppm. Analysis of (**151**) by ^{1}H NMR spectroscopy shows the presence of overlapping phosphorus-coupled resonances between δ 2.7 and δ 2.9 ppm, with no resonances upfield of TMS, while the ^{13}C NMR spectrum showed one phosphorus-coupled resonance at δ 22.1 ppm, and two phosphorus-coupled quartets at δ 126.0 ppm and δ 124.9 ppm, with phosphorus-fluorine coupling constants of 320 Hz. The mass spectrum of (**151**) was obtained, and the base peak occurred at 1099 a.m.u. This peak does not correspond to any obvious fragment ($Ru(dfmpe)_2$ has a mass of 833

a.m.u.). The mass spectrum also shows peaks arising from fragmentation of dfmpe, indicating that **(151)** does contain one or more dfmpe ligands. The data is consistent with a monomeric octahedral ruthenium complex containing two dfmpe ligands bound in one plane, however a dimer or higher oligomer cannot be ruled out. The remaining two axial coordination sites are occupied by non-equivalent groups, making the trifluoromethyl groups on one face of the complex magnetically non-equivalent to the trifluoromethyl groups on the opposite face of the complex. The groups occupying the axial coordination sites do not contain phosphorus or fluorine.

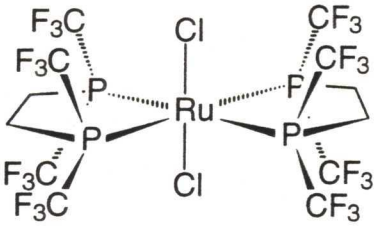


(151)

An infra-red spectrum of **(151)** showed no resonance in the carbonyl region, and addition of a solution of sodium tetraphenylborate in methanol failed to precipitate any ionic compound from solution. Attempts to crystallise **(151)** from a variety of solvents were unsuccessful. This compound remains to be identified conclusively, and further approaches to purify and characterise **(151)** have not been pursued.

The minor component of this mixture (comprising less than 20%, estimated by ^{31}P NMR and ^{19}F NMR) appears in the ^{31}P NMR spectrum as a single fluorine-coupled resonance at δ 90.5 ppm, and appears in the ^{19}F NMR spectrum as a single second-order multiplet at δ -47.1 ppm. No peaks in the ^{1}H NMR and ^{13}C NMR could be assigned to this compound due to the small amount of this compound present in the mixture. The mass spectrum of this

component of the mixture revealed a base peak at 871 a.m.u. and a smaller peak at 906 a.m.u., peaks corresponding to the $RuCl(dfmpe)_2$ fragment and the parent ion of $RuCl_2(dfmpe)_2$ **(150)** respectively. The mass spectrum also shows peaks arising from fragmentation of dfmpe, indicating that the complex does contain one or more dfmpe ligands. The data described is consistent with the desired *trans*- dichloride ruthenium complex, $RuCl_2(dfmpe)_2$ **(150)**.

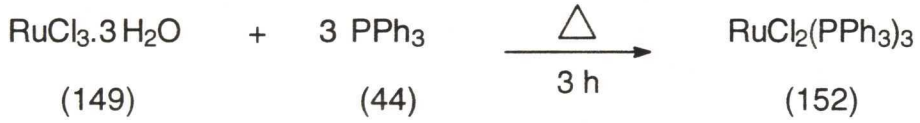


(150)

This synthetic approach to $RuCl_2(dfmpe)_2$ **(150)** was not pursued further, due to the small proportion of the desired dichloride **(150)** produced, and the difficulty encountered in separating this minor product from the other product in the mixture.

3.3.2 Reaction of dfmpe with $RuCl_2(PPh_3)_3$

Tris(triphenylphosphine)dichlororuthenium (II) **(152)** was synthesised by the method described by Hallman, Stephenson and Wilkinson.[102] Ruthenium trichloride trihydrate **(149)** reacted with excess triphenylphosphine **(44)** in refluxing methanol to form $RuCl_2(PPh_3)_3$ **(152)** as a brown air-stable solid (Scheme 3.9).



(149) (44) (152)

Scheme 3.9

Two equivalents of dfmpe **(50)** as a solution in dichloromethane were added to a suspension of $RuCl_2(PPh_3)_3$ **(152)** in toluene and stirred at room temperature for 1 h. The colour of the solution turned yellow immediately on addition of dfmpe **(50)**, and $RuCl_2(PPh_3)_3$ **(152)** dissolved. Analysis of the reaction mixture by ^{19}F NMR spectroscopy showed a mixture of fluorine-containing products, with no excess dfmpe **(50)** remaining. Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed the presence of displaced triphenylphosphine **(44)**, and two products with fluorine-coupled multiplets at δ 118.6 and δ 90.5 ppm, in the ratio approximately 4:1. These are the same products observed in the previous attempted synthesis of $RuCl_2(dfmpe)_2$ **(150)** (Section 3.3.1). As in the mixture obtained by reaction of dfmpe **(50)** with ruthenium trichloride trihydrate **(149)**, the resonance at δ 118.6 ppm represents the major product in the reaction, and the compound exhibiting the resonance at δ 90.5 ppm was only present in small quantities (approx. 20%). A ^{19}F NMR spectrum of the reaction mixture showed the resonances at δ -47.1 ppm and δ -50.3 ppm and δ -53.3 ppm previously assigned to the products **(150)** and **(151)** discussed in Section 3.3.1, amidst a number of other fluorine-containing products.

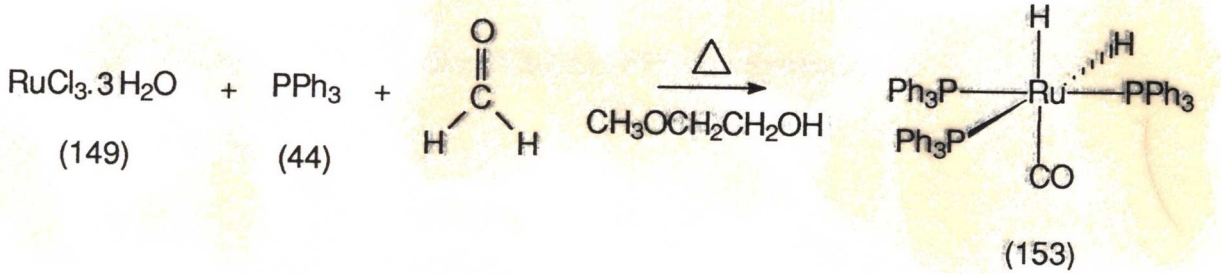
No further work was carried out towards separating $RuCl_2(dfmpe)_2$ **(150)** from the mixture or attempting to synthesise **(150)** directly by other methods.

3.3.3 Reaction of dfmpe with $RuH_2CO(PPh_3)_3$ (153)

An alternative strategy to form $RuH_2(dfmpe)_2$ **(113)**, other than by formation and subsequent reduction of $RuCl_2(dfmpe)_2$ **(150)**, was devised. Stepwise assembly of **(113)** was attempted, firstly by substituting two dfmpe **(50)** ligands onto a ruthenium complex already bearing two hydride ligands. $RuH_2CO(PPh_3)_3$ **(153)** contains four potentially displaceable

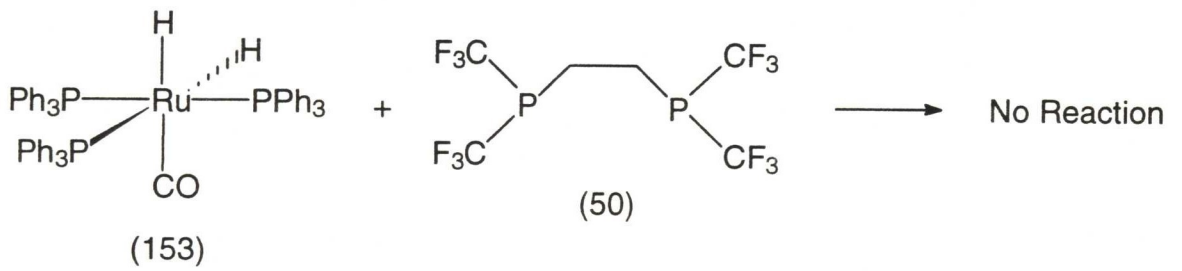
groups (three triphenylphosphine groups and a carbonyl group), and so may undergo substitution to form the required $RuH_2(dfmpe)_2$ **(113)**.

Carbonyldihydridotris(triphenylphosphine) ruthenium (II), $RuH_2CO(PPh_3)_3$, **(153)** was synthesised using the method described by Ahmad, Levison, Robinson and Uttley (Scheme 3.10).[103]



Scheme 3.10

Two equivalents of dfmpe **(50)** in dichloromethane were added to $RuH_2CO(PPh_3)_3$ **(153)** and stirred at room temperature for 48 h. Analysis of the crude reaction mixture by ^{19}F NMR spectroscopy showed dfmpe **(50)** as the only fluorine-containing product present (Scheme 3.11). Attempts to use higher temperatures or extended reaction periods resulted only in the decomposition of dfmpe **(50)**.

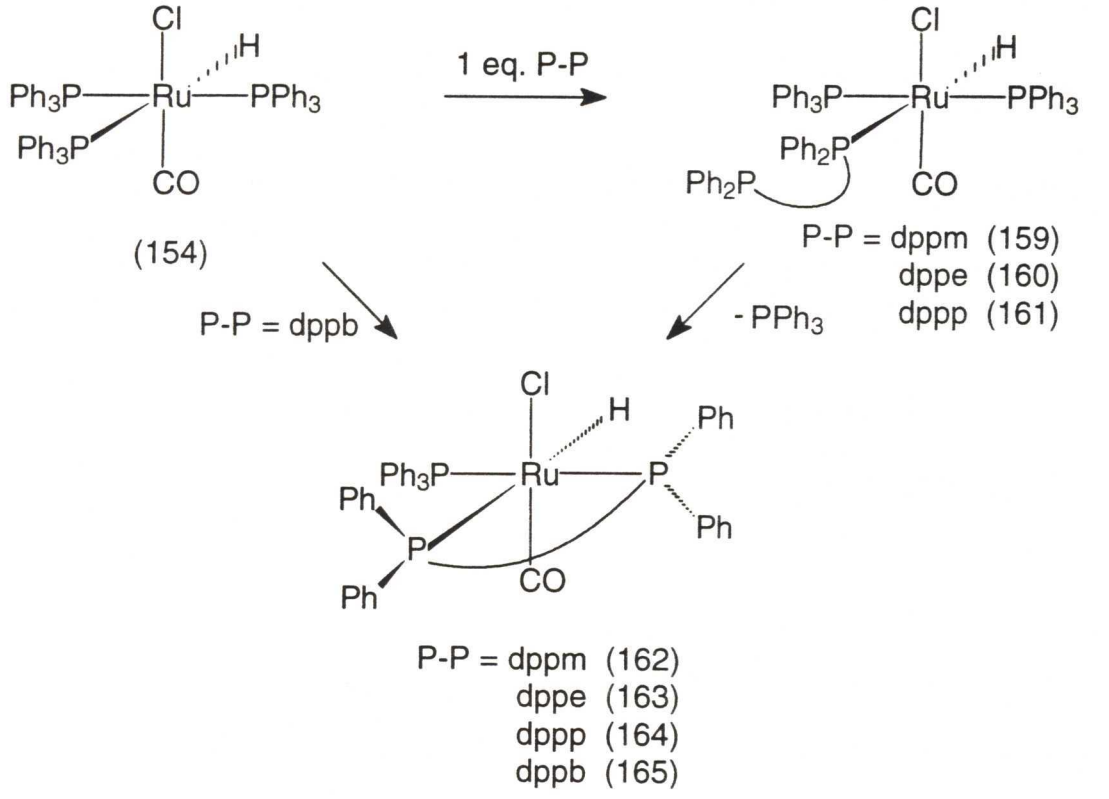


Scheme 3.11

$RuH_2(CO)(PPh_3)_3$ **(153)** was found to be unsuitable as a precursor complex for the synthesis of $RuH_2(dfmpe)_2$ **(113)**. Vigorous reaction conditions which could facilitate the substitution of dfmpe **(50)** for labile groups in $RuH_2(CO)(PPh_3)_3$ **(153)** could not be employed due to the availability of dfmpe **(50)** only as a solution in dichloromethane.

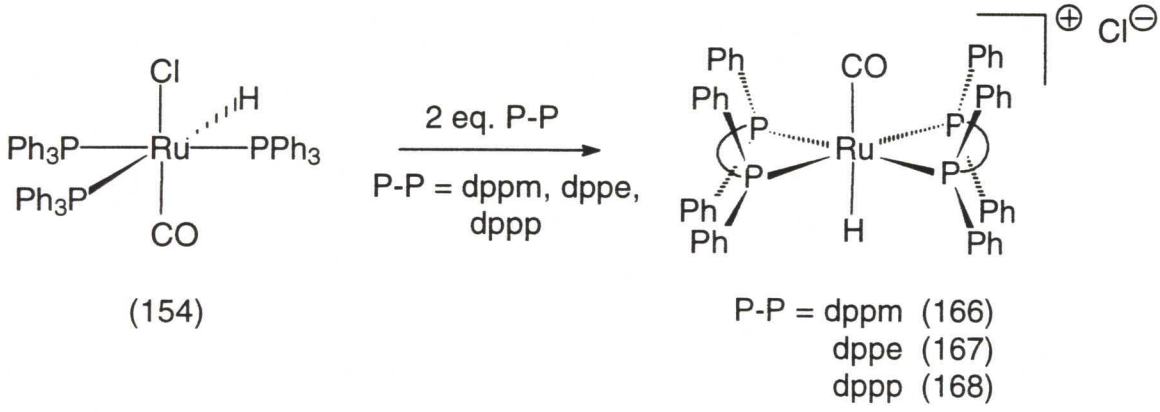
3.3.4 Reaction of dfmpe with $RuHCl(CO)(PPh_3)_3$: Synthesis of $RuHCl(CO)(PPh_3)(dfmpe)$

The synthesis of $RuH_2(dfmpe)_2$ **(113)** was attempted via the replacement of labile ligands on a ruthenium precursor complex with dfmpe **(50)**. The complex carbonylchlorohydridotris(triphenylphosphine) ruthenium (II), $RuHCl(CO)(PPh_3)_3$ **(154)** has been used by Santos *et al.* to synthesise a series of ruthenium complexes containing bisphosphine ligands.[104] The displacement of one or two triphenylphosphine groups from $RuHCl(CO)(PPh_3)_3$ **(154)** by one equivalent of the bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ (L-L) (n = 1, dppm **(156)**; n = 2, dppe **(16)**; n = 3, dppp **(157)**; n = 4, dppb **(158)**) leads to the formation of the hydrides $RuHCl(CO)(PPh_3)_2$(L-L) (L-L = dppm, **(159)**; L-L = dppe, **(160)**; L-L = dppp, **(161)**) or $RuHCl(CO)(PPh_3)$(L-L) (L-L = dppm, **(162)**; L-L = dppe, **(163)**; L-L = dppp, **(164)**; L-L = dppb, **(165)**)(Scheme 3.12).



Scheme 3.12

Reaction of $RuHCl(CO)(PPh_3)_3$ **(154)** with two equivalents of the bidentate phosphines $Ph_2P(CH_2)_nPPh_2$ (L-L) **(156)**, **(16)** and **(157)** for extended reaction times leads to the formation of $[Ru(CO)H(L\text{-}L)_2]^+Cl^-$ (L-L = dppm, **(166)**; L-L = dppe, **(167)**; L-L = dppp, **(167)**) (Scheme 3.13).

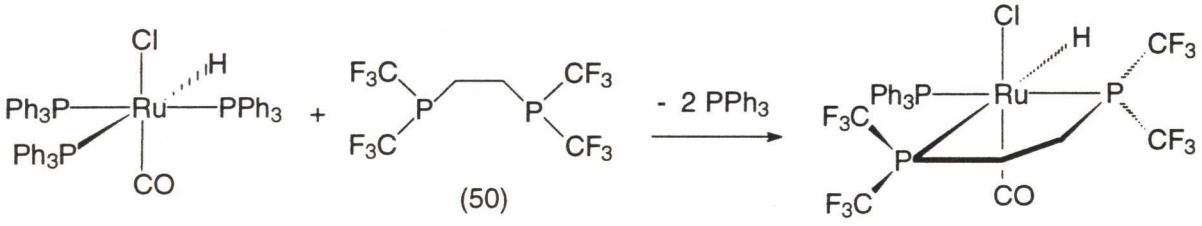


Scheme 3.13

The most sterically demanding of this series of bidentate phosphine ligands, dppb **(158)** does not form the corresponding ruthenium complex containing two bisphosphine ligands.

Carbonylchlorohydridotris(triphenylphosphine) ruthenium (II) **(154)** was prepared using the procedure of Ahmad, Levison, Robinson and Uttley.[103] Solutions of hydrated ruthenium trichloride **(149)** in 2-methoxyethanol and aqueous formaldehyde were added quickly and successively to a vigorously refluxing solution of 6 equivalents of triphenylphosphine **(44)** in 2-methoxyethanol, to form $RuHCl(CO)(PPh_3)_3$ **(154)** as an orange crystalline solid.

In an attempt to form $[RuH(CO)(dfmpe)_2]^+Cl^-$ **(169)**, an excess of dfmpe **(50)** in dichloromethane was added to carbonylchlorohydridotris(triphenylphosphine) ruthenium (II) **(154)**. The orange starting complex dissolved immediately, and the colour of the reaction mixture changed from colourless to yellow. ^1H NMR analysis of the reaction mixture after 2 h showed the formation of an unidentified hydride-containing intermediate, with no evidence of the required product, $[RuH(CO)(dfmpe)_2]^+Cl^-$ **(169)**. The reaction mixture was stirred for 24 h at room temperature, after which time ^1H NMR and ^{19}F NMR analysis of the reaction mixture showed the formation of $RuHCl(CO)(PPh_3)(dfmpe)$ **(155)**. Prolonged stirring of $RuHCl(CO)(PPh_3)(dfmpe)$ **(155)** in the presence of excess dfmpe **(50)** at room temperature showed no evidence for substitution of a second dfmpe ligand onto ruthenium (Scheme 3.14).



Scheme 3.14

When one equivalent of dfmpe **(50)** in dichloromethane was added to carbonylchloro-hydridotris(triphenylphosphine) ruthenium (II) **(154)**, the starting complex dissolved immediately. The reaction was stirred overnight, after which time ^{19}F NMR analysis showed that all dfmpe **(50)** had been consumed, and $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** was the sole product formed. 1,2-(Bis(bis(trifluoromethyl)phosphino)ethane)carbonylchlorohydrido-(triphenylphosphine) ruthenium (II) **(155)** was purified by column chromatography on flash silica, and washed with light petroleum to remove all traces of triphenylphosphine **(44)**. The product was obtained as an air-stable white powder, slightly soluble in light petroleum but soluble in all other organic solvents, and was recrystallised from light petroleum to afford colourless prisms in a yield of 43%.

The NMR spectra of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** (Figure 3.1) provide structural information about the arrangement of groups around the central ruthenium atom, and are worthy of comment.

The ^{19}F NMR spectrum of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** shows four phosphorus-coupled doublets, arising from the four unique CF_3 groups (Figure 3.1(a)). Two of the doublets are overlapping, between δ -48.8 and -49.2 ppm. The other two ^{19}F doublets are more separated, occurring at δ -53.3 ppm and δ -55.2 ppm. Selective external decoupling of the phosphorus resonances P_A and P_B while acquiring the fluorine spectrum of **(155)** indicates that the resonances at δ -48.9 and δ -55.2 ppm arise from trifluoromethyl groups on P_A, and those at δ -49.1 and δ -53.3 ppm arise from trifluoromethyl groups on P_B.

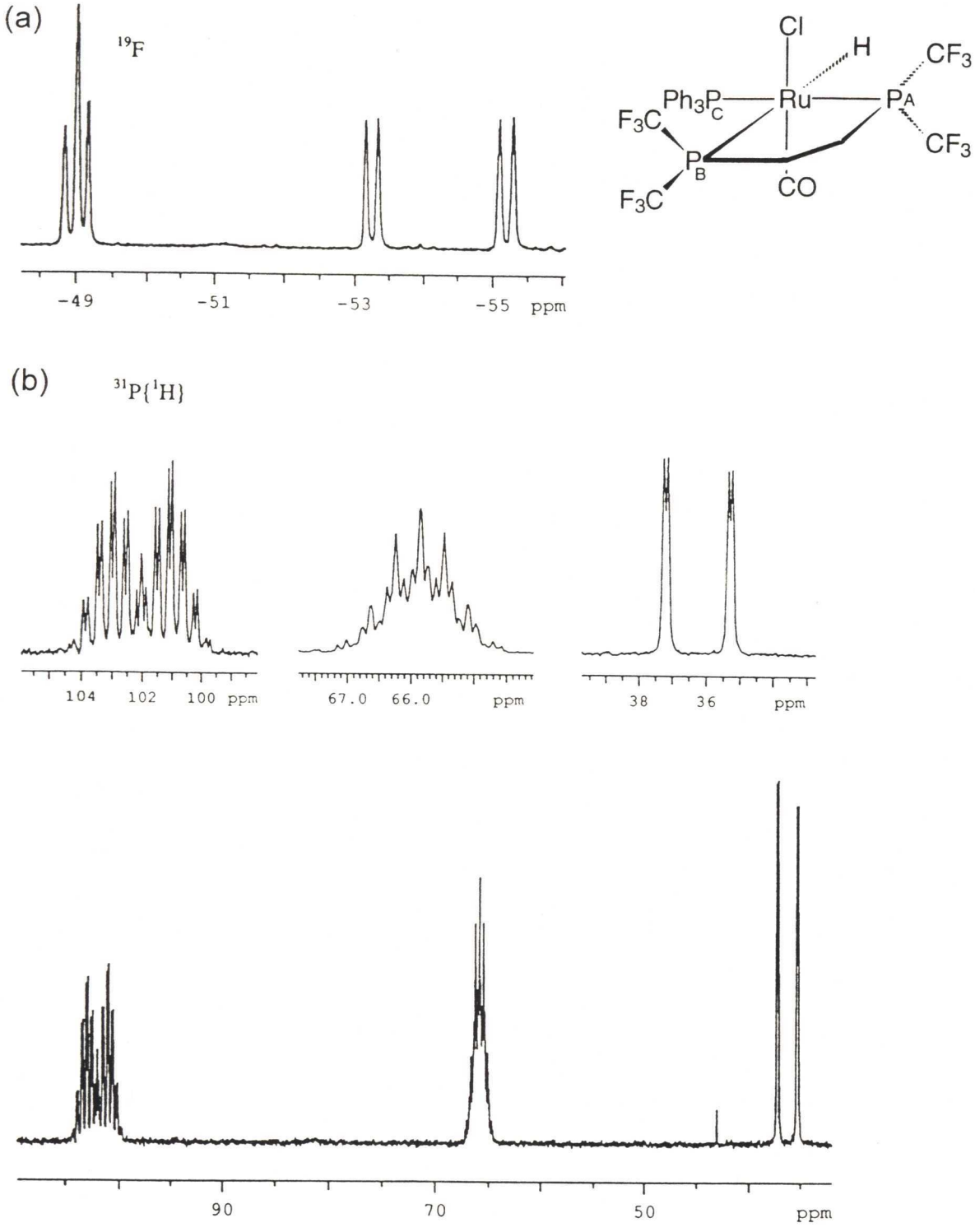


Figure 3.1 : (a) ^{19}F NMR spectrum of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** in $CDCl_3$ at 300K (b) $^{31}P\{^1H\}$ NMR spectrum of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** in $CDCl_3$ at 300K

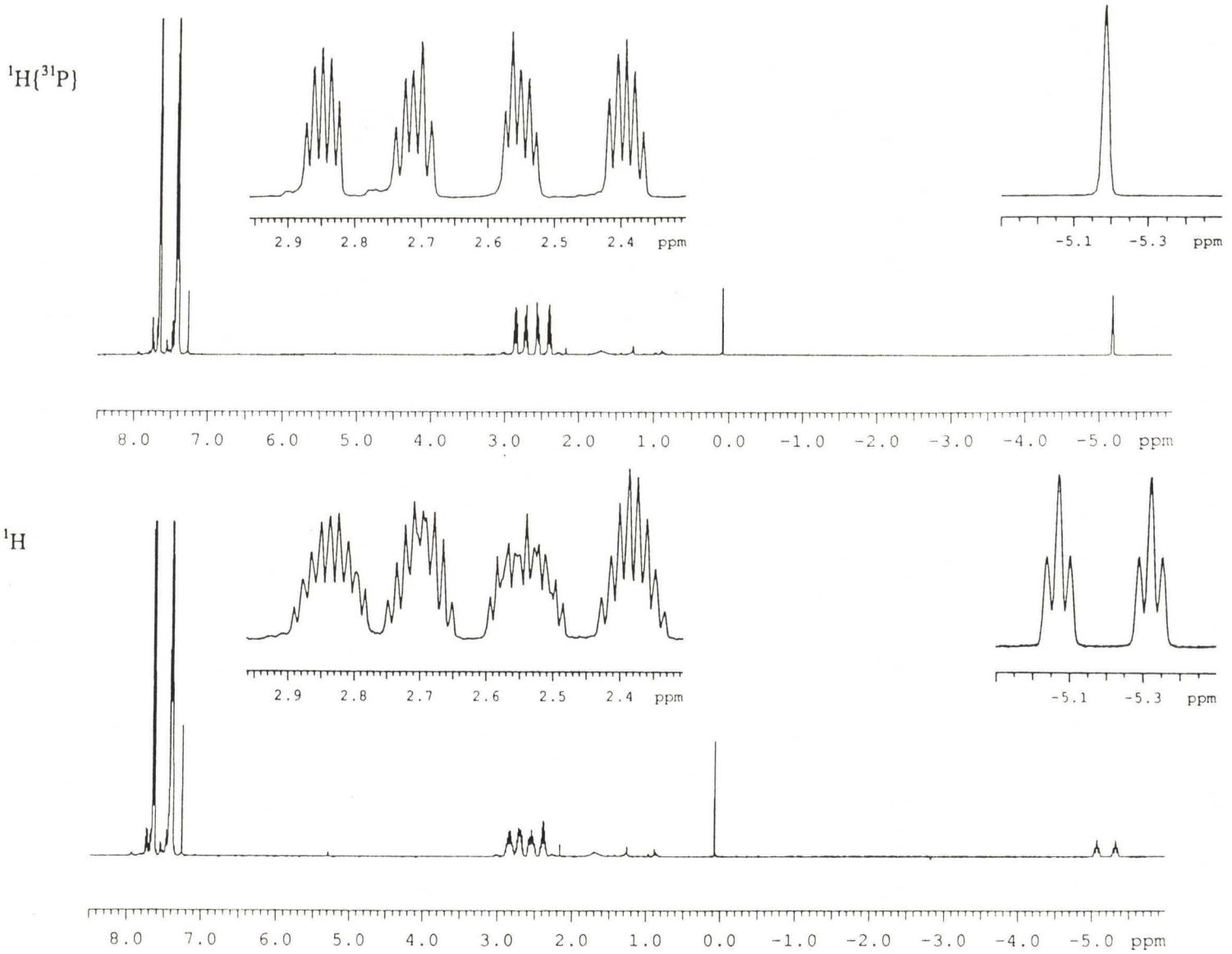


Figure 3.1(c) : ^1H NMR spectrum of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** in $CDCl_3$ at 300K

The $^{31}P\{^{1}H\}$ NMR spectrum of RuHCl(CO)(PPh_3)(dfmpe) (**155**) consists of three resonances due to three different phosphorus environments (Figure 3.1(b)). Two of the resonances, P_A and P_B are due to the bound dfmpe ligand. P_A occurs at δ 102.1 and is a doublet of doublets due to coupling to the other two phosphorus atoms, P_B and P_C, and a septet due to coupling to the six equivalent fluorine atoms comprising the two CF_3 groups on P_A. One phosphorus coupling to P_C is large (310 Hz) suggesting that P_A and P_C are mutually *trans*. P_B is similarly a doublet of doublet of septets at δ 65.9 ppm, however the two phosphorus couplings due to P_A and P_C are small (22 and 20 Hz). The phosphorus atom of the triphenylphosphine, P_C, is a doublet of doublets at δ 36.2 ppm, with the large coupling to P_A (310 Hz) and a small coupling to P_B (20 Hz) (Figure 3.2).

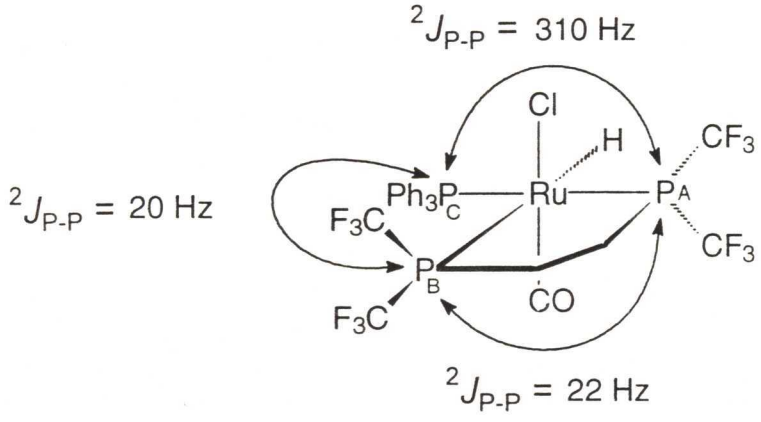


Figure 3.2 : P-P Coupling constants in RuHCl(CO)(PPh_3)(dfmpe) (**155**)

The ^{1}H NMR spectrum of RuHCl(CO)(PPh_3)(dfmpe) (**155**) shows three groups of signals (Figure 3.1(c)). The phenyl protons of the triphenylphosphine show a series of phosphorus-coupled peaks in the region δ 7.3-7.7 ppm. Each of the methylene protons on the dfmpe ligand is in a unique environment, and so exhibits a unique resonance, resulting in four phosphorus-coupled resonances in the region δ 2.3-2.9 ppm. The hydride resonance appears in the upfield region of the ^{1}H NMR spectrum, at δ -5.19 ppm. This resonance is coupled to

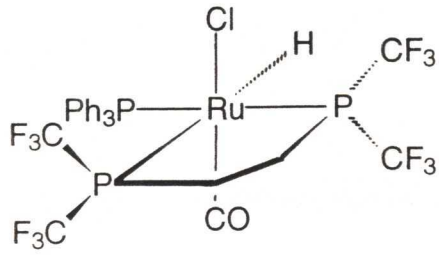
all three of the phosphorus atoms in the complex, and so appears as a doublet of doublet of doublets, or an apparent doublet of triplets. This hydride shows a large doublet coupling (150 Hz) to one phosphorus nucleus, and two smaller identical couplings of 19 Hz to the remaining two phosphorus nuclei. The hydride was located in the coordination sphere of the complex by a 2-dimensional phosphorus-proton NMR correlation experiment. The hydride lies *trans* to P_B, while the other two phosphorus atoms coupled more weakly to this hydride lie *cis* to this hydride.

The $^{13}C\{^{1}H,^{31}P\}$ NMR spectrum exhibits a characteristic downfield-shifted singlet due to a carbonyl, at δ 195.3. The carbon nuclei of the triphenylphosphine group of **(155)** resonate at δ 134.9, 133.8, 131.1 and 128.9 ppm. These resonances occur in the region expected for the four trifluoromethyl carbons of the bound dfmpe ligand, which were not further assigned. The methylene carbons on the ethylene bridge of the bound dfmpe ligand are chemically inequivalent, and exhibit resonances at δ 21.1 and 19.2 ppm.

An infra-red spectrum of this compound as a nujol mull showed a peak of medium intensity at 1992 cm^{-1}, and a peak at 1978 cm^{-1}.

The CI mass spectrum of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** showed a base peak at 793 a.m.u., consistent with the parent ion of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)**. A peak was also present at 759 a.m.u., arising from loss of a chlorine from the parent ion.

A crystal suitable for x-ray analysis was grown by slow evaporation of solvent, and the structure of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** in the solid state was analysed by x-ray diffraction. An ORTEP plot of this molecule is shown in Figure 3.3.



(155)

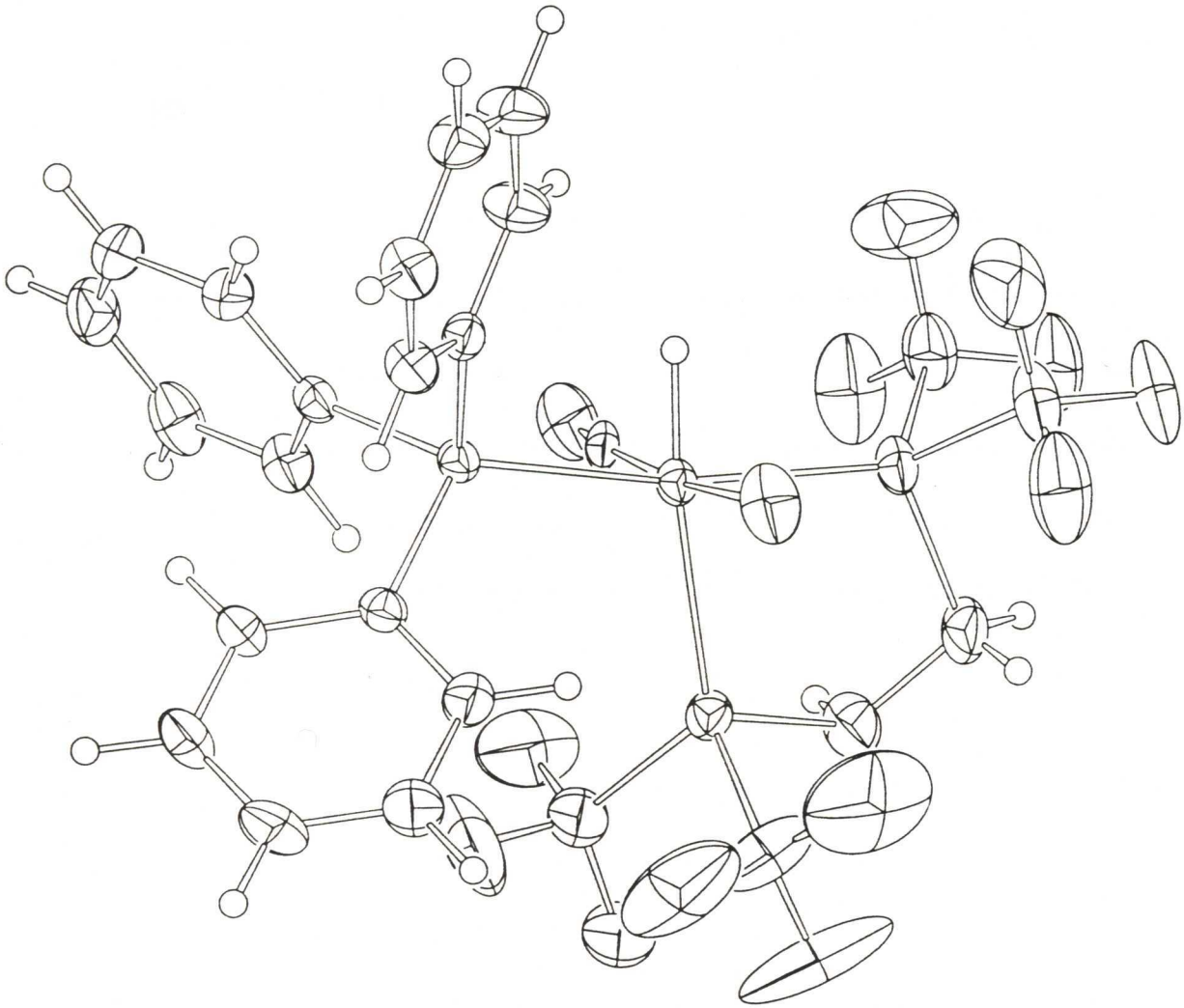


Figure 3.3 : ORTEP plot of $RuHCl(CO)(PPh_3)(dfmpe)$ **(155)**

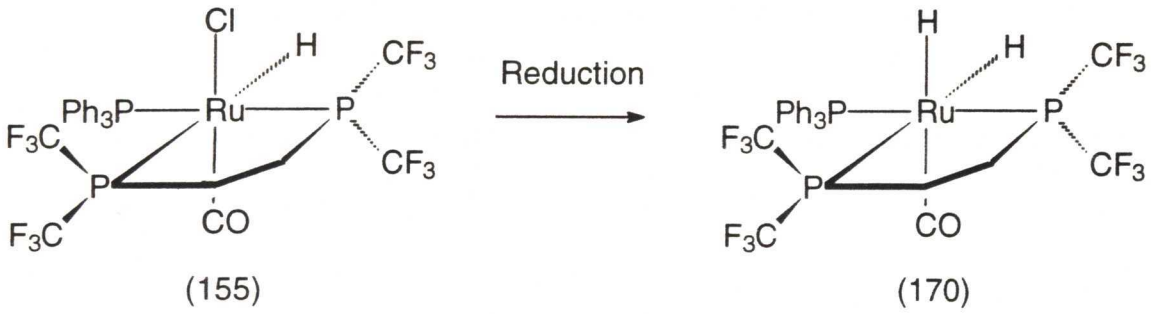
$RuHCl(CO)(PPh_3)$(dfmpe) **(155)** crystallises in the monoclinic space group $P2_1/n$, and exhibits disorder in the trifluoromethyl groups and also in the carbonyl and chloride groups. The latter disorder results from the lack of steric distinction between the chloride and carbonyl sites. As a result, the C-O bond appears artificially short (0.88 Å), and the Ru-Cl bond appears artificially long (2.42 Å). Crystallographic tables are given in Appendix A3.

The structure of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** determined by x-ray analysis (Figure 3.3) is consistent with that determined by NMR spectroscopy. The hydride ligand is in a *trans* orientation with respect to one of the phosphorus atoms of dfmpe, and the triphenylphosphine group is *trans* to the other dfmpe phosphorus atom. The carbonyl and chloride groups are also mutually *trans*.

It is interesting to note that in its reaction with $RuHCl(CO)(PPh_3)_3$ **(154)**, dfmpe **(50)** acts in a similar way as Santos and co-workers reported for dppb **(158)**.[104] Both dfmpe **(50)** and dppb **(158)** form the same isomer with this ruthenium precursor, and only displace two triphenylphosphine ligands. There may be some similarity between the steric requirements of dppb **(158)** and dfmpe **(50)**, although perhaps the electronic effect of dfmpe **(50)**, once bound to the ruthenium complex, deactivates the complex towards further substitution.

3.3.5 Synthesis of $RuH_2(CO)(PPh_3)$(dfmpe)

The synthesis of RuH_2(dfmpe)$_2$ **(113)** was attempted stepwise, by attempting to add the remaining dfmpe ligand and hydride to this molecule in two stages. Having assembled a ruthenium complex with one dfmpe ligand and one hydride in $RuHCl(CO)(PPh_3)$(dfmpe) **(155)**, reduction of the chloro group was attempted, to synthesise $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** (Scheme 3.15).



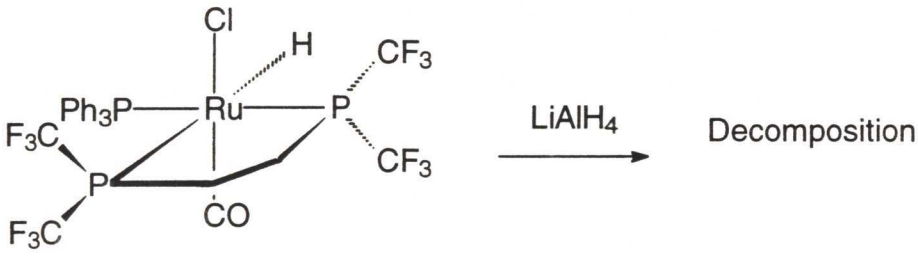
(155) (170)

Scheme 3.15

A number of reducing agents were used to try to effect the reduction of $RuHCl(CO)(PPh_3)(dfmpe)$ **(155)** to $RuH_2(CO)(PPh_3)(dfmpe)$ **(170)**.

3.3.5.1 Reduction of $RuHCl(CO)(PPh_3)(dfmpe)$ with lithium aluminium hydride

A small amount of solid lithium aluminium hydride was added to a solution of $RuHCl(CO)(PPh_3)(dfmpe)$ **(155)** in tetrahydrofuran, and the solution was allowed to stir at room temperature for 15 min. A ^{19}F NMR spectrum of the reaction mixture showed peaks arising from decomposition of dfmpe **(50)** , and new peaks in the region of the ^{19}F NMR spectrum characteristic of coordinated trifluoromethylphosphino groups. When more lithium aluminium hydride was added, the only peaks visible in the ^{19}F NMR spectrum were due to the decomposition of **(155)** and dfmpe **(50)** (Scheme 3.16).



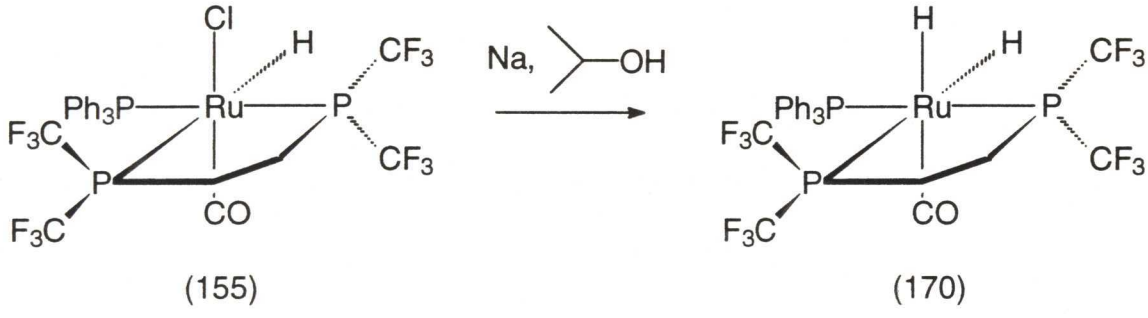
(155)

Scheme 3.16

3.3.5.2 Reduction of $RuHCl(CO)(PPh_3)(dfmpe)$ with sodium and 2-propanol

A mixture of sodium and 2-propanol has proved to be a useful combination of reagents for the reduction of chloro-ruthenium complexes to ruthenium hydrides. The reduction of $RuCl_2(dmpe)_2$ **(4)** to form dihydrido-bis(1,2-bis(dimethylphosphino)ethane) ruthenium(II), $RuH_2(dmpe)_2$ **(143)** has been reported to occur in high yield by use of sodium and 2-propanol.[100]

Freshly-cut sodium was added to a solution of $RuHCl(CO)(PPh_3)(dfmpe)$ **(155)** in 2-propanol and the reaction mixture was stirred at room temperature for 5 h. Analysis of the reaction mixture by ^{19}F NMR spectroscopy showed complete conversion of the starting material to a new product. The solvent was removed under vacuum, and the residue was washed with a small amount of light petroleum to remove sodium isopropoxide, a by-product of the reduction. The residue was analysed by ^{1}H, ^{31}P and ^{19}F NMR spectroscopy and found to be $RuH_2(CO)(PPh_3)(dfmpe)$ **(170)**, contaminated with a small amount of sodium isopropoxide (Scheme 3.17). The NMR spectra of this product were identical to those obtained from the reduction of $RuHCl(CO)(PPh_3)(dfmpe)$ **(155)** using sodium borohydride (Section 3.3.5.3).



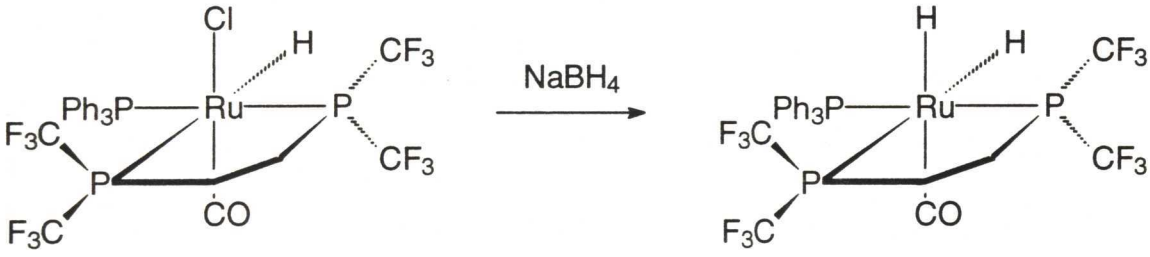
(155) (170)

Scheme 3.17

3.3.5.3 Reduction of RuHCl(CO)(PPh_3)(dfmpe) with sodium borohydride

Sodium borohydride has also been used to effect clean reduction of chloro-ruthenium complexes to their corresponding hydrido-ruthenium complexes.[105,106]

A solution of sodium borohydride in THF was added to a solution of RuHCl(CO)(PPh_3)(dfmpe) (**155**) in THF and stirred at room temperature for 20 h. Analysis of the crude reaction mixture by ^{19}F NMR throughout the course of the reaction showed clean conversion to one product which exhibited a similar ^{19}F NMR spectrum to (**155**). Removal of the solvent under vacuum and extraction of the residue into light petroleum afforded a white powder, which by NMR analysis was shown to be $RuH_2(CO)(PPh_3)$(dfmpe) (**170**) of >95% purity in a yield of 90% (Scheme 3.18).



(155) (170)

Scheme 3.18

$RuH_2(CO)(PPh_3)$(dfmpe) (**170**) is a white air-stable solid which is soluble in all organic solvents, more soluble than RuHCl(CO)(PPh_3)(dfmpe) (**155**). The $^{31}P\{^1H\}$ NMR spectrum of $RuH_2(CO)(PPh_3)$(dfmpe) (**170**) in C_6D_6 is very similar to that of RuHCl(CO)(PPh_3)(dfmpe) (**155**) (Figure 3.4(a)). The spectrum shows three resonances due to three different phosphorus environments, two dfmpe phosphorus atoms and one

triphenylphosphine phosphorus atom. One dfmpe phosphorus resonance, P_A, is a doublet of doublet of septets at δ 118.8 ppm and exhibits a large coupling to the triphenylphosphine phosphorus atom, P_C (247 Hz), indicating that it is *trans* to P_C. The other dfmpe phosphorus atom, P_B, exhibits a resonance at δ 89.6 ppm and appears as a doublet of doublet of septets due to coupling to the other two phosphorus atoms and coupling to the two attached CF_3 groups. Both phosphorus doublet couplings in the resonance of P_B are relatively small (20 and 21 Hz) indicating that P_B is the phosphorus atom *cis* to the other two phosphorus atoms. The phosphorus atom of the triphenylphosphine group, P_C, gives rise to a doublet of doublets at δ 51.8 ppm, and has a large coupling to P_A (247 Hz) and a small coupling to P_B (21 Hz). These assignments are indicated in Figure 3.5. It is interesting to note that all the ^{31}P NMR resonances for $RuH_2(CO)(PPh_3)$(dfmpe) (**170**) are shifted downfield relative to the ^{31}P NMR resonances of $RuHCl(CO)(PPh_3)$(dfmpe) (**155**).

The ^{19}F NMR spectrum of $RuH_2(CO)(PPh_3)$(dfmpe) (**170**) shows four phosphorus-coupled doublets, each due to one of the four unique CF_3 groups on the dfmpe ligand (Figure 3.4(b)). Again these ^{19}F NMR resonances are more dispersed than the ^{19}F NMR resonances of the trifluoromethyl groups in $RuHCl(CO)(PPh_3)$(dfmpe) (**155**). The resonances in the ^{19}F NMR spectrum occur at δ -56.9, -57.2, -59.1 and -60.2 ppm, with doublet couplings to the attached phosphorus atoms of 67, 68, 76 and 77 Hz respectively.

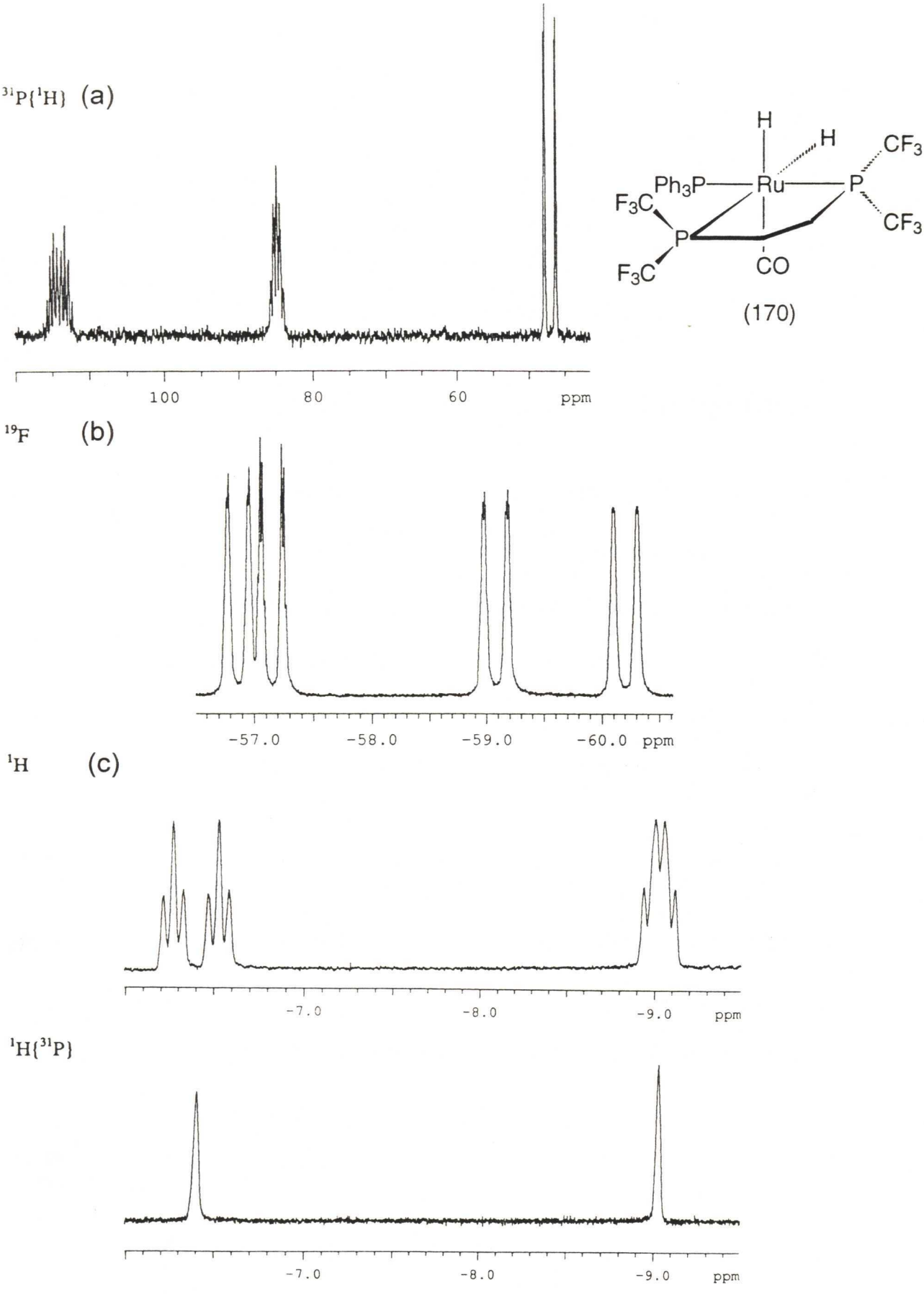


Figure 3.4 : (a) $^{31}P\{^{1}H\}$ NMR spectrum of $RuH_2(CO)(PPh_3)(dfmpe)$ **(170)** in C_6D_6 at 300K

(b) ^{19}F NMR spectrum of $RuH_2(CO)(PPh_3)(dfmpe)$ **(170)** in C_6D_6 at 300K

(c) ^{1}H NMR spectrum of $RuH_2(CO)(PPh_3)(dfmpe)$ **(170)** in C_6D_6 at 300K

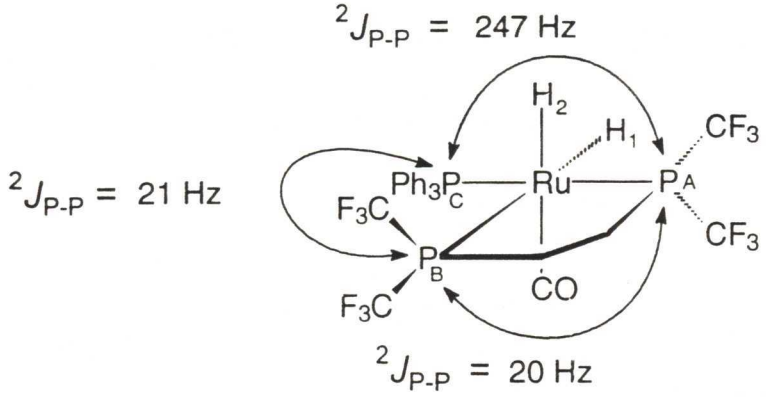


Figure 3.5 : P-P Coupling constants in $RuH_2(CO)(PPh_3)$(dfmpe) **(170)**

The ^1H NMR spectrum of $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** shows two sets of phosphorus-coupled resonances for the triphenylphosphine protons in the region δ 7.3-7.7 ppm, and phosphorus-coupled signals in the region δ 2.3-2.9 ppm due to the methylene protons on the dfmpe ligand (Figure 3.4(c)). The methylene resonances are not as well dispersed as are the corresponding methylene protons of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)**, and this results in some overlap. The high-field region of the ^1H NMR spectrum of **(170)** exhibits 2 hydrides, at δ -6.55 and -9.31 ppm. Each of these hydrides is a doublet of doublet of doublets, the resonance at δ -6.55 ppm having a large *trans* coupling of 102 Hz and two smaller couplings of 22 and 23 Hz, while the peak at δ -9.31 has three smaller couplings of 25, 20 and 25 Hz. The hydride at δ -6.55 ppm is therefore *trans* to P_A and so is assigned as H_1. The hydride at δ -9.31 ppm is *cis* to all three phosphorus atoms and so is assigned as H_2, *trans* to the carbonyl group. This assignment, shown in Figure 3.5, was confirmed by a 2-D phosphorus-proton correlation.

The $^{13}C\{^1H\}$ NMR spectrum of $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** exhibits the characteristic downfield-shifted singlet due to carbonyl peaks, at δ 199.2. There are four resonances due to the carbon nuclei of the three equivalent triphenylphosphine groups, at

δ 137.6, 134.3, 130.8 and 129.8 ppm. These resonances coincide with the four trifluoromethyl carbons, which with the large fluorine coupling make them difficult to identify conclusively. The methylene carbons are chemically inequivalent, and occur at δ 23.7 and 20.6 ppm.

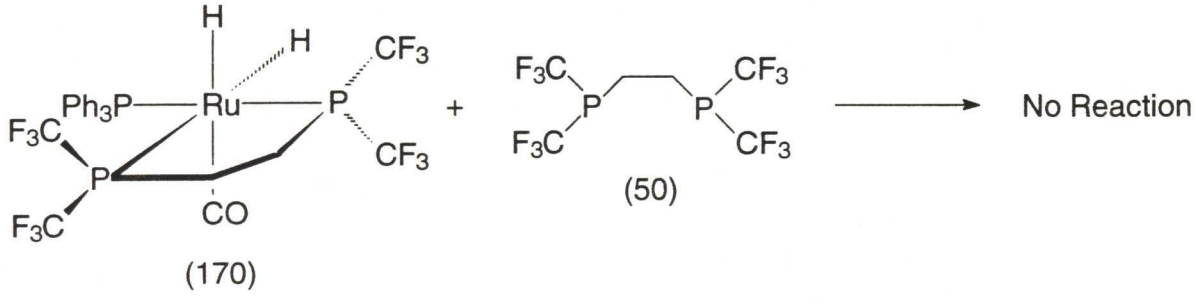
An infra-red spectrum of **(170)** as a nujol mull shows a band of medium strength at 2005 cm^{-1}, which was assigned to the C≡O stretch. Ru-H stretches were not observed, however these bands may have been obscured by the C≡O stretch.

The CI mass spectrum of $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** shows a base peak at 759 a.m.u., consistent with the parent ion of this compound.

3.3.6 Attempted synthesis of RuH_2(dfmpe)$_2$ via $RuH_2(CO)(PPh_3)$(dfmpe)

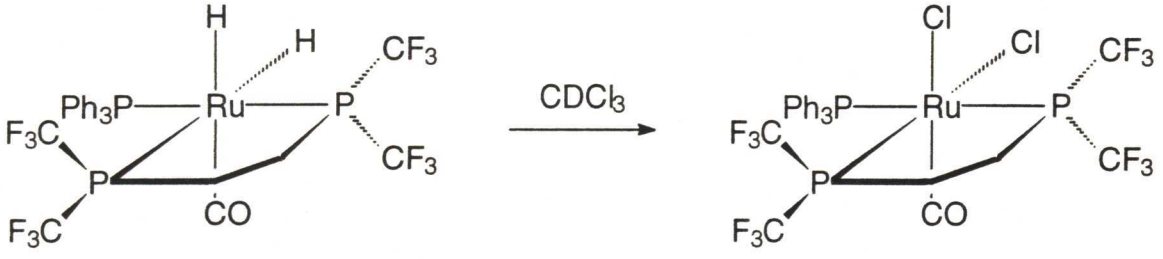
In an attempt to form the desired dihydride, RuH_2(dfmpe)$_2$ **(113)**, reactions were carried out to assess the lability of the carbonyl and triphenylphosphine groups on $RuH_2(CO)(PPh_3)$(dfmpe) **(170)**, by substitution for dfmpe **(50)**.

$RuH_2(CO)(PPh_3)$(dfmpe) **(170)** was stirred with one equivalent of dfmpe **(50)** in dichloromethane for 24 h at room temperature. Analysis of the reaction mixture by ^{19}F NMR spectroscopy showed only the presence of the starting dihydride complex **(170)** and dfmpe **(50)** (Scheme 3.19).



Scheme 3.19

$RuH_2(CO)(PPh_3)$(dfmpe) **(170)** was stable in non-chlorinated and alcoholic solvents for extended periods of time, however in $CDCl_3$ solution over a period of 2 days at room temperature, $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** decomposed to form a compound which was assigned as $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)** (Scheme 3.20).



(170) (171)

Scheme 3.20

The same product was observed as a minor by-product in the synthesis of $RuHCl(CO)(PPh_3)$(dfmpe) **(155)**, when a solution of dfmpe **(50)** in a mixture of dichloromethane and THF was refluxed with the precursor ruthenium complex $RuHCl(CO)(PPh_3)_3$ **(154)**. The dichloride species presumably arises from the chlorination of the hydrochloride ruthenium complex **(155)** once it is formed in the reaction mixture (Scheme 3.21).

(155) (171)

Scheme 3.21

$RuCl_2(CO)(PPh_3)$(dfmpe) **(171)** is an air-stable white powder which is soluble in chlorinated solvents such as dichloromethane, and can be purified by column chromatography on flash silica.

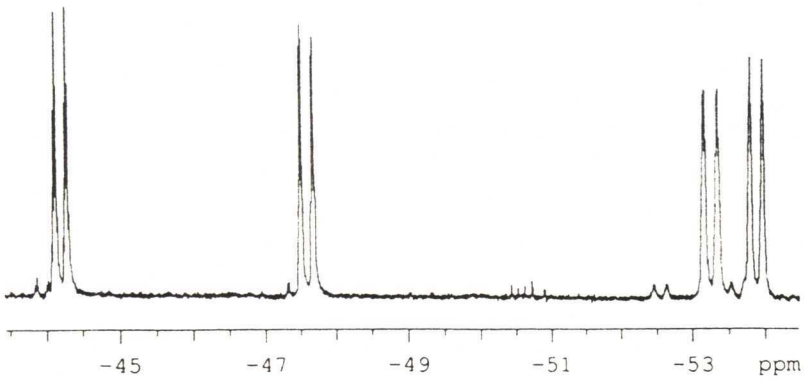
The CI mass spectrum of $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)** showed a base peak at 795 a.m.u., consistent with the fragment remaining after loss of chlorine from the parent ion of $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)**.

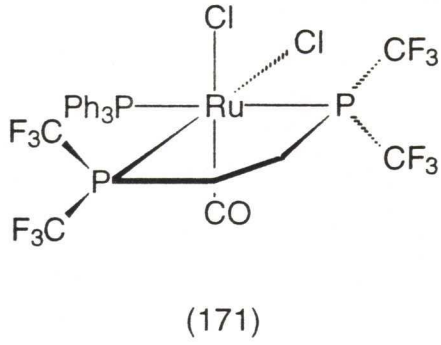
Addition of a solution of sodium tetraphenylborate in methanol to a solution of **(171)** in methanol failed to precipitate any new species, suggesting that the product is a neutral species, not ionic.

The ^{19}F NMR spectrum of **(171)** consists of four distinct doublets at δ -44.2, -47.6, -53.3 and -53.9 ppm, with fluorine-phosphorus coupling constants of 60, 66, 69 and 65 Hz respectively (Figure 3.6(a)). This shows that each of the trifluoromethyl groups on the dfmpe ligand is in a unique magnetic environment.

The ^{31}P NMR spectrum of $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)** again shows three characteristic resonances, similar in multiplicity to both $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** and $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** (Figure 3.6(b)). The ^{31}P NMR spectrum in $CDCl_3$ shows a resonance at δ 93.7 ppm which is a doublet of septets, and arises from the dfmpe phosphorus atom, P_B, which is *cis* to P_A and P_C. This resonance appears to have no coupling to P_A, the other dfmpe phosphorus atom. This phosphorus atom, P_A, occurs at δ 88.1 ppm and again is a doublet of septets, the doublet coupling of magnitude 390 Hz arising from coupling to the triphenylphosphine phosphorus atom, P_C, and the septet coupling of magnitude 63 Hz arising from coupling to the 6 fluorine atoms in the two trifluoromethyl groups bound to P_A. Again,

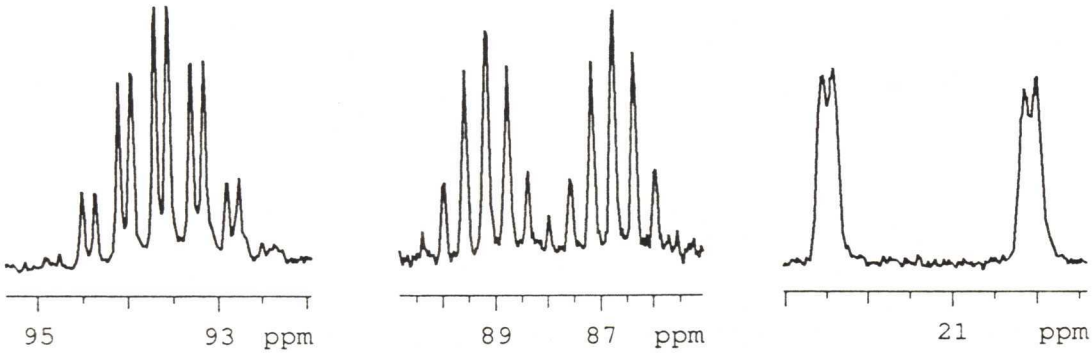
(a) ^{19}F





(171)

(b) $^{31}P\{^{1}H\}$



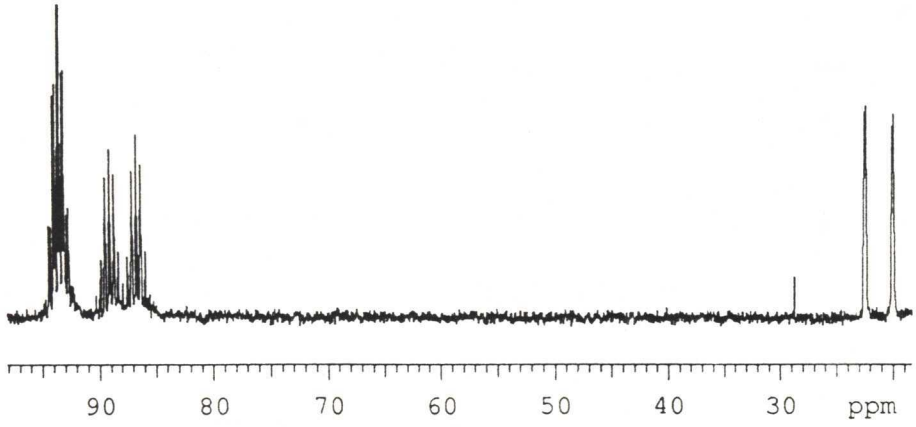


Figure 3.6 : (a) ^{19}F NMR spectrum of $RuCl_2(CO)(PPh_3)(dfmpe)$ **(171)** in $CDCl_3$ at 300K
(b) $^{31}P\{^{1}H\}$ NMR spectrum of $RuCl_2(CO)(PPh_3)(dfmpe)$ **(171)** in $CDCl_3$ at 300K

there is no apparent coupling to the other dfmpe phosphorus atom, P_B. The triphenylphosphine phosphorus atom, P_C, exhibits a doublet of doublets at δ 21.3 ppm, with coupling to P_A of 390 Hz and coupling to P_B of 23 Hz. The ^{31}P NMR spectrum of **(171)** therefore indicates a similar arrangement of the phosphorus atoms as in $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** and $RuH_2(CO)(PPh_3)$(dfmpe) **(170)**, that is a dfmpe ligand bound to ruthenium with a triphenylphoshine ligand attached in a *trans-* orientation relative to one of the dfmpe phosphorus atoms (Figure 3.7).

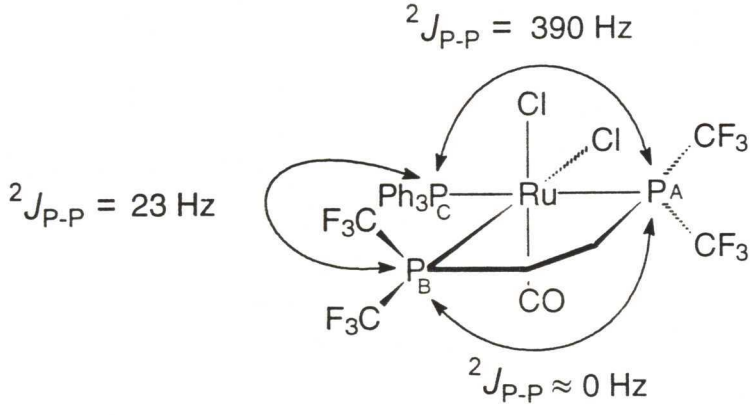


Figure 3.7 : P-P Coupling constants in $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)**

The ^1H NMR spectrum of $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)** in $CDCl_3$ shows resonances in the aromatic region at δ 7.3-7.7 ppm corresponding to the triphenylphoshine protons, and four distinct resonances at δ 3.05, 2.90, 2.75 and 2.30 ppm arising from the four unique methylene protons on the dfmpe 2-carbon chain. There are, however, no resonances in the region upfield of TMS, indicating that there are no metal-bound hydrides.

The $^{13}C\{^1H,^{31}P\}$ NMR spectrum exhibits a resonance due to the carbon of the carbonyl group at δ 193.0 ppm. The resonances due to the carbon nuclei of the three equivalent triphenylphosphine groups occur at δ 135.4, 132.8, 131.4 and 128.9 ppm. These resonances

coincide with the four trifluoromethyl carbons of the bound dfmpe ligand, which in addition to the large fluorine coupling make them difficult to identify. The methylene carbons of the bound dfmpe ligand are chemically inequivalent, and occur at δ 21.1 and 19.2 ppm.

An infra-red spectrum of this product as a nujol mull showed a carbonyl stretch of medium intensity at 2008 cm^{-1}.

Several attempts were made to crystallise this compound and although several crystals were obtained, none were of sufficient quality for structural determination by x-ray analysis.

Some spectroscopic properties of $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)**, $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** and $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** are summarised in Table 3.1.

Table 3.1 : Comparison of spectroscopic properties of $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)**, $RuHCl(CO)(PPh_3)$(dfmpe) **(155)** and $RuH_2(CO)(PPh_3)$(dfmpe) **(170)**.

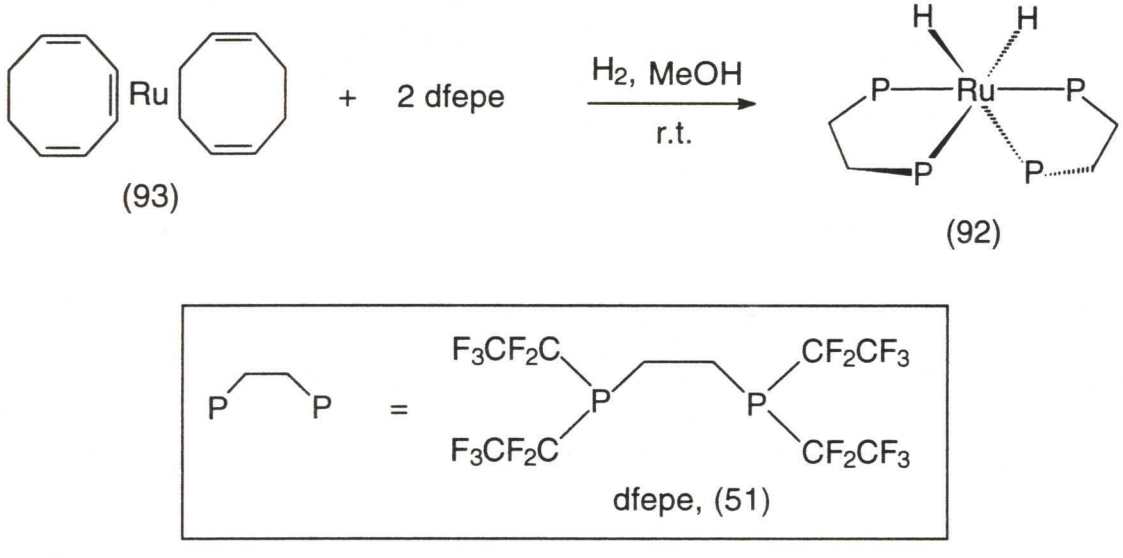
	$RuCl_2(CO)(PPh_3)$(dfmpe) **(171)**	$RuHCl(CO)(PPh_3)$(dfmpe) **(155)**	$RuH_2(CO)(PPh_3)$(dfmpe) **(170)**
^{31}P (ppm)	88.1, 93.7, 21.3	102.1, 65.9, 36.2	118.8, 89.6, 51.8
^{19}F (ppm)	-44.2, -47.6, -53.3, -53.9	2 × -49, -53.3, -55.2	-56.9, -57.2, -59.1, -60.2
^{13}C (**CO**) (ppm)	193.0	195.3	199.2
ν (CO) (cm^{-1})	2008.4	1992.2	2005.4

The NMR data shown in Table 3.1 shows a progressive trend towards low field for resonances of the dichloride **(171)**, the hydrochloride **(155)**, and the dihydride **(170)**. This data is consistent with the formulation of **(171)** as $RuCl_2(CO)(PPh_3)$(dfmpe). The infra-red stretches of the carbonyl groups for these three compounds do not appear to exhibit this trend.

Synthesis of $RuH_2(dfmpe)_2$ **(113)** by this route is complicated by the instability of $RuH_2(CO)(PPh_3)(dfmpe)$ **(170)** in solution. Prolonged reaction times at room temperature, or short reaction times at elevated temperatures result in decomposition of $RuH_2(CO)(PPh_3)(dfmpe)$ **(170)** to form $RuCl_2(CO)(PPh_3)(dfmpe)$ **(171)**. This route was therefore found to be unsuitable for the synthesis of $RuH_2(dfmpe)_2$ **(113)**.

3.3.7 Reaction of dfmpe with Ru(COD)(COT)

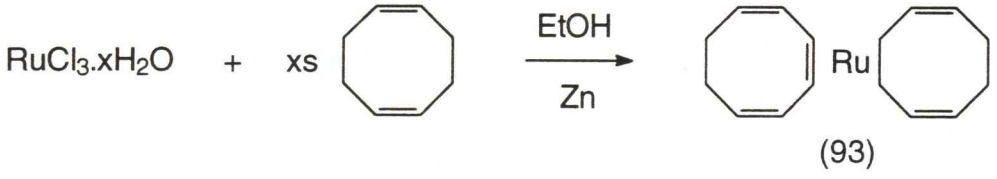
The synthesis of (η^4-cyclo-octa-1,5-diene)(η^6-cyclo-octa-1,3,5-triene)ruthenium (0), Ru(COD)(COT) **(93)**, was reported by Pertici and co-workers in 1980.[107] Ru(COD)(COT) **(93)** is an extremely air-sensitive complex but has previously been used in the synthesis of several ruthenium arene and bisphosphine complexes.[108] Under one atmosphere of hydrogen gas, the ruthenium-bound cycloalkenes are reduced to a mixture of cyclooctane and cyclooctene, leaving the metal centre vulnerable to coordination by other ligands.[108b] In particular, Roddick and co-workers have reported the use of this complex in the synthesis of $RuH_2(dfepe)_2$ **(92)** (Scheme 3.22).[56]



Scheme 3.22

Ru(COD)(COT) (**93**) was synthesised using a modification of the procedure described by Pertici and Vitulli.[109]

An excess of 1,5-cyclooctadiene was added to a solution of ruthenium trichloride trihydrate in ethanol. Zinc dust was added and the mixture was heated under reflux with vigorous magnetic stirring for 3 hours. Extraction into hexane yielded a bright yellow solution containing the required Ru(COD)(COT) (**93**). This solution was calibrated by ^{1}H NMR spectroscopy by integration against an internal standard (trinitrotoluene, 0.03 mmol.ml^{-1}) and found to contain Ru(COD)(COT) (**93**) (0.95 mmol, 73%) (Scheme 3.23).

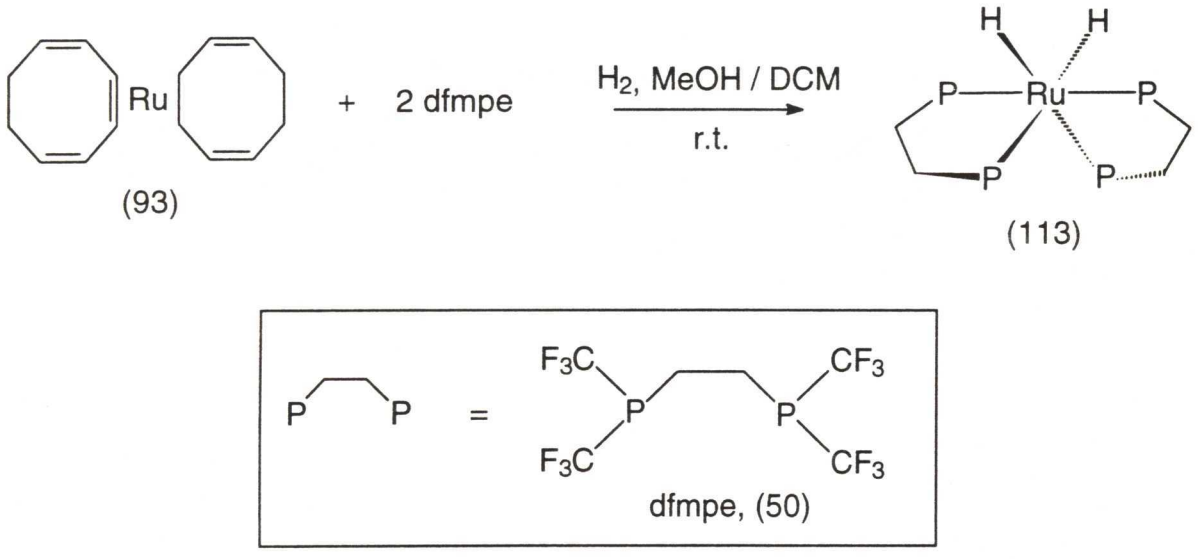


Scheme 3.23

Ru(COD)(COT) (**93**) is very air-sensitive and attempts to purify or crystallise this complex resulted in extensive decomposition and reduced yields of the compound. As a result, the solution of Ru(COD)(COT) (**93**) in hexane was used in subsequent reactions without further purification.

A solution of Ru(COD)(COT) (**93**) in hexane was added to a flask and the solvent removed under vacuum. A solution of 2.2 equivalents of dfmpe (**50**) in dichloromethane was added to this residue, and the vessel was evacuated and filled with 1 atm H_2 gas. The reaction mixture was left stirring overnight at room temperature. ^{1}H NMR analysis of the crude reaction mixture showed the presence of a phosphorus-coupled multiplet at -9.9 ppm,

indicating the formation of a metal-bound hydride. The product formed was identified as $RuH_2(dfmpe)_2$ **(113)** (Scheme 3.24).



Scheme 3.24

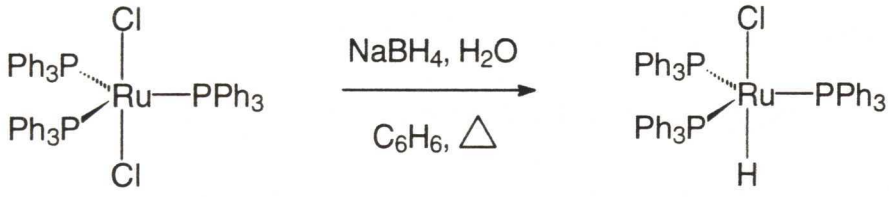
The crude reaction mixture was purified by column chromatography in hexane and subsequent sublimation under high vacuum.

Although this method does produce $RuH_2(dfmpe)_2$ **(113)**, this synthesis is not reproducible and results in erratic yields. Ru(COD)(COT) **(93)** is a very air-sensitive compound and often the mixture of cyclooctanes and cyclooctenes present at the completion of the reaction make the product difficult to purify. In addition, all attempts to increase the scale of the synthesis of Ru(COD)(COT) **(93)** were unsuccessful. A more reliable and high yielding reaction pathway for the synthesis of $RuH_2(dfmpe)_2$ **(113)** was sought.

3.3.8 Reaction of dfmpe with $RuHCl(PPh_3)_3$: Synthesis of $RuHCl(dfmpe)_2$

Hydridochlorotris(tristriphenylphosphine)ruthenium (II), $RuHCl(PPh_3)_3$ **(172)**, was synthesised by the reduction of dichlorotris(tristriphenylphosphine)ruthenium (II) **(152)** by

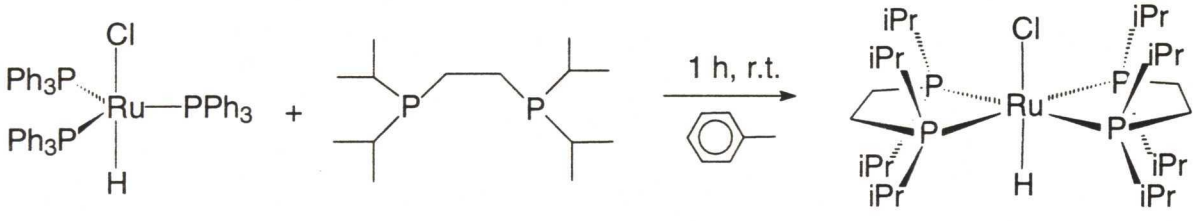
sodium borohydride in refluxing benzene, following the procedure of Hallman, McGarvey and Wilkinson (Scheme 3.25).[110]



(152) (172)

Scheme 3.25

$RuHCl(PPh_3)_3$ **(172)** has been used for the preparation of the ruthenium hydride complex **(173)** containing 1,2-bis(diisopropylphosphino)ethane, dippe **(174)**, reported in 1994 by Puerta and co-workers (Scheme 3.26).[111]

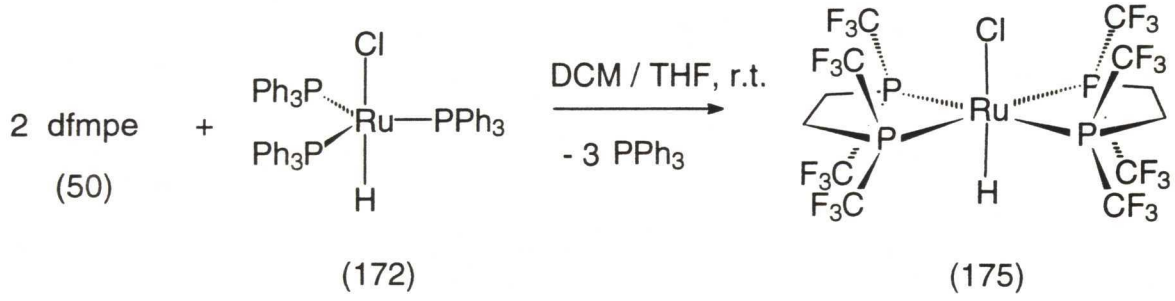


(172) (174) (173)

Scheme 3.26

Two equivalents of dfmpe **(50)** in dichloromethane were added to $RuHCl(PPh_3)_3$ **(172)** in benzene and the reaction was stirred at room temperature. The reaction was monitored by ^{19}F NMR spectroscopy and was complete after 30 min, with $RuHCl(dfmpe)_2$ **(175)** present as the sole fluorine-containing product in the reaction mixture (Scheme 3.27). The colour of the reaction mixture lightened from deep purple to yellow as the reaction proceeded. The crude

reaction mixture was filtered through dry flash silica and the silica was washed with more dichloromethane to elute any $RuHCl(dfmpe)_2$ (**175**) remaining on the column. The solvent was removed and the residue was washed exhaustively with light petroleum to remove triphenylphosphine. The residue from the light petroleum washings was dried under vacuum and found to be pure $RuHCl(dfmpe)_2$ (**175**), isolated in 65% yield . Failure to dry the flash silica before use resulted in drastic reduction of the yield of this reaction.



(172) (175)

Scheme 3.27

$RuHCl(dfmpe)_2$ (**175**) is an air-stable, colourless solid, which is soluble in organic solvents, but only sparingly soluble in light petroleum, and can be recrystallised from hexane to form colourless prisms. An attempt to purify $RuHCl(dfmpe)_2$ (**175**) by sublimation at 7×10^{-5} Torr at 75°C resulted only in slight decomposition, and the compound failed to sublime.

The ^{31}P NMR spectrum of $RuHCl(dfmpe)_2$ (**175**) shows one fluorine-coupled resonance at δ 96.2 ppm, indicating that all four phosphorus atoms are chemically equivalent (Figure 3.8(a)).

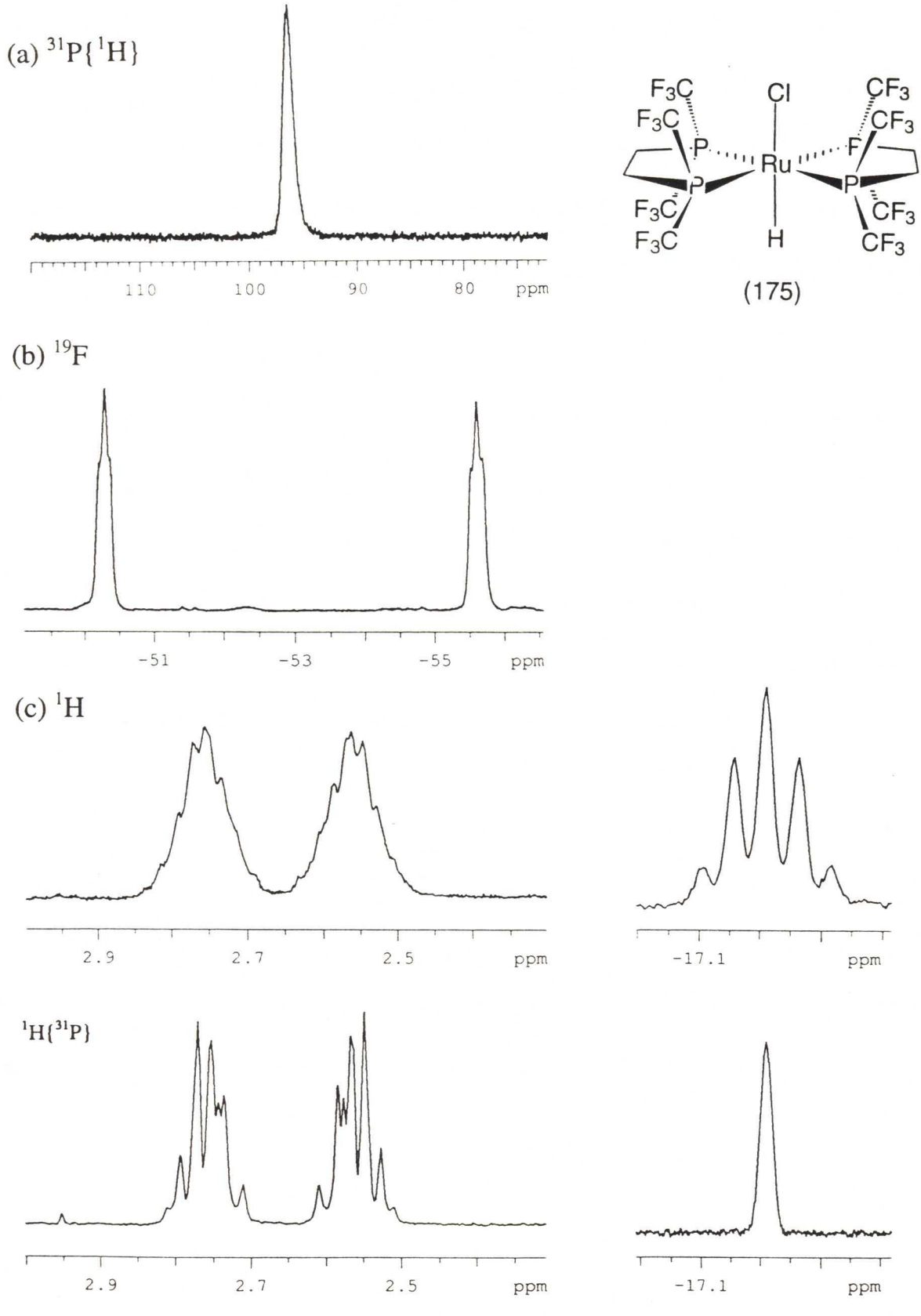


Figure 3.8 : (a) $^{31}P\{^{1}H\}$ NMR spectrum of $RuHCl(dfmpe)_2$ (**175**) in $CDCl_3$ at 300K
(b) ^{19}F NMR spectrum of $RuHCl(dfmpe)_2$ (**175**) in $CDCl_3$ at 300K
(c) ^{1}H NMR spectrum of $RuHCl(dfmpe)_2$ (**175**) in $CDCl_3$ at 300K

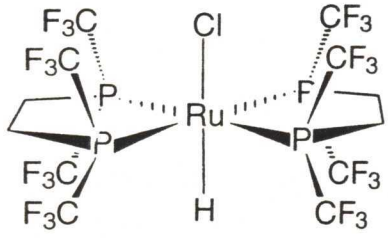
The ^{19}F NMR spectrum of $RuHCl(dfmpe)_2$ (**175**) shows two peaks, again one peak arising from the four CF_3 groups pointing towards the chloride group, and the other arising from the four CF_3 groups pointing towards the hydride group (Figure 3.8(b)). The two ^{19}F resonances appear as triplet-like multiplets due to second-order phosphorus coupling. The phosphorus nuclei are magnetically inequivalent with respect to the fluorine nuclei, resulting in a complex ^{19}F NMR spectrum.

The ^{1}H NMR spectrum of (**175**) shows a quintet at δ -17.21 ppm, which collapses to a singlet on phosphorus decoupling (Figure 3.8(c)). The ^{1}H NMR spectrum of $RuHCl(dfmpe)_2$ (**175**) also shows two phosphorus-coupled resonances at δ 2.75 and 2.56 ppm, each of which arises from four equivalent protons. One of these resonances results from the methylene protons on the dfmpe ligands on one face of the *trans* complex (**175**), and the other resonance results from the dfmpe methylene protons on the other face of this complex.

The $^{13}C\{^{1}H,^{31}P\}$ NMR spectrum of $RuHCl(dfmpe)_2$ (**175**) in d_8-THF consists of a broad quartet at δ 126.0 ppm (with a carbon-fluorine coupling constant of 320 Hz, typical for trifluoromethyl groups), arising from overlap of the two groups of trifluoromethyl carbon nuclei. The only other feature of this spectrum is a resonance at δ 21.3 ppm, which arises due to the four equivalent methylene carbon nuclei on the dfmpe ethylene bridge.

The infra-red spectrum of (**175**) as a nujol mull exhibits a weak stretch at 1978 cm^{-1}, which was assigned as the Ru-H stretch.

Crystals suitable for x-ray analysis were grown by slow solvent evaporation of a saturated solution of $RuHCl(dfmpe)_2$ (**175**). The structure of $RuHCl(dfmpe)_2$ (**175**) was analysed by x-ray diffraction, and Figure 3.9 shows an ORTEP plot of the structure



(175)

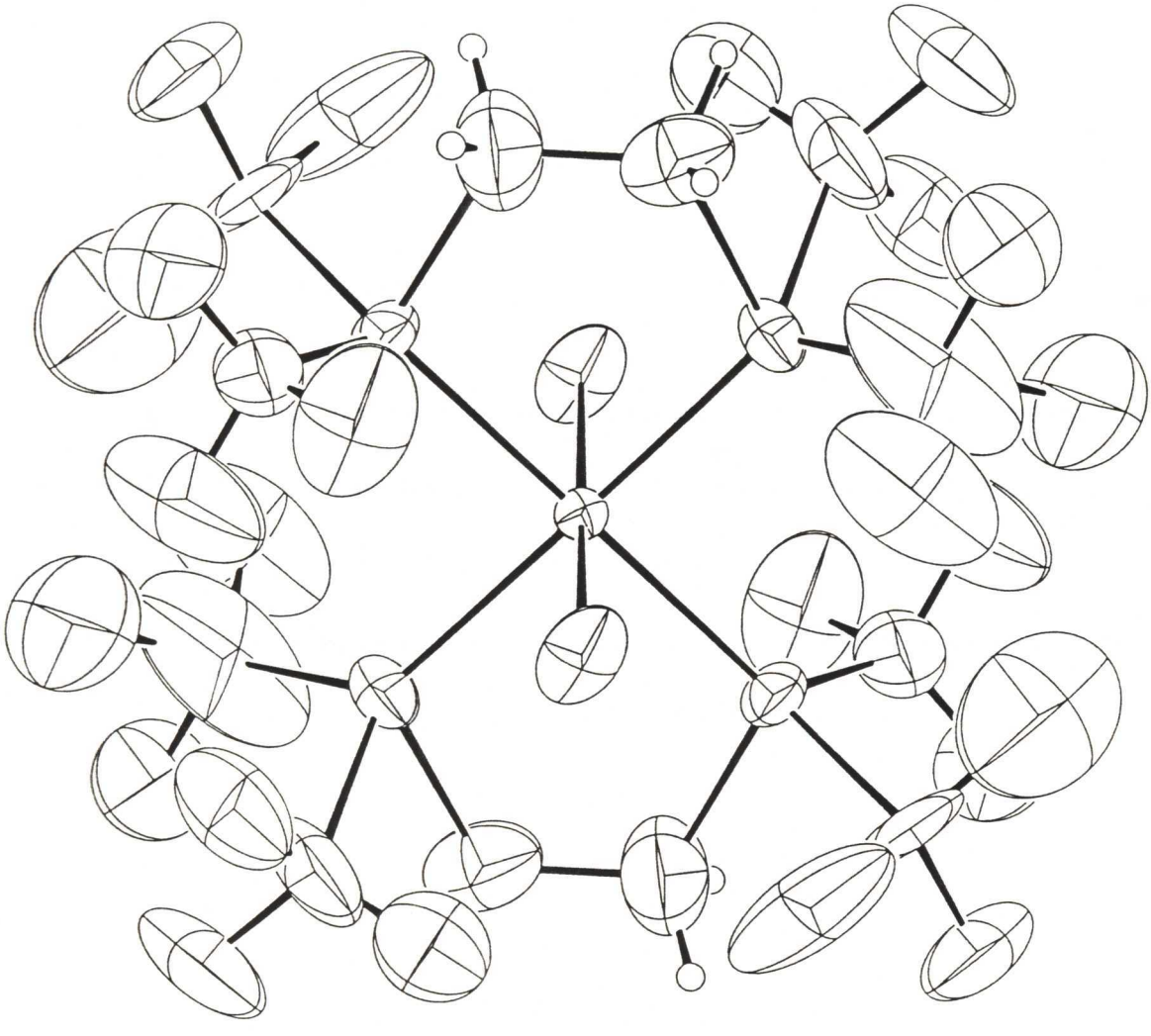
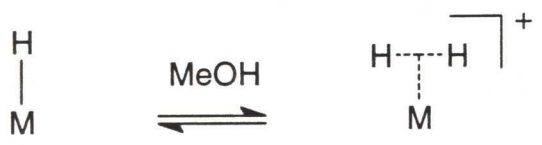


Figure 3.9 : ORTEP plot of $RuHCl(dfmpe)_2$ (**175**)

determined. *Trans*-chlorohydridobis[1,2-bis(bis(trifluoromethyl)phosphino)-ethane]ruthenium (II), $RuHCl(dfmpe)_2$ (**175**) crystallises in the centrosymmetric space group $P2_1/n$, with the ruthenium atom lying on a crystallographic centre of inversion and with half a molecule in the asymmetric unit. Consequently, the chloro and hydrido substituents are disordered in their (half) occupancies of the axial sites in the octahedral coordination. As a result, the hydride substituent could not be located from difference Fourier maps. The chloro substituent cleanly refines to half occupancy, thereby confirming the molecular stoichiometry. The problem of structure refinement is further compounded by disorder in the orientations of the trifluoromethyl substituents. Data was refined to give an R factor of 4.8%. Full crystallographic details are given in Appendix A4.

3.3.9 Reactions of $RuHCl(dfmpe)_2$

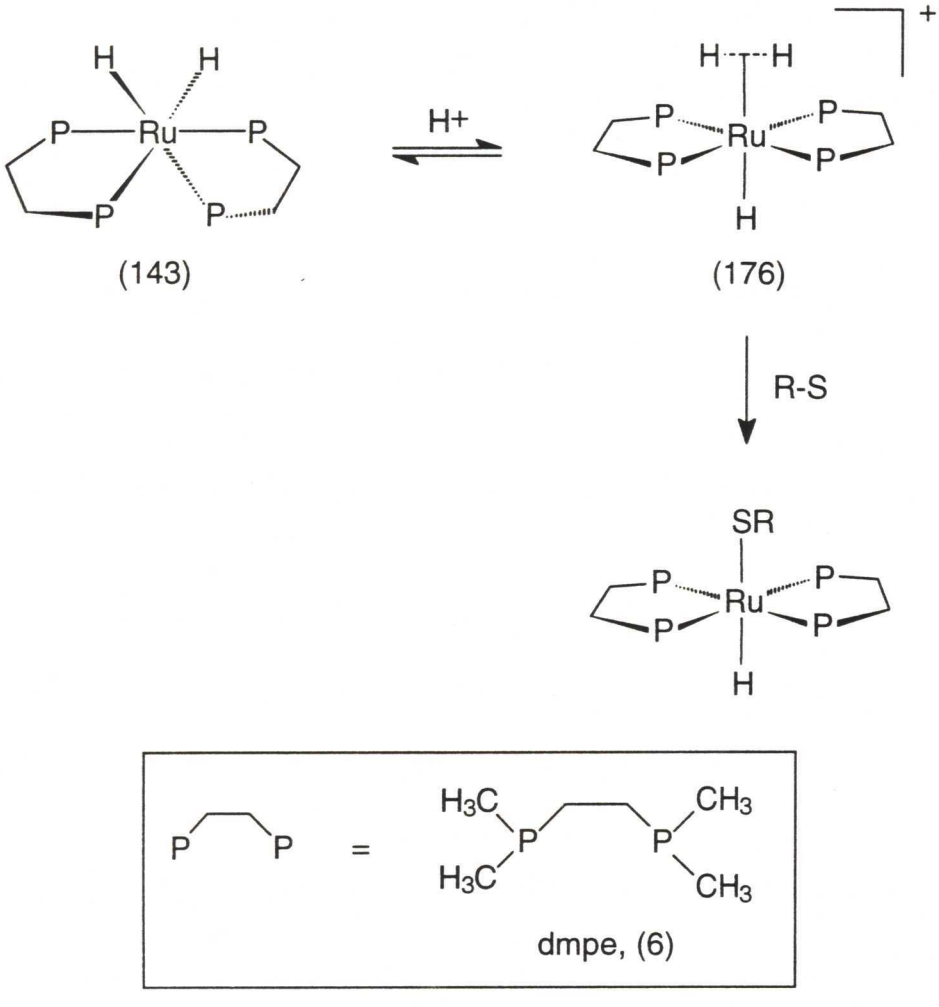
In the presence of organic acids such as methanol, iron and ruthenium complexes containing hydride ligands have been reported to undergo protonation to form a cationic complex containing a η^2- bound dihydrogen molecule (Scheme 3.28). Substitution of dihydrogen in complexes of this type by nucleophiles such as halides, thiols and acetylenes occurs readily under mild conditions to form a variety of new complexes.



Scheme 3.28

Field and Yau have reported the reversible protonation of $RuH_2(dmpe)_2$ (**143**) by methanol and ethanol to give the molecular hydrogen complex,

trans-[RuH(H_2)(dmpe)$_2$]$^+$ (**176**), which has a classical σ-bonded hydride ligand and an η^2-coordinated H_2 ligand.[100] Substitution of the weakly bound η^2-H_2 ligand from this compound by alkanethiols and arenethiols was reported to form *trans*-monothiolate hydrides (Scheme 3.29).[100]



Scheme 3.29; R = Ph, n-Pr, t-butyl, $HSCH_2CH_2CH_2$-, 3-HS-C_6H_4-, $HOCH_2CH_2$-.

RuHCl(dfmpe)$_2$ (**175**) in the presence of methanol was examined by NMR spectroscopy, to assess whether the compound can be protonated to form a molecular hydrogen complex.

3.3.9.1 Reaction of $RuHCl(dfmpe)_2$ with CD_3OD

A sample of $RuHCl(dfmpe)_2$ (**175**) was dissolved in CD_3OD and left at room temperature for 30 min. Analysis by ^{31}P NMR and ^{1}H NMR spectroscopy showed similar spectra to those obtained in $CDCl_3$. The ^{31}P NMR spectrum of $RuHCl(dfmpe)_2$ (**175**) in CD_3OD exhibits a single resonance at δ 98.4 ppm, not significantly different from the shift of δ 96.3 ppm that this compound exhibits in $CDCl_3$. Similarly, the hydride resonance of $RuHCl(dfmpe)_2$ (**175**) in CD_3OD appears as a quintet at -17.2 ppm, as it does in $CDCl_3$.

No evidence for the formation of a molecular hydrogen complex of $RuHCl(dfmpe)_2$ (**175**) in methanol solution was obtained.

3.3.9.2 Reaction of $RuHCl(dfmpe)_2$ with phenylacetylene in methanol

The reaction of $RuHCl(dfmpe)_2$ (**175**) with phenylacetylene in the presence of methanol was examined, to investigate the possibility of displacement by phenylacetylene of molecular hydrogen from the molecular hydrogen complex, if it is formed.

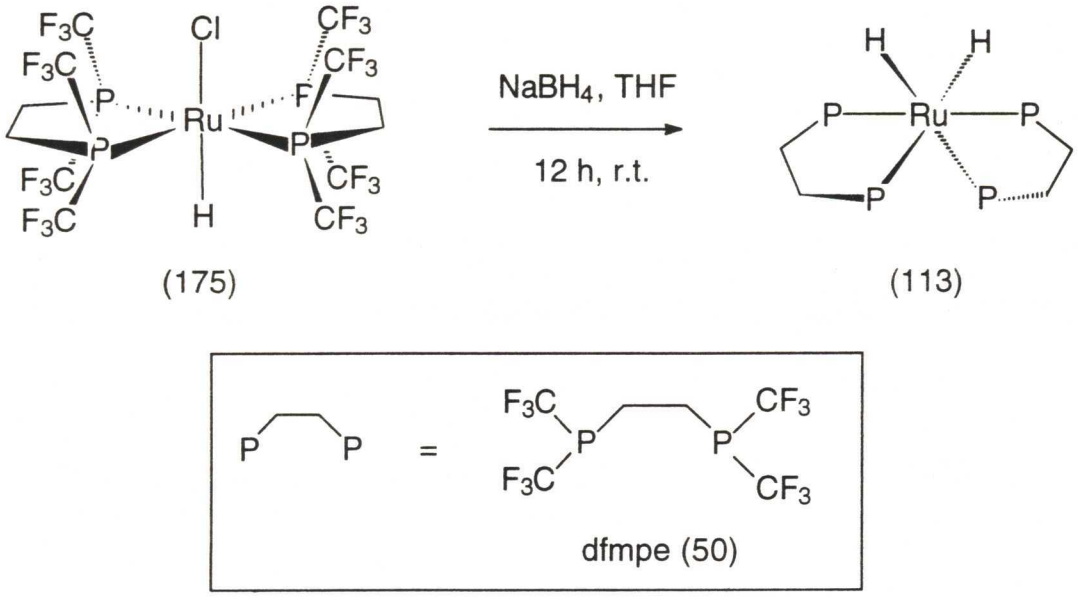
$RuHCl(dfmpe)_2$ (**175**) was dissolved in 0.5 ml of deuterated methanol in an NMR tube fitted with a concentric rotary valve. Excess phenylacetylene was added, and the ^{19}F NMR spectrum of the sample was recorded. Analysis of this sample by ^{19}F NMR spectroscopy showed that $RuHCl(dfmpe)_2$ (**175**) was the only fluorine-containing compound present. The sample was heated at 90°C for 45 min, and analysis by ^{19}F NMR spectroscopy showed that almost complete decomposition of $RuHCl(dfmpe)_2$ (**175**) had occurred. Analysis by ^{31}P NMR spectroscopy showed that a number of phosphorus-containing products arising from decomposition of $RuHCl(dfmpe)_2$ (**175**) had formed, among them free dfmpe (**50**). No new

ruthenium complexes were observed resulting from addition of phenylacetylene to $RuHCl(dfmpe)_2$ **(175)**.

3.3.10 Reduction of $RuHCl(dfmpe)_2$: Synthesis of $RuH_2(dfmpe)_2$

The reduction of $RuHCl(dfmpe)_2$ **(175)** was attempted to form the required compound, $RuH_2(dfmpe)_2$ **(113)**. Several reducing agents and solvents were investigated to find the optimum conditions to carry out this conversion. Sodium borohydride in THF, sodium borohydride in 2-propanol and sodium in 2-propanol were found to effect the conversion of $RuHCl(dfmpe)_2$ **(175)** to $RuH_2(dfmpe)_2$ **(113)**. Attempted reduction of $RuHCl(dfmpe)_2$ **(175)** with sodium borohydride in methanol resulted only in partial reaction of the starting hydrochloride complex, and showed no formation of $RuH_2(dfmpe)_2$ **(113)**. Yields of $RuH_2(dfmpe)_2$ **(113)** were highest when sodium borohydride was employed in 2-propanol, as the reaction of $RuHCl(dfmpe)_2$ **(175)** with sodium borohydride in THF produced quantities of THF-insoluble material, and resulted in isolated yields of $RuH_2(dfmpe)_2$ **(113)** of only 30%.

A solution of $RuHCl(dfmpe)_2$ **(175)** in 2-propanol was added to excess sodium borohydride in 2-propanol and the reaction mixture was stirred at room temperature for 16 h. ^{19}F NMR analysis of the crude reaction mixture showed that $RuHCl(dfmpe)_2$ **(175)** was completely converted to $RuH_2(dfmpe)_2$ **(113)**, and that $RuH_2(dfmpe)_2$ **(113)** was the only fluorine-containing product present (Scheme 3.30). The solvent was removed under vacuum and the residue was extracted exhaustively with light petroleum. The combined extracts were sublimed to afford $RuH_2(dfmpe)_2$ **(113)** as a white powder in 55% yield. The NMR spectra were identical to those observed for this compound when synthesised by reaction of Ru(COD)(COT) **(93)** with dfmpe **(50)** under H_2 gas (Section 3.3.7).



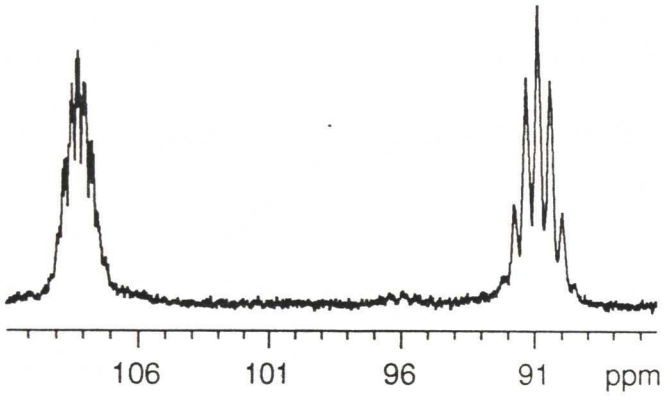
Scheme 3.30

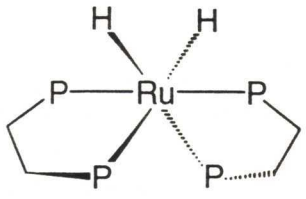
$RuH_2(dfmpe)_2$ **(113)** is a white, air-stable compound, soluble in all organic solvents and able to be purified by column chromatography. It sublimes at 50°C at 4×10^{-5} Torr as a white powder. Several attempts to crystallise this compound were made, and crystals were obtained from various solvents including hexane and toluene, but none were of sufficient quality for x-ray analysis.

The properties of $RuH_2(dfmpe)_2$ **(113)** are very different to those of its alkyl analogue, $RuH_2(dmpe)_2$ **(143)**. $RuH_2(dfmpe)_2$ **(113)** is stable indefinitely in the presence of air and moisture, whereas $RuH_2(dmpe)_2$ **(143)** is an extremely air-sensitive compound, able to tolerate only seconds in the air before a colour change to black occurs.[112] Whereas $RuH_2(dmpe)_2$ **(143)** exists as a mixture of *cis* and *trans* isomers, $RuH_2(dfmpe)_2$ **(113)** exists exclusively as the *cis* isomer.

The NMR spectra of $RuH_2(dfmpe)_2$ **(113)** are shown in Figure 3.10. The $^{31}P\{^1H\}$ NMR spectrum of **(113)** shows two distinct fluorine-coupled resonances at δ 90.9 ppm and 108.2 ppm, each due to two equivalent phosphorus atoms (Figure 3.10(a)).

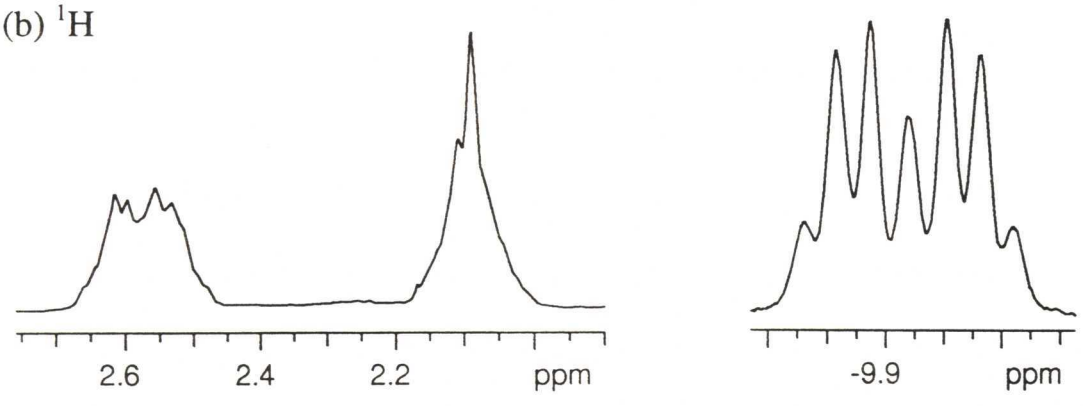
(a) $^{31}P\{^{1}H\}$





(113)

(b) ^{1}H



(c) ^{19}F

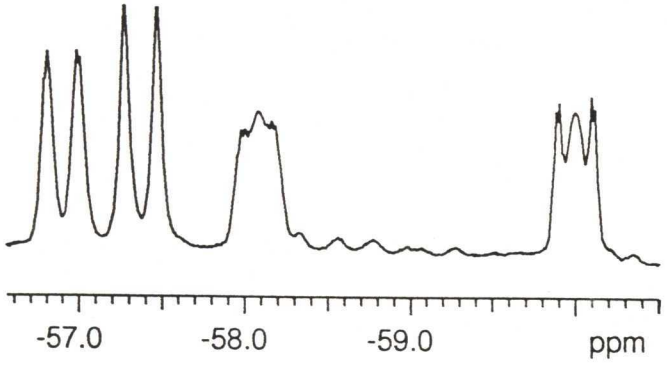


Figure 3.10 : (a) $^{31}P\{^{1}H\}$ NMR spectrum of $RuH_2(dfmpe)_2$ (**113**) in $CDCl_3$ at 300K
(b) ^{1}H NMR spectrum of $RuH_2(dfmpe)_2$ (**113**) in $CDCl_3$ at 300K
(c) ^{19}F NMR spectrum of $RuH_2(dfmpe)_2$ (**113**) in $CDCl_3$ at 300K

The ^{1}H NMR spectrum of $RuH_2(dfmpe)_2$ **(113)** shows a phosphorus-coupled resonance at -9.9 ppm due to the two metal bound hydrides (Figure 3.10(b)). The resonance collapses to a singlet with phosphorus decoupling. The appearance of this hydride resonance is almost identical to the hydride resonance exhibited by the analogous protonated complex, $RuH_2(dmpe)_2$ **(143)**, both in chemical shift and in phosphorus coupling.[101] The ^{1}H NMR spectrum of $RuH_2(dfmpe)_2$ **(113)** also exhibits two phosphorus-coupled resonances at 2.09 ppm and 2.58 ppm, due to two equivalent CH_2 groups on the ethylene back-bone of the dfmpe ligands (Figure 3.10(b).

The ^{19}F NMR spectrum of $RuH_2(dfmpe)_2$ **(113)** shows four phosphorus-coupled resonances, each representing two CF_3 groups (Figure 3.10(c)). Two of these resonances appear as doublets, while the other two appear as more complex multiplets.

The $^{13}C\{^{1}H,^{31}P\}$ NMR spectrum of **(113)** in $CDCl_3$ shows two multiplets at δ 127.1 and 123.9 ppm due to the two groups of equivalent trifluoromethyl carbon nuclei, and two multiplets at δ 23.5 and 22.2 ppm due to the two groups of equivalent methylene carbon nuclei.

The infrared spectrum of $RuH_2(dfmpe)_2$ **(113)** run as a KBr disk shows a weak band at 1931 cm^{-1} which is assigned to a Ru-H stretch.

A High Resolution Mass Spectrum was obtained on the $Ru(dfmpe)_2$ fragment, with the experimental mass of 833.82230 a.m.u. (expected mass 833.82368 a.m.u.).

3.4 Reactions of $RuH_2(dfmpe)_2$

$RuH_2(dfmpe)_2$ **(113)** was examined in an attempt to assess its use in hydrocarbon activation reactions. Samples of $RuH_2(dfmpe)_2$ **(113)** were subjected to u.v. radiation in the presence of substrates such as deuterium gas, carbon monoxide and triethylsilane, as well as compounds containing C-H bonds such as alkanes, alkenes and arenes.

The ability of $RuH_2(dfmpe)_2$ **(113)** to form a molecular hydrogen complex and undergo substitution of hydrogen by nucleophiles was examined by the reaction of **(113)** with organic acids.

3.4.1 Photolysis of $RuH_2(dfmpe)_2$ in the presence of D_2 gas

$RuH_2(dfmpe)_2$ **(113)** was irradiated in the presence of D_2 gas in order to assess the photochemical lability of the hydride ligands.

A solution of $RuH_2(dfmpe)_2$ **(113)** in pentane was degassed, placed under an atmosphere of D_2 gas and subjected to ultraviolet irradiation overnight. Analysis by ^2H NMR spectroscopy revealed the incorporation of deuterium into the hydride positions of $RuH_2(dfmpe)_2$ **(113)** (Figure 3.11(a)).

This experiment indicates that $RuH_2(dfmpe)_2$ **(113)** eliminates the two hydrides as hydrogen gas under photochemical conditions, and then recombines with hydrogen gas or deuterium gas to regenerate $RuH_2(dfmpe)_2$ **(113)** or $RuD_2(dfmpe)_2$ **(177)** respectively. This is strong evidence for the formation of the four-coordinate species, $Ru(dfmpe)_2$ **(178)** (Scheme 3.31).

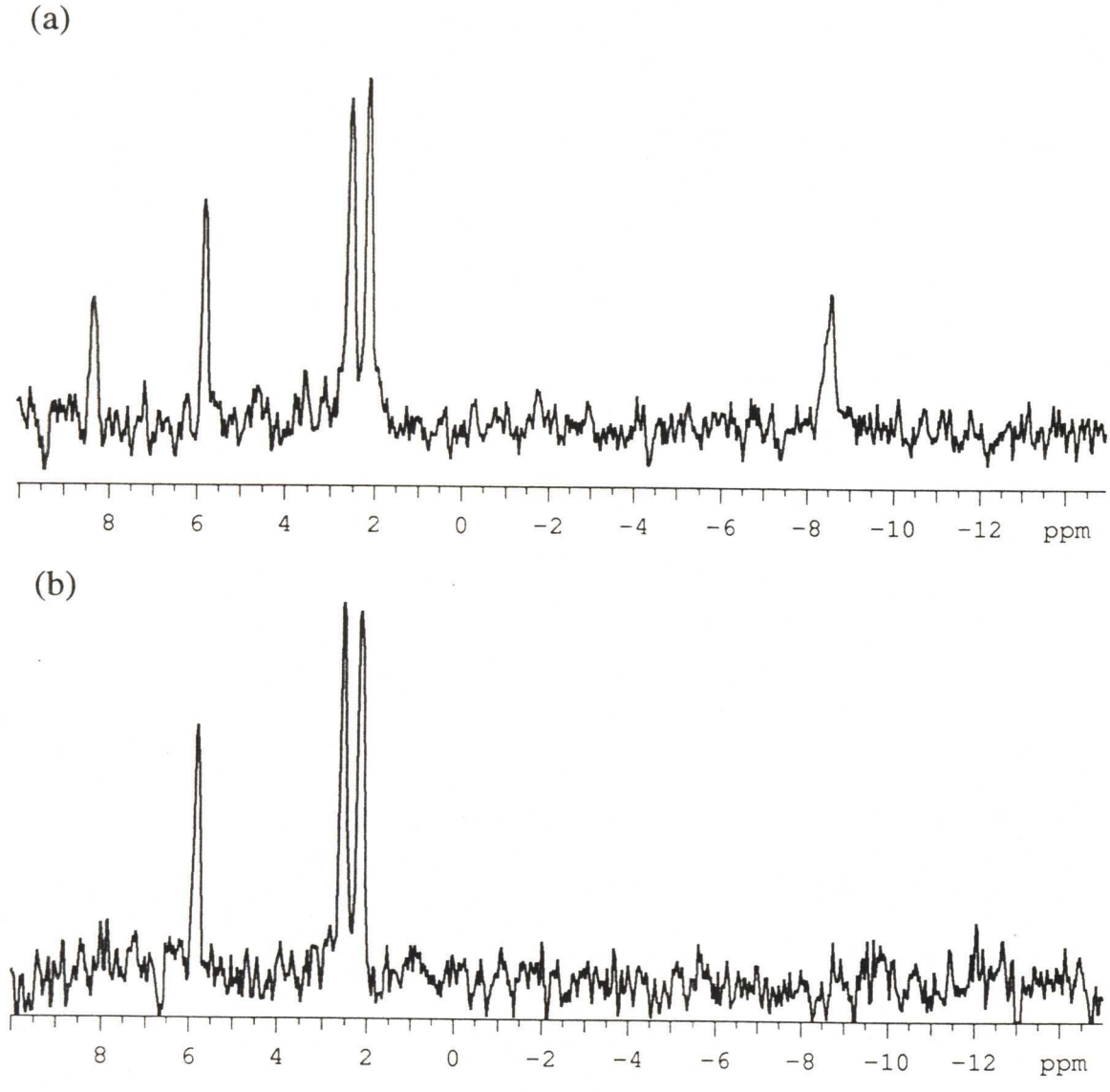
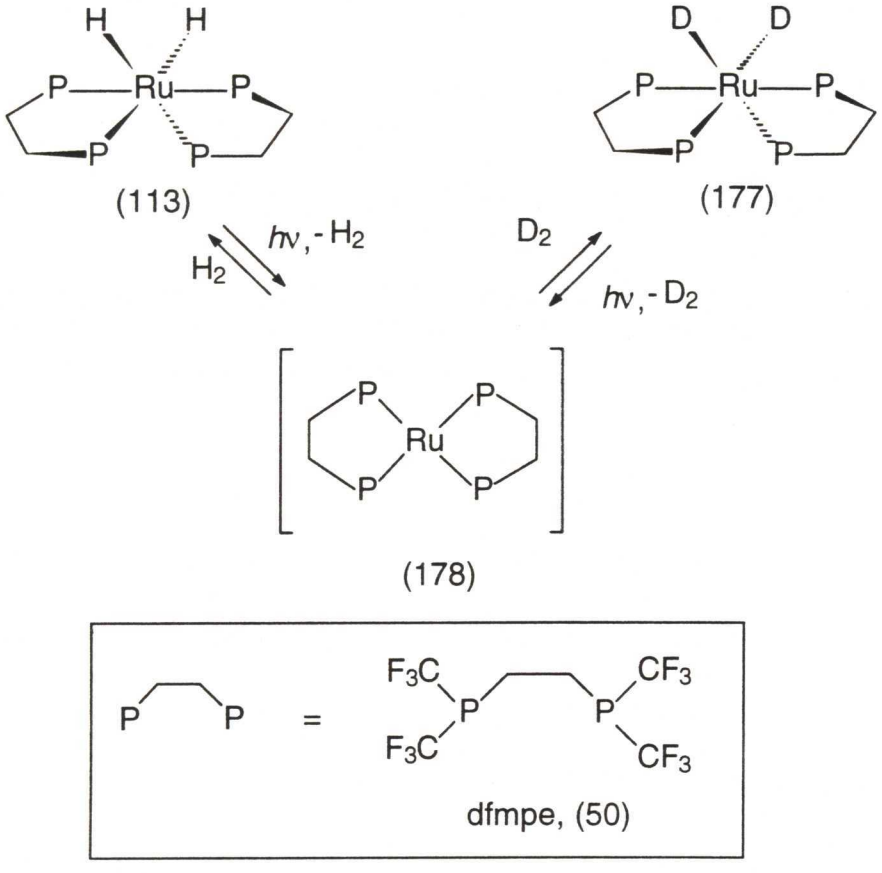


Figure 3.11 : (a) ^{2}H NMR spectrum of $RuH_2(dfmpe)_2$ **(113)** in pentane under 1 atm D_2 gas at 300K, after u.v. irradiation at room temperature for 16 h.

(b) ^{2}H NMR spectrum of $RuH_2(dfmpe)_2$ **(113)** in pentane under 1 atm D_2 gas at 300K, after being kept at room temperature for 43 h.



Scheme 3.31

An identical sample of $RuH_2(dfmpe)_2$ in pentane was prepared, put under 1 atm of D_2 gas and left at room temperature in the dark for an extended period of time. Analysis by ^2H NMR spectroscopy revealed no incorporation of deuterium into the hydride positions of $RuH_2(dfmpe)_2$ **(113)** (Figure 3.11(b)). This experiment suggests that the reversible removal of hydrogen and replacement for deuterium is only a photochemical process.

3.4.2 Photolysis of $RuH_2(dfmpe)_2$ in the presence of carbon monoxide

A sample of $RuH_2(dfmpe)_2$ **(113)** in THF was prepared, back-filled with carbon monoxide, and subjected to ultraviolet radiation at room temperature for 42 h. Analysis by ^{19}F NMR spectroscopy revealed the presence of $RuH_2(dfmpe)_2$ **(113)** as the major compound present, and also the presence of small products arising from the decomposition of the complex

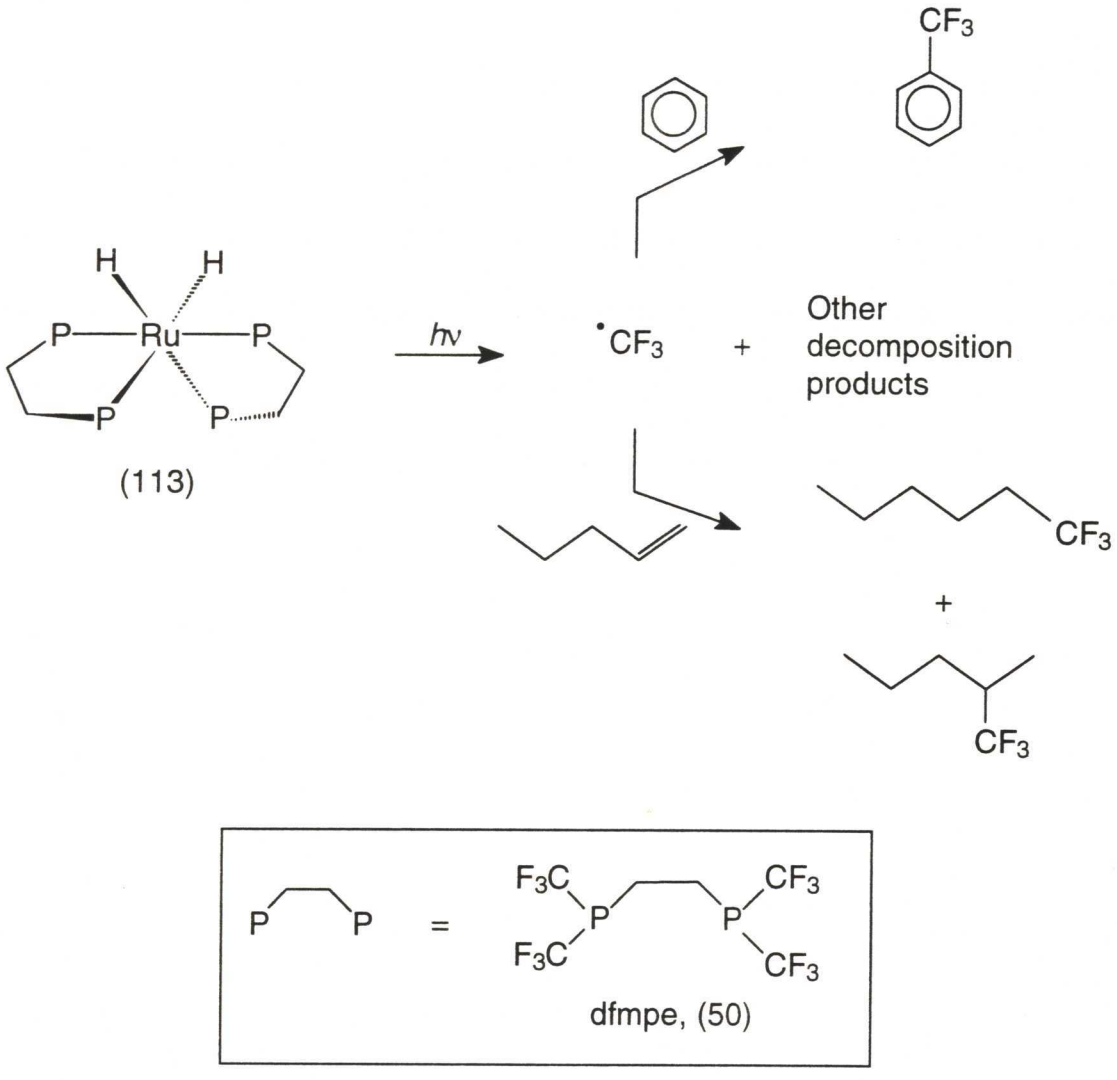
to dfmpe (**50**). Prolonged photolysis led only to a slow increase in the decomposition of $RuH_2(dfmpe)_2$ (**113**). No complexes containing carbon monoxide were observed.

3.4.3 Photolysis of $RuH_2(dfmpe)_2$ in the presence of organic substrates

The photolysis of $RuH_2(dfmpe)_2$ (**113**) in the presence of organic substrates was investigated, to assess the use of this complex in the activation of C-H bonds of organic compounds.

In a typical reaction, $RuH_2(dfmpe)_2$ (**113**) was dissolved in an organic substrate in an NMR tube fitted with a concentric teflon valve, and the solution was degassed by three freeze-pump-thaw cycles. The sample was then subjected to ultra-violet radiation at room temperature for an extended period of time (up to 16 h). Throughout this time, the sample was removed periodically from the lamp and analysed by ^{19}F NMR spectroscopy.

In the cases of cyclopentene, toluene, benzene, 1-pentene, triethylsilane and phenylacetylene, irradiation of samples for prolonged periods of time showed no evidence of reaction. The ^{19}F NMR spectra in all cases contained resonances only from $RuH_2(dfmpe)_2$ (**113**). When a more powerful lamp was used, decomposition of $RuH_2(dfmpe)_2$ (**113**) was observed in the ^{19}F NMR spectrum over a period of 12 h. In the reactions involving aromatic or unsaturated substrates, new products were observed in the ^{19}F NMR spectra which upon G.C./M.S. analysis were revealed to arise from generation of trifluoromethyl radicals and subsequent radical attack of this species onto the double bond of the substrate. Thus in the prolonged irradiation of $RuH_2(dfmpe)_2$ (**113**) in benzene, α,α,α-trifluorotoluene was identified in the G.C./M.S. spectrum (Scheme 3.32). Similarly, trifluorohexanes were identified in the reaction mixture after extended photolysis of $RuH_2(dfmpe)_2$ (**113**) in the presence of 1-pentene (Scheme 3.32).

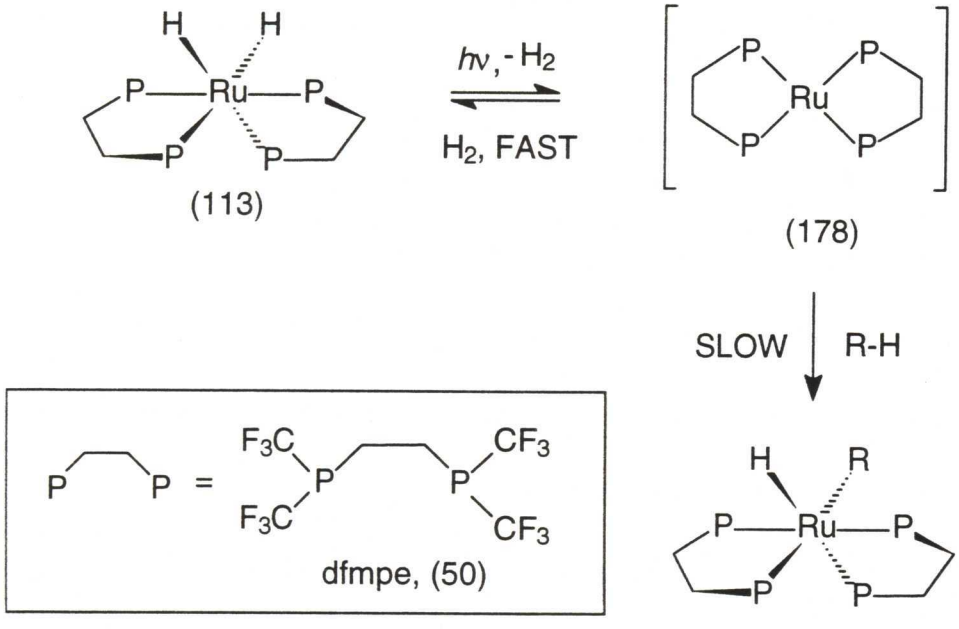


Scheme 3.32

$RuH_2(dfmpe)_2$ **(113)** was not found to possess the required photochemical activity for the activation of alkanes or other organic substrates.

Laser flash photolysis experiments have been carried out on $RuH_2(dfmpe)_2$ **(113)** by Professor Robin N. Perutz at the University of York. Laser flash photolysis allows intermediates with very short lifetimes to be observed in photoinitiated reactions, and often kinetic information about reactions involving these intermediates can be obtained. Preliminary results from experiments involving $RuH_2(dfmpe)_2$ **(113)** indicate that an intermediate is formed

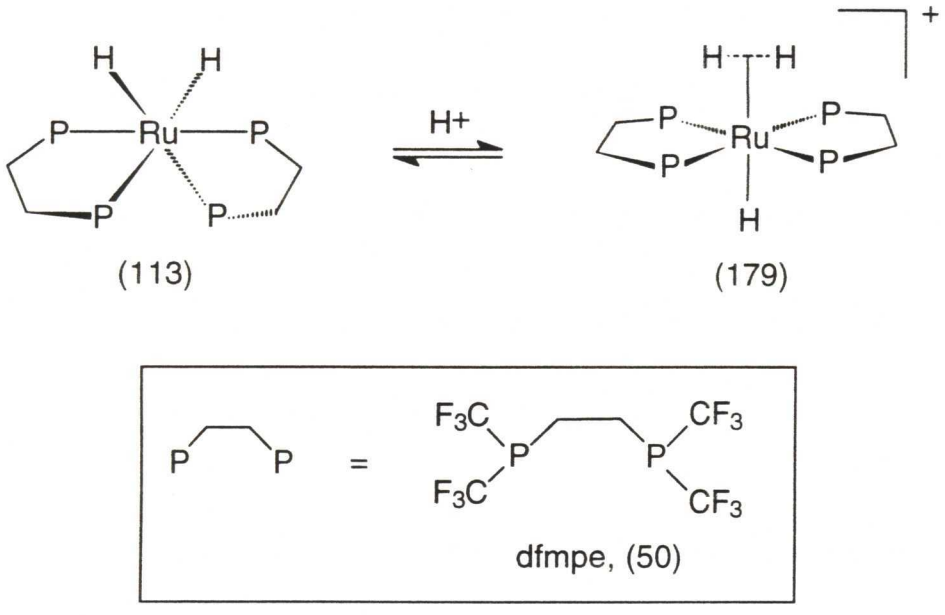
upon photolysis of this compound under flash conditions, and that the back-reaction of this intermediate with hydrogen gas is very fast (diffusion-controlled).[113] These results are consistent with those observed when $RuH_2(dfmpe)_2$ **(113)** is photolysed in the presence of organic substrates, as the back-reaction of $Ru(dfmpe)_2$ **(178)** with hydrogen (or deuterium) occurs too fast for successful competition by the organic substrate. Consequently, exchange of deuterium for hydrogen is observed photochemically, but no products arising from C-H activation of organic substrates are observed (Scheme 3.33).



Scheme 3.33

3.4.4 Reaction of $RuH_2(dfmpe)_2$ with organic acids

Reactions of $RuH_2(dfmpe)_2$ **(113)** with organic acids were carried out to determine whether $RuH_2(dfmpe)_2$ **(113)** could be protonated by acids to form a molecular-hydrogen complex, $[RuH_2H(dfmpe)_2]^+$ **(179)** in the same way as $RuH_2(dmpe)_2$ **(143)** (Scheme 3.34).



Scheme 3.34

A ^{19}F NMR spectrum of $RuH_2(dfmpe)_2$ **(113)** in d_4-methanol revealed only resonances arising from $RuH_2(dfmpe)_2$ **(113)**. This provides no evidence that a molecular hydrogen complex of $RuH_2(dfmpe)_2$ **(113)** is formed in methanol. Stronger acids were used in an attempt to protonate $RuH_2(dfmpe)_2$ **(113)**. ^{19}F NMR spectra of **(113)** dissolved in trifluoroacetic acid and triflic acid showed only peaks due to $RuH_2(dfmpe)_2$ **(113)** and these acids, and no evidence of the formation of new complexes.

To investigate the possibility of a fast equilibrium occurring between $RuH_2(dfmpe)_2$ **(113)** and its protonated form **(179)**, $RuH_2(dfmpe)_2$ **(113)** was dissolved in CD_3OD and the solvent removed. This procedure was repeated twice, and a ^2H NMR spectrum of the sample was acquired. This spectrum showed no deuterium resonance in the hydride region of the ^2H NMR spectrum, indicating that there is no incorporation of deuterium into the hydride of $RuH_2(dfmpe)_2$ **(113)** which would be expected if **(113)** is in equilibrium with the molecular hydrogen complex **(179)** in methanol solution. A solution of

$RuH_2(dfmpe)_2$ (**113**) in a mixture of phenylacetylene and methanol similarly showed only $RuH_2(dfmpe)_2$ (**113**) in the ^{19}F NMR spectrum, even after extended photolysis.

No evidence for the formation of a protonated form of $RuH_2(dfmpe)_2$ (**113**) in organic acids was obtained.

3.5 Summary of coordination properties of dfmpe

The coordination properties of dfmpe (**50**) are very different to those of the methyl analogue, dmpe (**6**). These properties demonstrate the influence fluorination can have on an organic compound. In contrast to the extensive coordination chemistry dmpe (**6**) exhibits with iron, no iron complexes containing dfmpe (**50**) have yet been isolated, or even observed.

Dfmpe (**50**) was found to complex readily to ruthenium by displacement of labile ligands. Several routes to the synthesis of $RuH_2(dfmpe)_2$ (**113**) were attempted, leading to the synthesis of $RuHCl(CO)(PPh_3)(dfmpe)$ (**155**), $RuH_2(CO)(PPh_3)(dfmpe)$ (**170**) and $RuCl_2(CO)(PPh_3)(dfmpe)$ (**171**). A crystal structure of $RuHCl(CO)(PPh_3)(dfmpe)$ (**155**) was obtained. The synthesis of $RuH_2(dfmpe)_2$ (**113**) was achieved by the reaction of Ru(COD)(COT) (**93**) with dfmpe (**50**) under an atmosphere of hydrogen gas, however this synthesis was not reliable.

The synthesis of $RuH_2(dfmpe)_2$ (**113**) was best carried out by synthesis of $RuHCl(dfmpe)_2$ (**172**) and subsequent reduction of this complex with sodium borohydride in 2-propanol. Good yields of $RuH_2(dfmpe)_2$ (**113**) are readily obtained using this method.

$RuH_2(dfmpe)_2$ (**113**) is very different in properties to its alkyl analogue,

$RuH_2(dmpe)_2$ **(143)**. $RuH_2(dfmpe)_2$ **(113)** is an air-stable and robust compound, in direct contrast to $RuH_2(dmpe)_2$ **(143)**. $RuH_2(dfmpe)_2$ **(113)** loses dihydrogen under photochemical conditions, but does not form NMR-observable intermediates when photolysed in the presence of alkanes, alkenes or arenes. In this respect, $RuH_2(dfmpe)_2$ **(113)** is similar to $RuH_2(dfepe)_2$ **(92)**, which also exchanges hydrogen for deuterium photochemically, but has not been reported to activate organic substrates.

Preliminary laser flash photolysis experiments indicate that the intermediate formed upon irradiation of $RuH_2(dfmpe)_2$ **(113)** reacts extremely rapidly with hydrogen, too fast to allow competitive activation of C-H bonds of organic substrates.

No evidence was found for the protonation of $RuH_2(dfmpe)_2$ **(113)** by strong organic acids, again in contrast to $RuH_2(dmpe)_2$ **(113)**. The differences in reactivity of $RuH_2(dfmpe)_2$ **(113)** compared to $RuH_2(dmpe)_2$ **(143)** arises from the drastic change to the electronic character of the metal centre imparted by the presence of the trifluoromethylphosphino groups.

The use of trifluoromethylated phosphines has been shown to cause great changes to the physical and chemical properties of organometallic complexes. The use of dfmpe **(50)** in organometallic complexes used to carry out activation of C-H bonds of organic substrates has resulted in reduced reactivity of these complexes in the desired reaction.

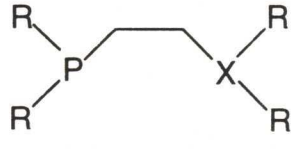
CHAPTER 4 : SYNTHESIS OF BIFE

4.1 Introduction

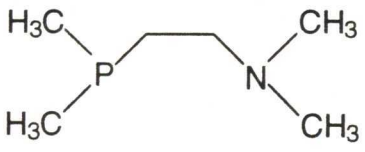
4.1.1 Mixed phosphines

Part of the reason for the widespread use of phosphines as ancillary ligands for organometallic complexes is the influence these ligands have on the reactivity of metal complexes. The ability to vary both the steric and electronic donor properties of a ligand enables modification of the reactivity and accessibility of a metal centre. Modification of the reactivity of metal bisphosphine complexes may be achieved by varying the nature of the four donor groups surrounding the metal atom, either by design of a ligand incorporating different donor atoms, or by using a common donor atom but varying the substituents on each donor atom. The synthesis of such *mixed ligands* incorporating one or more phosphorus donor atoms presents a highly challenging task.

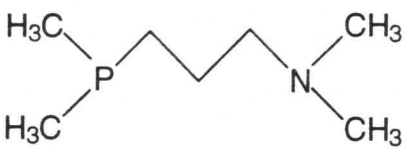
4.1.2 Mixed bidentate ligands containing one phosphorus atom and another hetero-atom



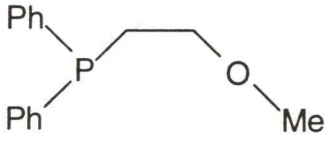
The synthesis of phosphines containing another heteroatom is a difficult task, and there are few reports in the literature dealing with compounds of this class. Examples of mixed-donor phosphorus/heteroatom chelating ligands which have been previously reported include phosphorus/nitrogen chelating ligands **(180)** and **(181)**,[114] and phosphorus/oxygen chelating ligands **(182)** and **(183)**.[115]



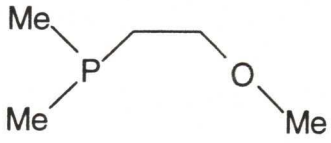
(180)



(181)



(182)



(183)

The difficulty in synthesising mixed phosphorus/heteroatom chelates has severely limited investigation of the coordination properties of these compounds. Mixed phosphine ligands of this type will not be discussed further.

4.1.3 Types of mixed bisphosphines

Subtle modification of the steric and electronic environment of a metal complex can be achieved through synthesis and coordination of *mixed bisphosphines*, that is bisphosphines of the form $R_1R_2P\text{-}PR_3R_4$, in which not all the groups bound to phosphorus, R_1, R_2, R_3, or R_4, are identical.

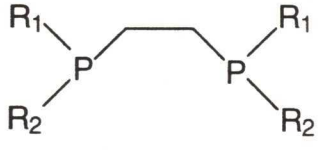
The advantages of phosphines as ancillary ligands for organometallic complexes, combined with the ever increasing range of synthetic methods available for the synthesis of sophisticated phosphines, makes the mixed bisphosphine an attractive class of ligand. In addition, the structure of the bisphosphine ligand itself, containing two phosphorus substituents and a bridging group which may be varied independently, is amenable to variation, and allows the fine-tuning of metal complexes containing bisphosphines.

The effect of the substituents on the phosphorus atoms of bisphosphines is particularly dramatic in complexes of the form $M(P\text{-}P)_2$, which have four phosphorus atoms bound to the metal atom. Incorporation of a variety of phosphine substituents in a bisphosphine can enable tuning of the ligand to suit a particular metal atom, or even to suit a particular reaction. Modification of bisphosphines in the way discussed results in more subtle changes in the steric and electronic environment of a metal complex than is available through use of simple, symmetrical mono- and bisphosphines. In the following discussion, the bisphosphines discussed all contain the ethylene group as the bridging unit.

There are several alternatives when considering bisphosphines containing different substituents. These bisphosphines can be divided into categories based on the symmetry of the bisphosphine ligand.

1) Symmetrical bisphosphines.

A bisphosphine (**184**) can be envisaged in which both phosphorus atoms are identical, and bear two different substituents, R^1 and R^2. The steric and electronic properties of both phosphorus donor atoms would be identical, and would presumably be intermediate between the steric and electronic properties of the $-P(R^1)_2$ and $-P(R^2)_2$ groups.

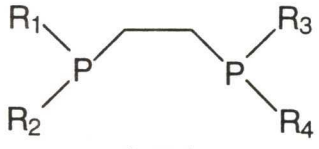


(184)

The synthesis of this type of bisphosphine would be difficult.

2) Fully unsymmetrical bisphosphines.

There are several types of unsymmetrical bisphosphines which could be envisaged. The most unsymmetrical bisphosphine, (**185**), is one which contains four unique groups, R^1, R^2, R^3 and R^4 bound to the two phosphorus donor atoms.

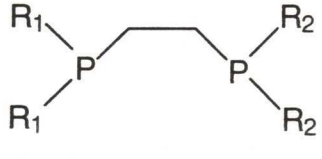


(185)

The synthesis of compounds such as **(185)** and the symmetrical mixed bisphosphine **(184)** is very challenging. There are few reports of the synthesis of **(184)** and no reports of the synthesis of **(185)** in the literature.

3) Unsymmetrical bisphosphines.

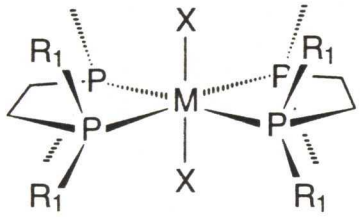
The other (synthetically more accessible) type of unsymmetrical bisphosphine **(186)** contains two groups, R^1, on one phosphorus atom, and two groups , R^2, on the other phosphorus atom, where $R^1 \neq R^2$.



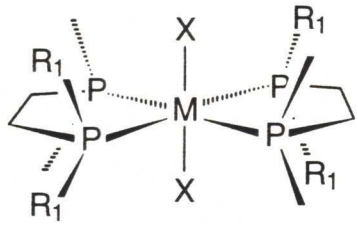
(186)

The formation of metal complexes of the form $M(P\text{-}P)_2$ containing unsymmetrical bisphosphines of this type introduces the possibility of stereochemical isomers. For example, an octahedral trans- complex such as $MX_2(P\text{-}P)_2$ could adopt

either the *syn* isomer **(187a)**, in which like groups, R^1 are in a *cis*- orientation, or the *anti* isomer **(187b)**, in which the like groups are *trans* to each other.

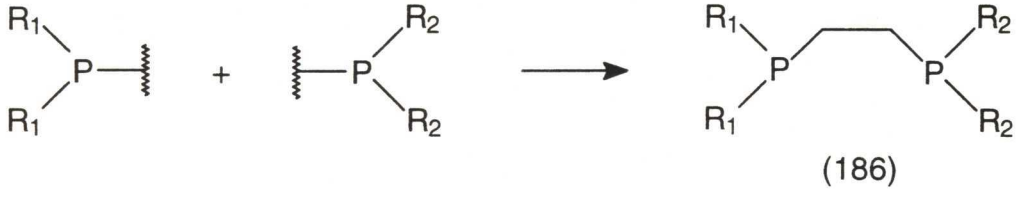


(187a)



(187b)

The synthesis of this type of unsymmetrical phosphine is also difficult, but methodology exists to carry out such syntheses. A possible route to the synthesis of such ligands involves the formation of monophosphines, $-P(R_1)_2$ and $-P(R_2)_2$ using traditional phosphine synthetic methods, followed by a coupling of the two phosphino groups with an alkyl bridge to form the unsymmetrical bisphosphine **(186)** (Scheme 4.1).



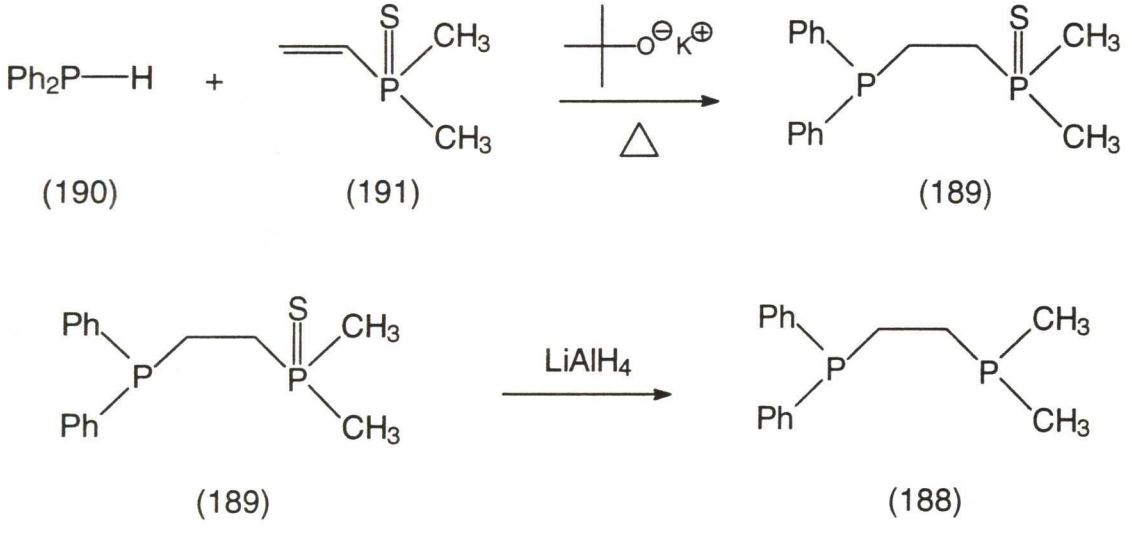
(186)

Scheme 4.1

Syntheses of mixed bisphosphines of this third type have previously been carried out, and the following discussion deals with the synthesis of unsymmetrical bisphosphines in this class.

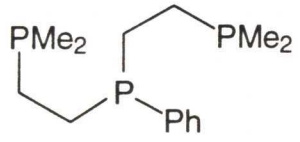
4.1.4 Previous syntheses of unsymmetrical mixed bisphosphines

Due to the difficulties involved in synthesising phosphines in general, the literature describing the synthesis of unsymmetrical bis-phosphines is scant. The first synthesis of unsymmetrical bis-phosphines was reported in 1973 by King *et al.*[116] (Dimethylphosphino)ethyldiphenylphosphine **(188)** was synthesised by the base-catalysed addition of diphenylphosphine to vinyldimethylphosphine sulfide, and subsequent deprotection of the phosphine sulfide **(189)** with lithium aluminium hydride (Scheme 4.2).

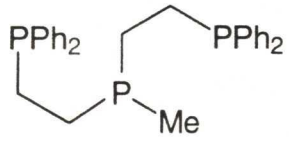


Scheme 4.2

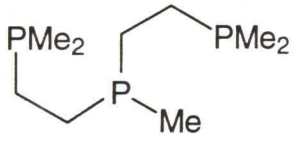
Analogous base-catalysed additions were carried out by King *et al* to synthesise the mixed polydentate ligands **(192)** - **(195)**, each with a mixture of methyl and phenyl substituents on the phosphorus atoms.[116]



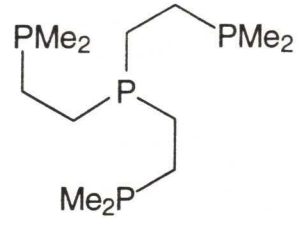
(192)



(193)

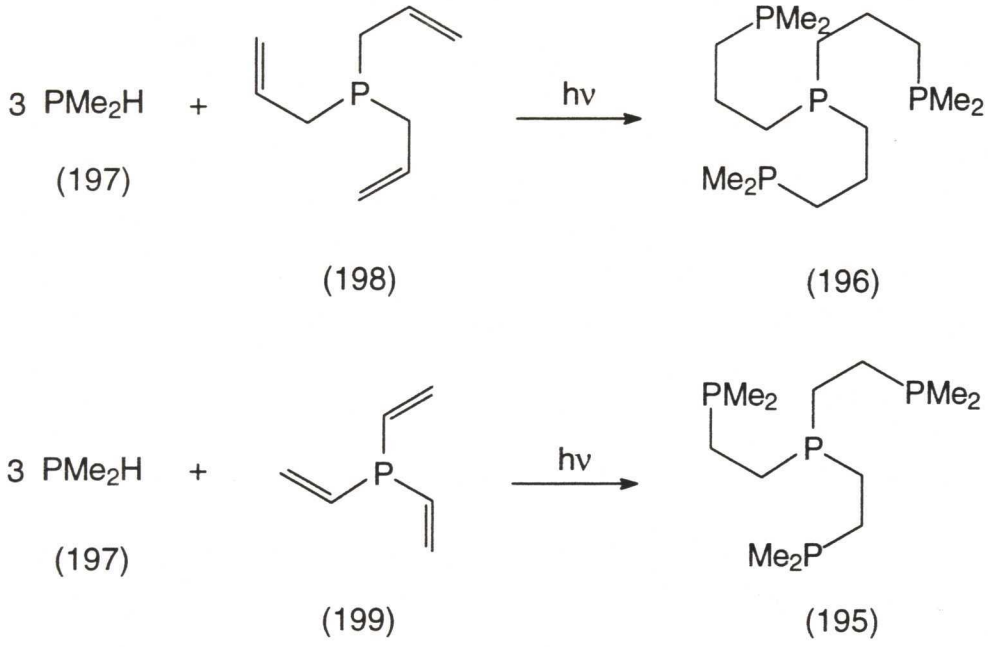


(194)



(195)

Some elegant work in this area was reported by Bampos, Field and co-workers in 1993.[117] Improved syntheses of the symmetrical ligands **(196)** and **(195)** were developed, by photochemical addition of dimethylphosphine **(197)** to triallylphosphine **(198)** and trivinylphosphine **(199)** (Scheme 4.3).

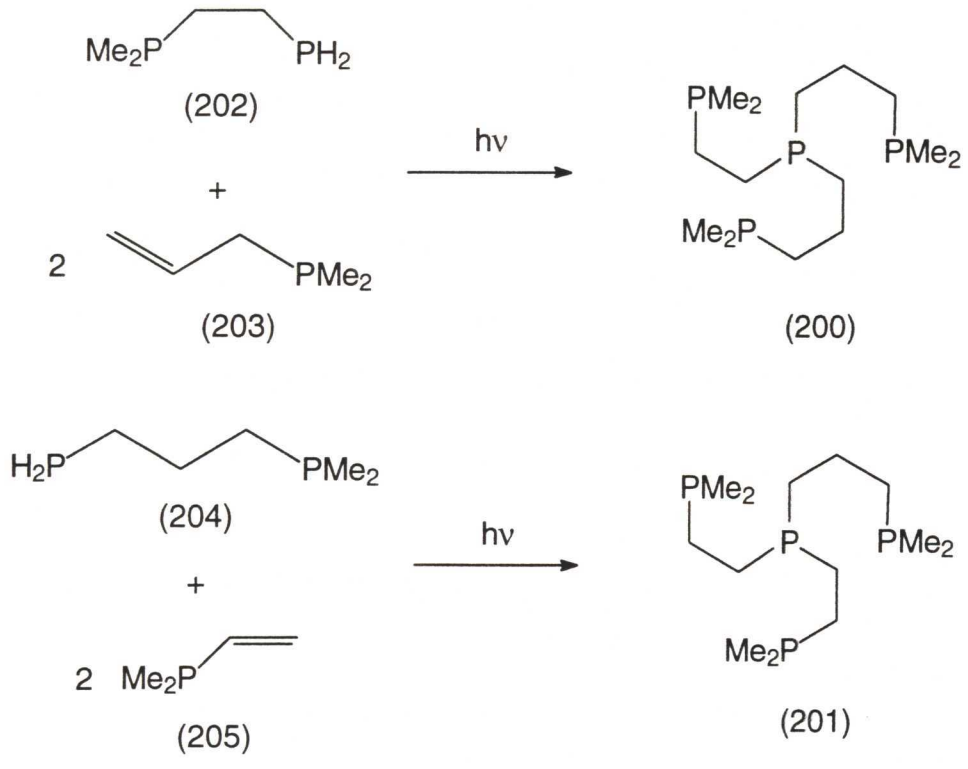


(197) (198) (196)

(197) (199) (195)

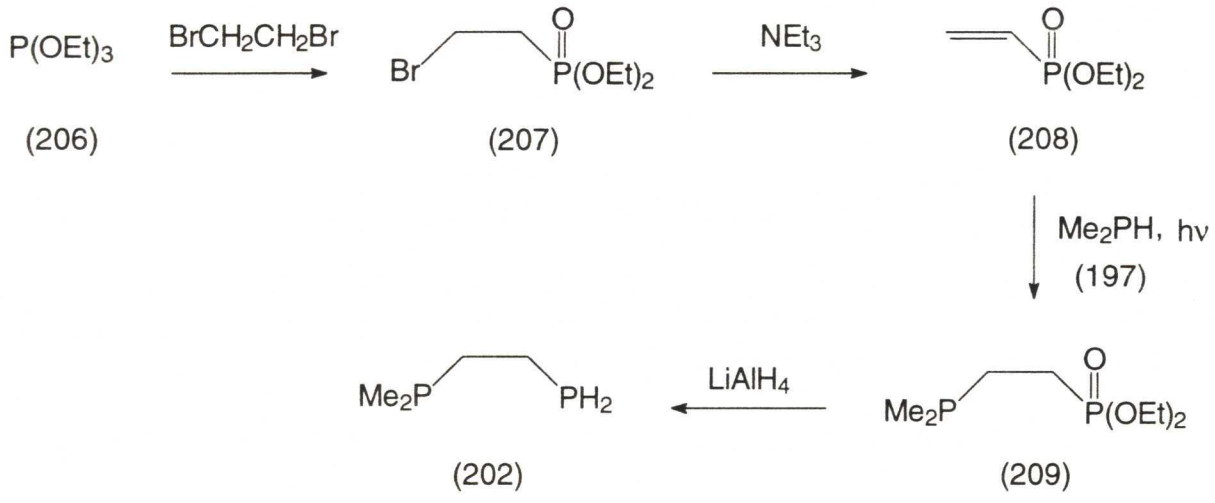
Scheme 4.3

Extension of this method and the development of other methods for phosphine synthesis enabled the synthesis of more sophisticated polydentate phosphines. The two unsymmetrical tetradentate phosphines (**200**) and (**201**), in which the radial alkyl chains are not all the same length, have been synthesised (Scheme 4.4).[117]



Scheme 4.4

Synthesis of (**200**) and (**201**) requires the synthesis of (**202**) and (**204**), unsymmetrical bisphosphines containing both a dimethylphosphino group and a primary phosphino group. The methodology for the synthesis of these synthetically important bisphosphines is illustrated in Scheme 4.5 with the synthesis of (2-(dimethylphosphino)ethyl)phosphine, $Me_2PCH_2CH_2PH_2$ (**202**).[117]



Scheme 4.5

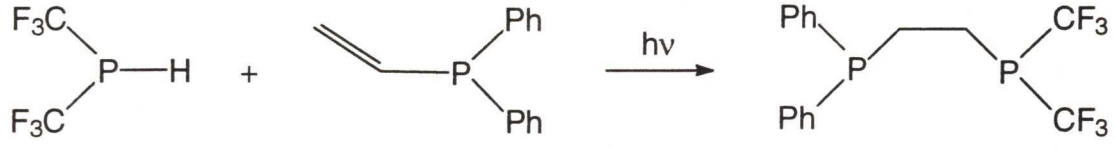
(2-(Dimethylphosphino)ethyl)phosphine, $Me_2PCH_2CH_2PH_2$ (**202**), is a useful synthetic intermediate in the synthesis of unsymmetrical bisphosphines.

4.1.5 Mixed bisphosphines containing fluorinated groups

The incorporation of fluorinated substituents into bisphosphines such as dfmpe (**50**) results in dramatic changes in the properties of the phosphorus donor atoms, and leads to marked changes in the reactivity of metal complexes containing fluorinated phosphines (see Chapter 3). The synthesis of mixed bisphosphines containing one or more fluoroalkyl groups may lead to a bisphosphine exhibiting properties intermediate between those of the alkyl bisphosphines, and those of the perfluoroalkyl phosphines. The reactivity of organometallic complexes containing such mixed fluorinated phosphines is similarly expected to be different to the reactivity of metal complexes containing fully alkylated or fully fluorinated bisphosphines. By appropriate choice of the alkyl and fluoroalkyl groups comprising the bisphosphine, fine-tuning of metal complexes containing mixed alkylated/fluoroalkylated may be achieved.

Only a small number of mixed bisphosphines containing perfluoroalkyl or perfluoroaryl groups have been synthesised, due to the synthetic difficulties involved.

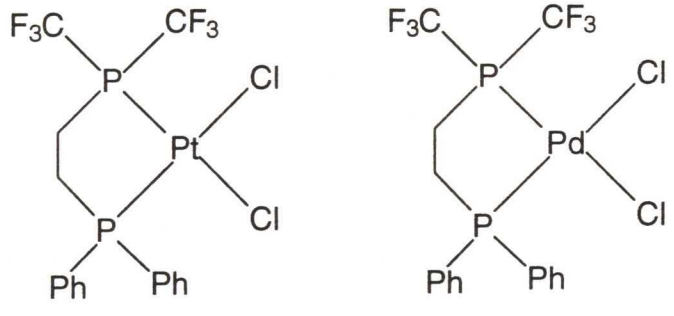
The synthesis of the first mixed phosphine incorporating a perfluoroalkyl group was carried out by Manojlovic-Muir *et al* in 1975.[118] Manojlovic-Muir and co-workers synthesised 1-(bis(trifluoromethyl)phosphino)-2-(diphenylphosphino)ethane (**210**) by the photochemical addition of bis(trifluoromethyl)phosphine to diphenylvinylphosphine (Scheme 4.6).[118]



(118) (211) (210)

Scheme 4.6

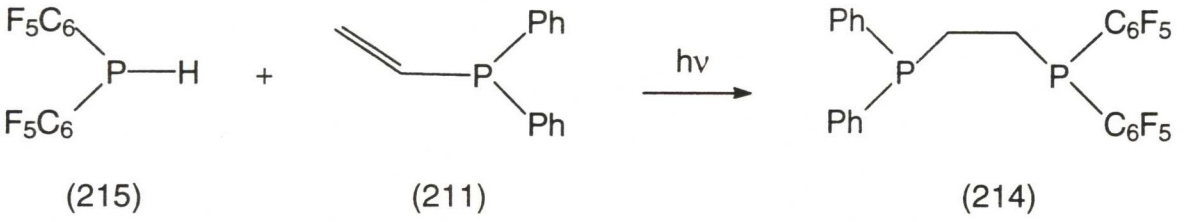
Manojlovic-Muir *et al* also reported the synthesis of the platinum[119] and palladium[118] complexes (**212**) and (**213**) with 1-(bis(trifluoromethyl)phosphino)-2-(diphenylphosphino)ethane (**210**).



(212) (213)

The analogous ligand 1-bis(pentafluorophenyl)phosphino-2-(diphenyl-phosphino)ethane (**214**), has also been reported by Manojlovic-Muir *et al* via the

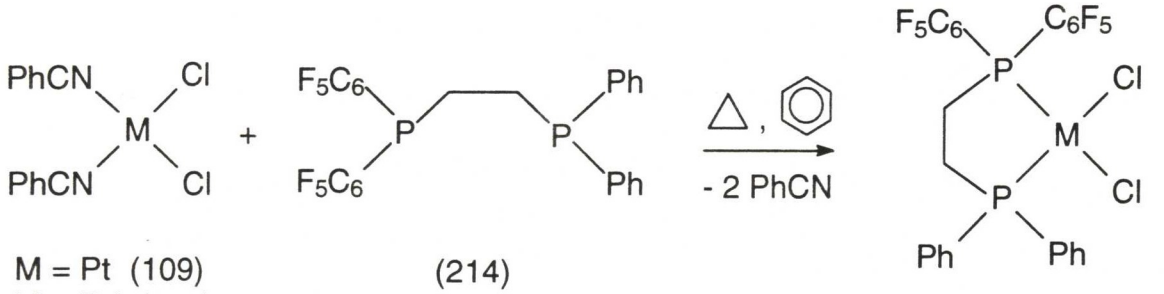
photochemical addition of bis(pentafluorophenyl)phosphine (**215**) to diphenylvinylphosphine (**211**) (Scheme 4.7).[119]



(215) (211) (214)

Scheme 4.7

Manojlovic-Muir *et al* also reported the synthesis of platinum[119] and palladium[118] complexes (**216**) and (**217**) containing $Ph_2PCH_2CH_2P(C_6F_5)_2$ (**214**) by the thermal reaction of (**214**) with $PtCl_2(PhCN)_2$ (**109**) and $PdCl_2(PhCN)_2$ (**218**) respectively (Scheme 4.8).



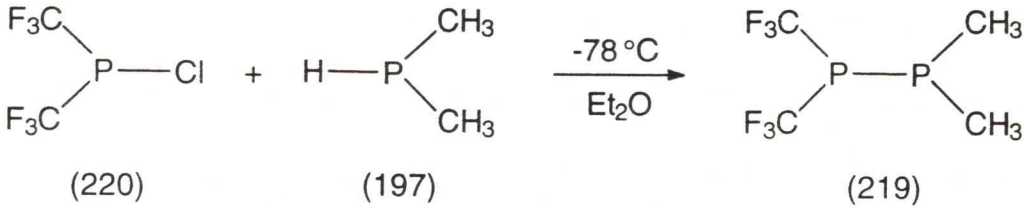
M = Pt (109)
M = Pd (218)

(214)

M = Pt (216)
M = Pd (217)

Scheme 4.8

The unsymmetrical diphosphine, bis(trifluoromethyl)dimethyldiphosphine (**219**), was reported in 1962 by Grant and Burg,[120] by the direct reaction of dimethylphosphine (**197**) and bis(trifluoromethyl)chlorophosphine (**220**) at low temperature in ether (Scheme 4.9).

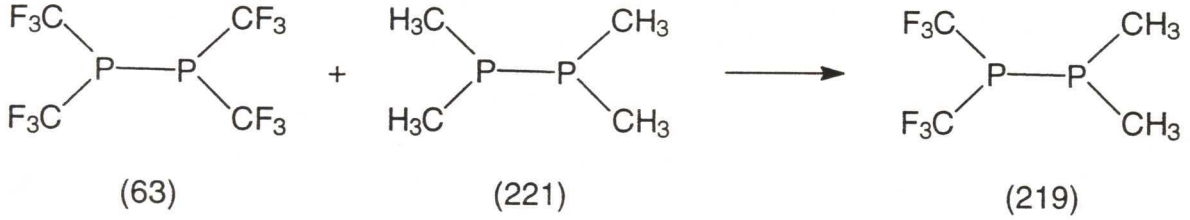


(220) (197) (219)

Scheme 4.9

Grant and Burg report that the unsymmetrical diphosphine (**219**) has very different properties from either tetramethyldiphosphine (**221**) or tetrakis(trifluoromethyl)-diphosphine (**63**).[120] In particular, bis(trifluoromethyl)dimethyldiphosphine (**219**) has a lower thermal stability than either of the symmetrical phosphines (**221**) and (**63**), decomposing at 110°C compared to over 300°C for both (**221**) and (**63**). This property is a consequence of having two very different groups in one molecule.

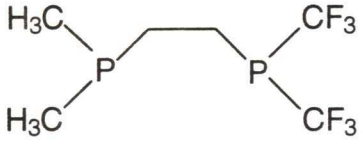
Bis(trifluoromethyl)dimethyldiphosphine (**219**) was synthesised by a different route in 1989. Avens *et al* reported that a disproportionation reaction can occur between two different symmetrical diphosphines if their basicities are very different.[71] The reaction of tetramethyldiphosphine (**221**) and tetrakis(trifluoromethyl)diphosphine (**63**) in a sealed tube at room temperature was reported to give clean conversion to bis(trifluoromethyl)dimethyl-diphosphine (**219**) (Scheme 4.10).



(63) (221) (219)

Scheme 4.10

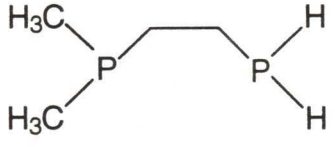
There have been no reports of the synthesis of (2-(dimethylphosphino)ethyl)-bis(trifluoromethyl)phosphine, (bife) (**222**). This ligand would be interesting in that it imposes the least steric demands on a metal centre of this class of bidentate ligand, and contains two groups differing greatly in electronic character. Bife (**222**) is an analogue of both dmpe (**6**) and dfmpe (**50**), and is expected to exhibit properties somewhere intermediate between the properties of (**6**) and (**50**).



bife, (222)

4.2 Preparation of $Me_2PCH_2CH_2P(CF_3)_2$ (bife)

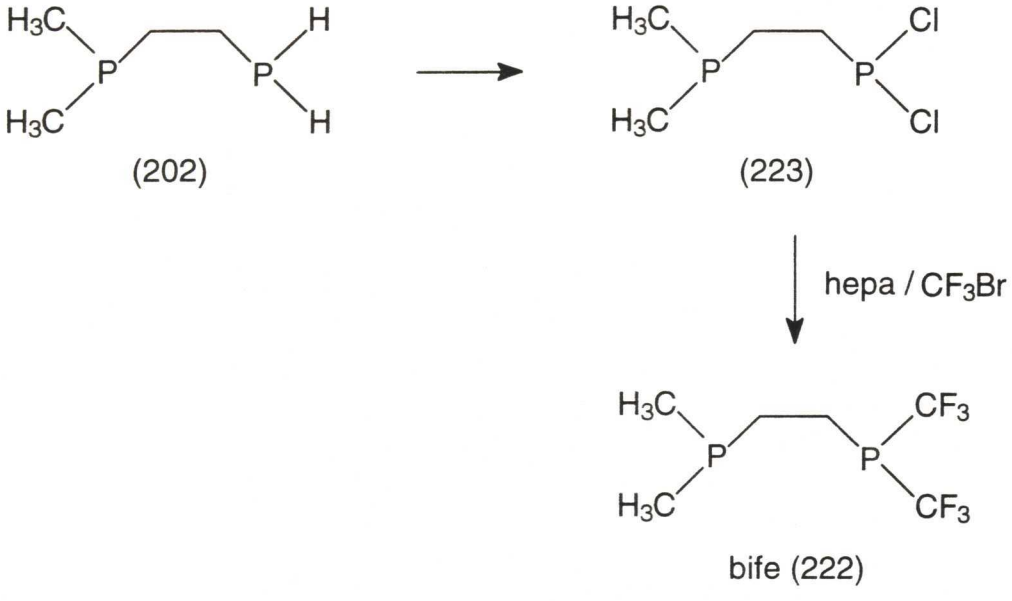
A synthetic scheme was required for the synthesis of the mixed unsymmetrical bisphosphine, bife (**222**), which consists of a dimethylphosphino group and a bis(trifluoromethyl) group bridged by an ethylene group. The initial synthetic steps to this ligand were developed by Bampos and Field in their synthesis of (2-(dimethyl-phosphino)ethyl)phosphine (**202**), an intermediate used to assemble polydentate phosphines.



(202)

(2-(Dimethylphosphino)ethyl)phosphine (**202**) already contains the dimethylphosphino group present in the target compound, bife (**222**), and has a synthetically useful primary

phosphino group on the other end of this compound. The conversion of this primary phosphino group to a bis(trifluoromethyl) group is required for the synthesis of bife (**222**). The trifluoromethylation reaction developed in this work and used to synthesise dfmpe (**50**) (Section 2.3) may be applicable to the synthesis of bife (**222**), if the dichloro compound (**223**) can be synthesised from (2-(dimethylphosphino)ethyl)phosphine (**202**) (Scheme 4.11).

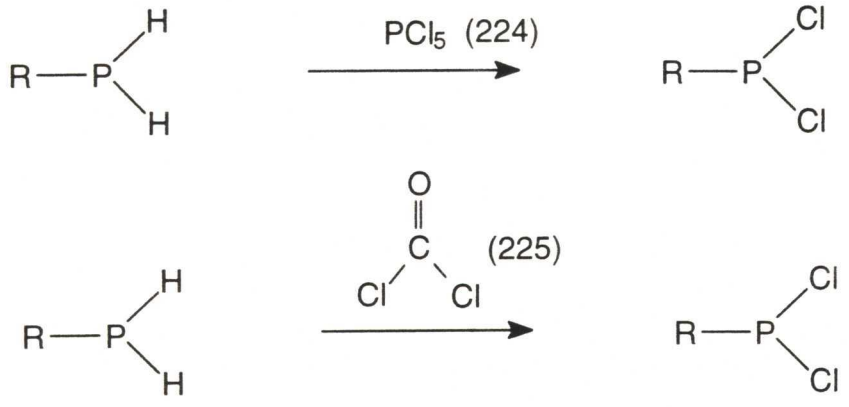


Scheme 4.11

A reagent is needed to convert (2-(dimethylphosphino)ethyl)phosphine (**202**) to (2-(dimethylphosphino)ethyl)dichlorophosphine (**223**).

4.2.1 Chlorination of primary phosphines

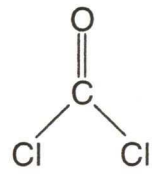
The conversion of a primary phosphine to the corresponding dichlorophosphine has been carried out in high yield using both phosphorus pentachloride (**224**) and phosgene (**225**) (Scheme 4.12).[121,122]



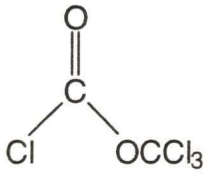
Scheme 4.12

Reagents such as SO_2Cl_2 are unsuitable for this conversion as they result in the oxidation of the phosphorus centre from phosphorus(III) to phosphorus(V).[75] While the toxicity and volatility of phosgene (**225**) often acts as a deterrent to using this reagent, liquid or solid phosgene substitutes (**226**) and (**227**) have recently become available which are safer and easier to handle. Trichloromethyl chloroformate , $ClC(O)OCCl_3$ (**226**), ("diphosgene")[123] has already proved its use as a phosgene substitute in many common phosgene reactions,[124] but as a liquid, its handling and storage are still dangerous.

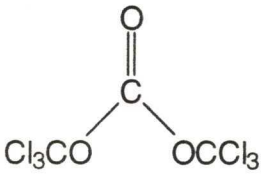
Recently, a phosgene substitute known as bis(trichloromethyl) carbonate, $Cl_3COC(O)OCCl_3$ (**227**), ("triphosgene") has become commercially available[125] and is reported to be much easier and safer to handle than phosgene (**225**) itself.[126] Triphosgene (**227**) is a white, crystalline solid (m.p. 81-83°C) which, as well as carrying out reactions where phosgene has been previously used, has been useful in situations where it is advantageous to weigh out an exact amount of the chlorinating agent.[127,128]



Phosgene (225)



Diphosgene (226)



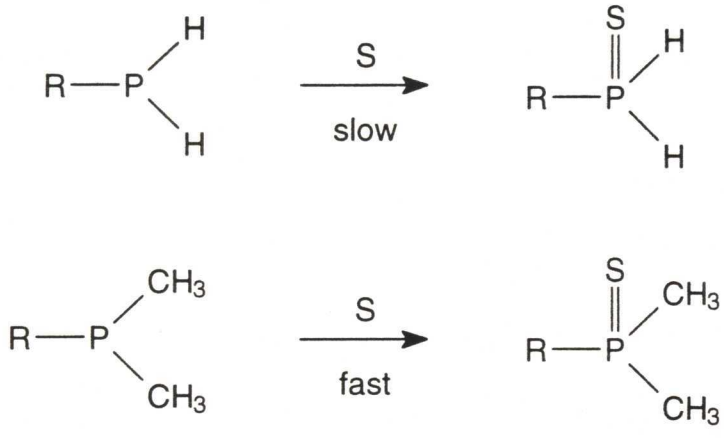
Triphosgene (227)

Triphosgene (**227**) and phosphorus pentachloride (**224**) were investigated as chlorinating reagents for the conversion of (2-(dimethylphosphino)ethyl)phosphine (**202**) to (2-(dimethylphosphino)ethyl)dichlorophosphine (**223**).

4.2.2 Protection of $Me_2PCH_2CH_2PH_2$

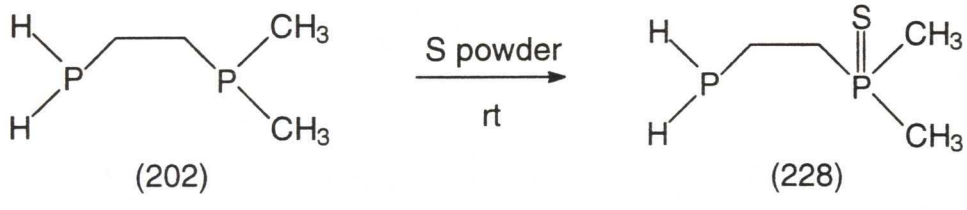
The reaction of $Me_2PCH_2CH_2PH_2$ (**202**) with chlorinating agents such as triphosgene (**227**) and phosphorus pentachloride (**224**) to form $Me_2PCH_2CH_2PH_2$ (**202**) has the potential to effect undesirable chlorination and concurrent oxidation of the dimethylphosphino group of (**202**), as well as the desired chlorination of the primary phosphino group of (**202**). Protection of this group was found to be necessary. Sulfurisation has traditionally been the method of choice for the protection of phosphines, since sulfur can be removed easily with a variety of reagents when protection is no longer required.

The basicity of tertiary phosphines is greater than that of primary phosphines,[129] due to the greater electron-releasing character of alkyl groups surrounding a tertiary phosphine. Reaction of the dimethylphosphino group of $Me_2PCH_2CH_2PH_2$ (**202**) with elemental sulfur occurs substantially faster than sulfurisation of the primary phosphine end of (**202**) (Scheme 4.13).



Scheme 4.13

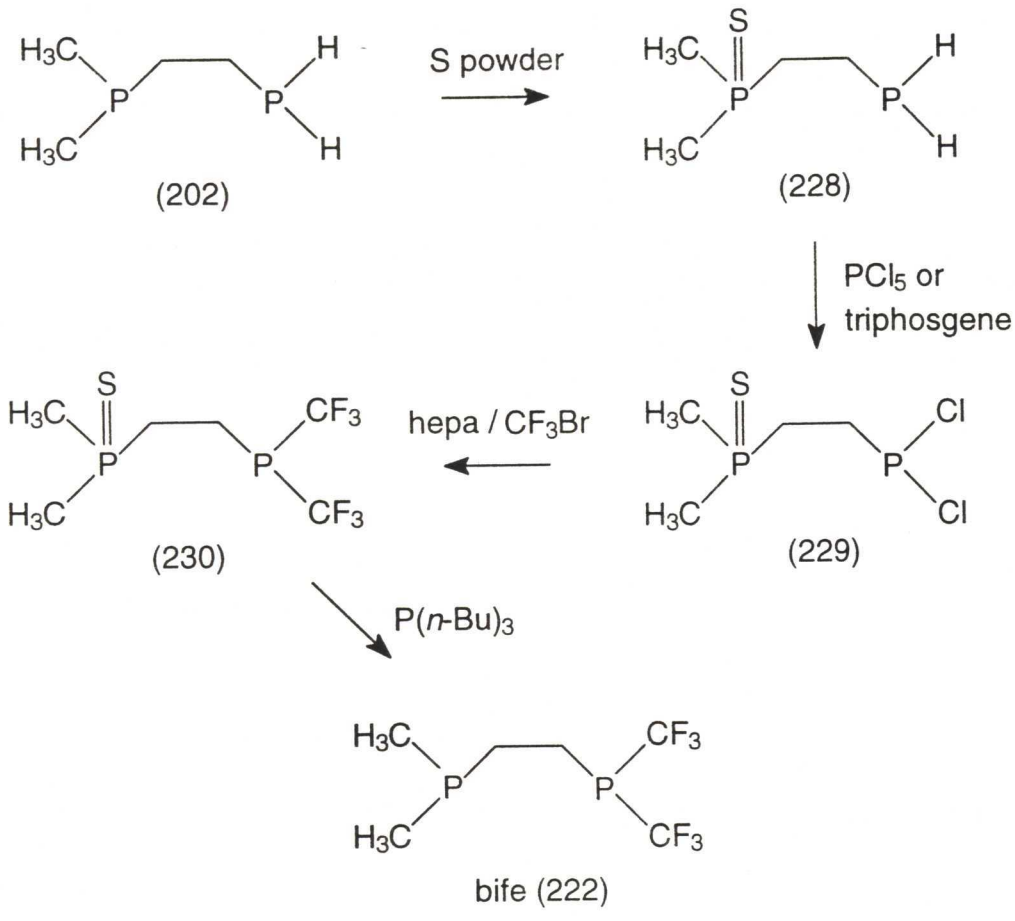
It is possible to selectively sulfurise the dimethylphosphino group of $Me_2PCH_2CH_2PH_2$ **(202)** to form $Me_2P(S)CH_2CH_2PH_2$ **(228)** by allowing the reaction of **(202)** with sulfur to proceed for only a short time (Scheme 4.14).[129]



(202) (228)

Scheme 4.14

Reaction of triphosgene **(227)** or phosphorus pentachloride **(224)** with the mono-sulfide $Me_2P(S)CH_2CH_2PH_2$ **(228)** is expected to form $Me_2P(S)CH_2CH_2PCl_2$ **(229)**. The method developed in this work for the trifluoromethylation of chlorophosphines can then be used to convert **(229)** into $Me_2P(S)CH_2CH_2P(CF_3)_2$ **(230)**, which upon desulfurisation with *n*-butylphosphine affords the required ligand, $Me_2PCH_2CH_2P(CF_3)_2$, bife **(222)** (Scheme 4.15).



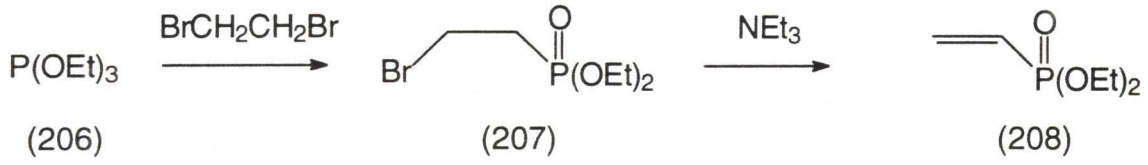
Scheme 4.15

(2-(Dimethylphosphino)ethyl)bis(trifluoromethyl)phosphine, $Me_2PCH_2CH_2P(CF_3)_2$, bife **(222)** was synthesised from 2-(dimethylphosphino)ethylphosphine, $Me_2PCH_2CH_2PH_2$ **(202)**, which in turn was synthesised by the procedure developed by Bampos and Field.[117]

4.2.3 Preparation of $CH_2CHP(O)(OEt)_2$

Diethyl (2-bromoethyl)phosphonate, $BrCH_2CH_2P(O)(OEt)_2$ **(207)** was synthesised by the reaction of triethyl phosphite **(206)** with a large excess of 1,2-dibromoethane in an Arbuzov reaction (Scheme 4.16). The mono-substituted phosphonate **(207)** was separated and purified by distillation in 90% yield. Elimination of HBr from diethyl (2-bromoethyl)-

phosphonate (**207**) was achieved by treatment with triethylamine in benzene (Scheme 4.16). Diethyl vinylphosphonate (**208**) was obtained in 80% yield by distillation under high vacuum.



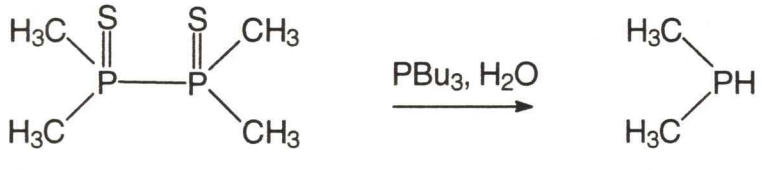
(206) (207) (208)

Scheme 4.16

4.2.4 Preparation of Me_2PH

Dimethylphosphine (**197**) was prepared by the reductive cleavage of tetramethyldiphosphine disulfide[130] (**231**) with *n*-butylphosphine in the presence of water (Scheme 4.17).[131]

Tetramethyldiphosphine disulfide (**231**), two equivalents of tri-*n*-butylphosphine and water were slowly heated to 140°C until the reaction mixture became homogeneous. The temperature of the reaction mixture was raised to 210°C and dimethylphosphine (**197**) was collected in 66% yield as it distilled from the reaction mixture under nitrogen. Dimethylphosphine (**197**) was obtained as a pyrophoric odorous compound which could be stored for long periods at low temperature, and was most conveniently handled in solution.



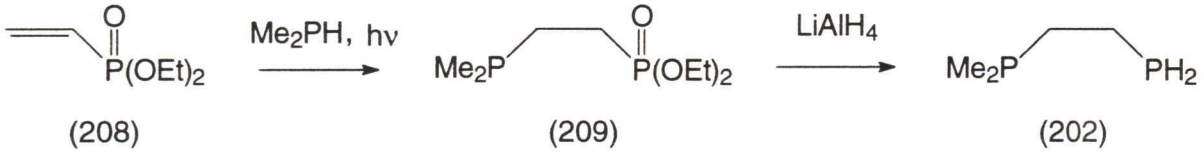
(231) (197)

Scheme 4.17

4.2.5 Preparation of $Me_2PCH_2CH_2PH_2$

Diethyl 2-(dimethylphosphino)ethylphosphonate, $Me_2PCH_2CH_2P(O)(OEt)_2$ (**209**) was prepared by the photochemical addition of dimethylphosphine (**197**) to diethyl vinylphosphonate (**208**), using a modification of the method of Bampos and Field (Scheme 4.18).[117] Irradiation of dimethylphosphine (**197**) and diethyl vinylphosphonate (**208**) for 2.5 h at room temperature afforded complete conversion to $Me_2PCH_2CH_2P(O)(OEt)_2$ (**209**), which after distillation under high vacuum was obtained as a colourless, air-sensitive oil in a yield of approximately 80%.

2-(Dimethylphosphino)ethylphosphine, $Me_2PCH_2CH_2PH_2$ (**202**) was prepared by reduction of diethyl 2-(dimethylphosphino)ethylphosphonate (**209**) with lithium aluminium hydride at 0°C, again following a modification of the method of Bampos and Field.[117] The volatility of 2-(dimethylphosphino)ethylphosphine (**202**) made it convenient to store and handle this product as an ethereal solution. The concentration of (**202**) in the ether solution was determined by integration against an internal standard (dimethyl phenylphosphonate) in the $^{31}P\{^1H\}$ NMR spectrum, and was found to be 0.24 $mmol.ml^{-1}$, representing a yield of 80%.

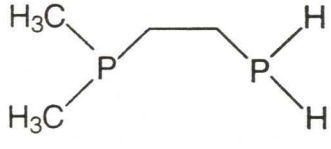


(208) (209) (202)

Scheme 4.18

The $^{31}P\{^1H\}$ NMR spectrum of $Me_2PCH_2CH_2PH_2$ (**202**) (Figure 4.1) is typical of the spectra obtained for unsymmetrically substituted bisphosphines, and is illustrative of the utility of $^{31}P\{^1H\}$ NMR spectroscopy as an analytical tool for unsymmetrical bisphosphines. The

$^{31}P\{^{1}H\}$ NMR spectrum of (**202**) consists of two resonances due to the two unique phosphorus environments present in the molecule. The dimethylphosphino nucleus exhibits a resonance at δ -49.7 ppm, and the phosphorus of the primary phosphino group gives rise to a resonance at δ -130.8 ppm. These two resonances are coupled to each other with a coupling constant of 15 Hz. This data is identical to that described for this compound in the literature.[117] Both the chemical shift of the $^{31}P\{^{1}H\}$ NMR resonances of compounds of this class, and the coupling constant between the two resonances are sensitive to the substituents on the phosphorus nuclei. As a result, $^{31}P\{^{1}H\}$ NMR spectroscopy is very informative in the analysis of asymmetrical bisphosphines.



(202)

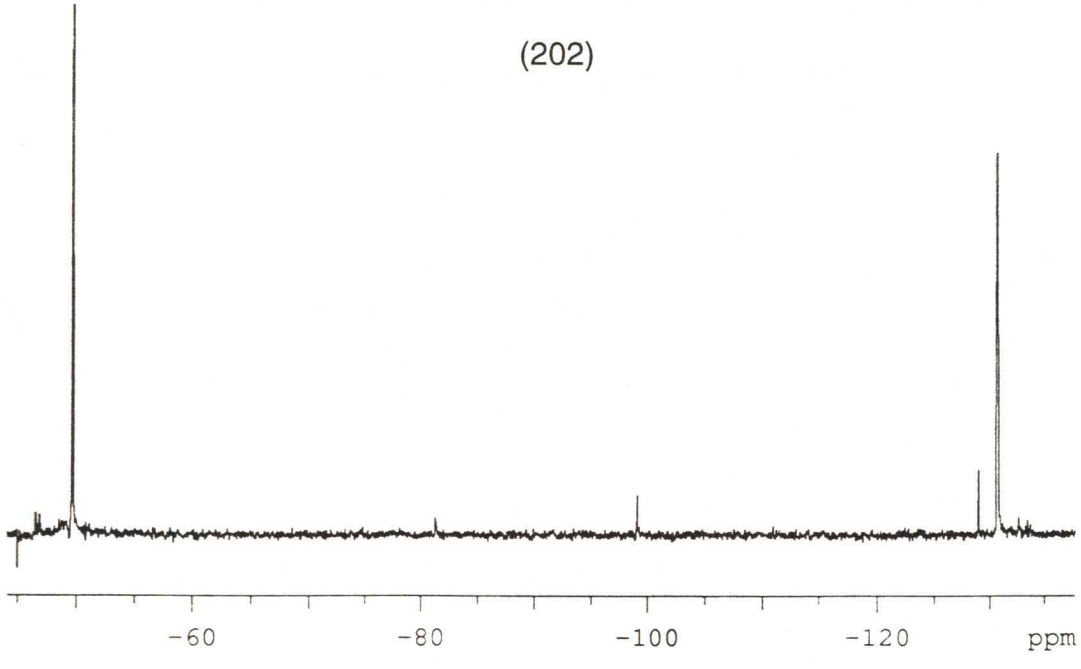
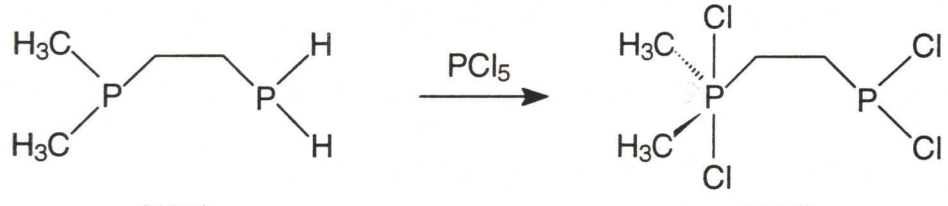


Figure 4.1 : $^{31}P\{^{1}H\}$ NMR spectrum of $Me_2PCH_2CH_2PH_2$ (**202**) in ether at 300K

4.2.6 Attempted preparation of $Me_2PCH_2CH_2PCl_2$

The conversion of $Me_2PCH_2CH_2PH_2$ (**202**) to $Me_2PCH_2CH_2PCl_2$ (**223**) was attempted using phosphorus pentachloride.

A solution of $Me_2PCH_2CH_2PH_2$ (**202**) in ether was added to a suspension of two equivalents of phosphorus pentachloride (**224**) in toluene at room temperature. The addition was accompanied by the evolution of gas, warming of the reaction mixture and the precipitation of a small amount of polymerised material from solution. Analysis of the crude reaction mixture by ^{31}P NMR spectroscopy showed a resonance at δ 175 ppm, the region for a $-PCl_2$ group, but showed no resonance in the expected region for a PMe_2 group (δ -50 ppm). Instead, the $^{31}P\{^1H\}$ NMR spectrum showed a resonance at δ 0 ppm, indicating that while the desired chlorination of the primary phosphine had occurred, undesirable oxidation of the dimethylphosphino group had also occurred to form (**232**) (Scheme 4.19).



(202) (232)

Scheme 4.19

When less than one equivalent of phosphorus pentachloride (**224**) was used in this reaction, $^{31}P\{^1H\}$ NMR analysis of the reaction mixture showed the disappearance of the peak at δ -50 ppm due to the dimethylphosphine group, and the appearance of a peak at δ 0 ppm.

The peak at δ -133 ppm due to the $-PH_2$ group was still present, indicating that the undesired oxidation of the dimethylphosphino group occurs before the chlorination of the primary phosphino group in the chlorination of $Me_2PCH_2CH_2PH_2$ (**202**).

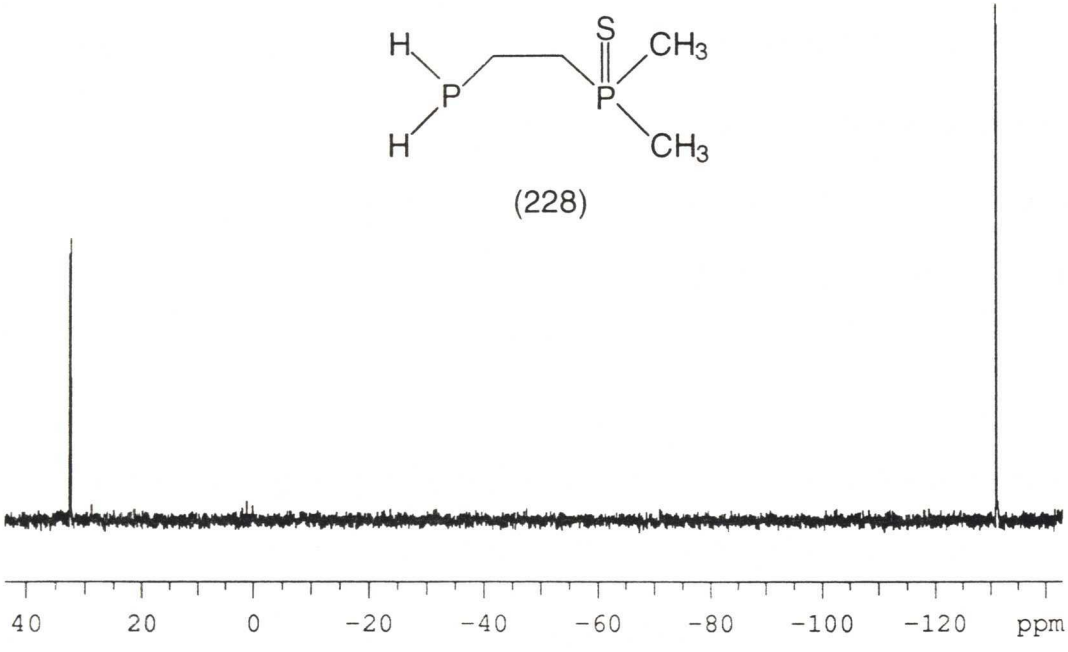
Protection of the more reactive dimethylphosphino group in $Me_2PCH_2CH_2PH_2$ (**202**) from oxidation by the chlorinating reagent was therefore required. The selective monosulfurisation of (**202**) was carried out by the reaction of (**202**) with sulfur powder at room temperature.

4.2.7 Preparation of $Me_2P(S)CH_2CH_2PH_2$

A solution of 2-(dimethylphosphino)ethylphosphine (**202**) in ether was added to a suspension of sulfur powder in ether at room temperature. The solution became cloudy and the sulfur powder dissolved immediately upon addition of $Me_2PCH_2CH_2PH_2$ (**202**). The solution was stirred at room temperature for 30 min, filtered, and the solvent was removed under reduced pressure. The residue was washed with hexane to afford 2-(dimethylphosphine-sulfide)ethylphosphine (**228**) as a white, air-sensitive, odorous solid in 88% yield. $Me_2P(S)CH_2CH_2PH_2$ (**228**) is insoluble in pentane and hexane, but soluble in other organic solvents. The compound was found to be >95% pure by ^1H NMR and ^{31}P NMR spectroscopy, and was used in subsequent reaction without further purification.

The $^{31}P\{^1H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2PH_2$ (**228**) in C_6D_6 shows a doublet at δ 34.1 ppm due to the dimethylphosphine(sulfide) group, and a characteristically upfield doublet at δ -129.7 ppm due to the $-PH_2$ group (Figure 4.2). The P-P coupling between the two ^{31}P nuclei is 17 Hz, and the $^1J_{P\text{-}H}$ coupling in the proton-coupled ^{31}P NMR spectrum is 192 Hz. The ^1H NMR spectrum of $Me_2P(S)CH_2CH_2PH_2$ (**228**) in C_6D_6 shows a phosphorus-

coupled resonance for the two equivalent methyl groups at δ 1.22 ppm, the four methylene protons in the region δ 1.70-1.52 ppm, and a strongly phosphorus-coupled resonance at δ 2.82 ppm arising from the -P**H**$_2$ protons.



(228)

Figure 4.2 : $^{31}P\{^{1}H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2PH_2$ (**228**) in C_6D_6 at 300K

The $^{13}C\{^{1}H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2PH_2$ () in C_6D_6 consists of three resonances. The methylene carbon nucleus α to the phosphinesulfide group shows a resonance at δ 38.7 ppm, and exhibits coupling to the α- and β-phosphorus nuclei of 49.2 and 4.2 Hz respectively. The methylene carbon adjacent to the -PH_2 group is shifted upfield to δ 7.7 ppm, and exhibits coupling to the two phosphorus nuclei of 11.0 and 5.1 Hz. The resonance due to the two equivalent methyl carbon nuclei occurs as a phosphorus-coupled doublet at δ 21.0 ppm ($^{1}J_{C\text{-}P}$ = 53.4 Hz).

If $Me_2P(S)CH_2CH_2PH_2$ **(228)** was stirred for long periods at room temperature in the presence of excess sulfur powder, a white precipitate crystallised out of the ether solution. This white solid was soluble in THF, and on the basis of $^{31}P\{^1H\}$ NMR analysis was formulated as 2-(dimethylphosphinesulfide)ethylphosphinesulfide, $Me_2P(S)CH_2CH_2P(S)H_2$ **(233)**. The $^{31}P\{^1H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2P(S)H_2$ **(233)** in d_8-THF consists of two mutually-coupled resonances at δ 38.0 and -12.2 ppm ($^3J_{P\text{-}P}$ = 58 Hz). The resonance at δ 38.0 ppm arises from the dimethylphosphinesulfide group, while the resonance at -12.2 ppm appears as a triplet in the proton-coupled ^{31}P NMR spectrum ($^1J_{H\text{-}P}$ = 453 Hz) and is assigned as the resonance arising from the phosphorus of the -**P**$(S)H_2$ group.

The disulfide **(233)** was isolated as an odorous, white solid which was insoluble in ether, but soluble in THF. The insolubility of $Me_2P(S)CH_2CH_2P(S)H_2$ **(233)** in ether enabled easy separation of this by-product from the mono-sulfide **(228)**.

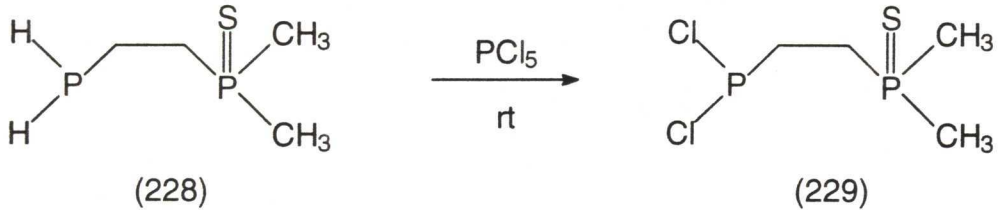
Isolation of the mono-sulfide **(228)** allows the subsequent chlorination reaction to be carried out in the presence of a solvent other than ether. $Me_2P(S)CH_2CH_2PH_2$ **(228)** also provides a convenient purification stage in the synthesis of bife **(222)**.

4.2.8 Preparation of $Me_2P(S)CH_2CH_2PCl_2$

Both phosphorus pentachloride **(224)** and triphosgene **(227)** were used in an attempt to convert the protected monosulfide 2-(dimethylphosphinesulfide)ethylphosphine, $Me_2P(S)CH_2CH_2PH_2$ **(228)** to 2-(dimethylphosphinesulfide)ethyldichlorophosphine, $Me_2P(S)CH_2CH_2PCl_2$ **(229)**.

4.2.8.1 Chlorination of $Me_2P(S)CH_2CH_2PH_2$ using phosphorus pentachloride

Phosphorus pentachloride (**224**) was used to chlorinate $Me_2P(S)CH_2CH_2PH_2$ (**228**), in an attempt to form $Me_2P(S)CH_2CH_2PCl_2$ (**229**) (Scheme 4.20).



(228) (229)

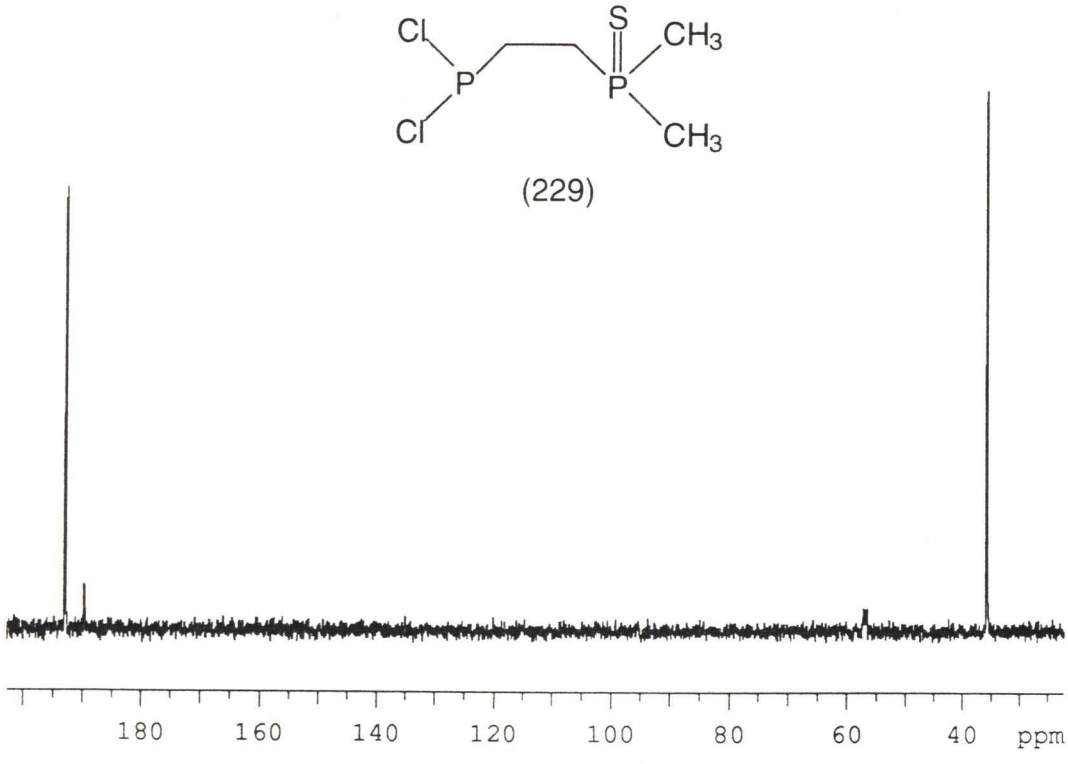
Scheme 4.20

A solution of 2-(dimethylphosphinesulfide)ethylphosphine (**228**) in toluene was added to a suspension of 2 equivalents of phosphorus pentachloride (**224**) in toluene over 15 min. The reaction mixture warmed to 70°C and a precipitate formed. The solution was filtered, and the solvent was removed under reduced pressure to afford 2-(dimethylphosphinesulfide)-ethyldichlorophosphine (**229**) as a yellow-green solid in 52% yield.

$Me_2P(S)CH_2CH_2PCl_2$ (**229**) is an air-sensitive solid which is sparingly soluble in aromatic solvents and soluble in chlorinated solvents.

The $^{31}P\{^1H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2PCl_2$ (**229**) in C_6D_6 shows a doublet at δ 36.2 ppm due to the dimethylphosphine(sulfide) group, similar in chemical shift to the corresponding resonance of $Me_2P(S)CH_2CH_2PH_2$ (**228**) (Figure 4.3). The phosphorus resonance arising from the dichlorophosphino group now occurs at δ 193.2 ppm. The P-P coupling between these two ^{31}P nuclei is 22 Hz. The ^1H NMR spectrum of $Me_2P(S)CH_2CH_2PCl_2$ (**229**) in C_6D_6 shows a phosphorus-coupled resonance for the two

equivalent methyl groups at δ 1.32 ppm and the two groups of methylene protons in the region δ 2.54-2.43 ppm (-C**H**$_2$PCl$_2$) and δ 1.96-1.87 ppm (-C**H**$_2$P(S)(CH$_3$)$_2$).



(229)

Figure 4.3 : $^{31}P\{^1H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2PCl_2$ (**229**) in C_6D_6 at 300K

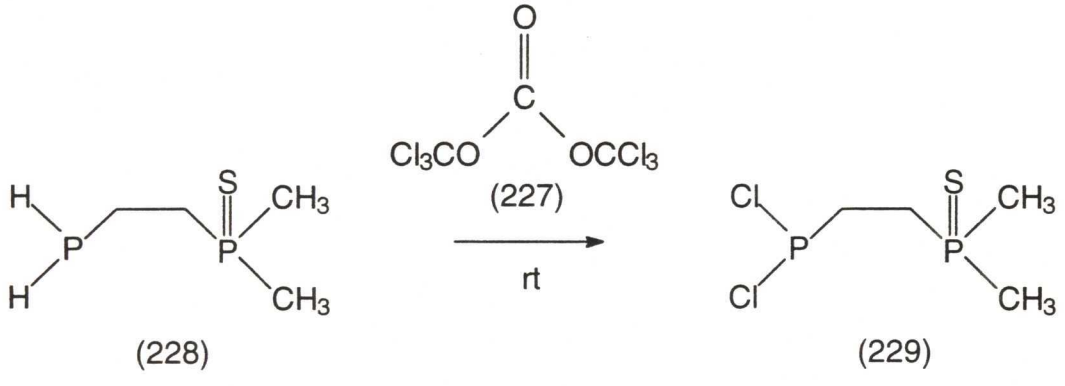
The $^{13}C\{^1H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2PCl_2$ (**229**) in C_6D_6 consists of three resonances. The methylene carbon nucleus α to the phosphinesulfide group shows a resonance at δ 35.4 ppm, similar to the shift of the corresponding resonance in the ^{13}C NMR spectrum of $Me_2P(S)CH_2CH_2PH_2$ () (δ 38.7 ppm). The coupling of this nucleus to the α- and β-phosphorus nuclei are also similar to those in $Me_2P(S)CH_2CH_2PH_2$ (**228**), 49 Hz and 4 Hz respectively (compared to 49.2 and 4.2 Hz for (**228**)). The methylene carbon adjacent to the

-PCl_2 group resonates at δ 27.8 ppm, and exhibits coupling to the two phosphorus nuclei of 51 Hz and 10 Hz. The resonance due to the two equivalent methyl carbon nuclei occurs as a phosphorus-coupled doublet at δ 20.5 ppm ($^1J_{C\text{-}P}$ = 55 Hz).

Owing to the insoluble nature of phosphorus pentachloride (**224**), this reagent could not be easily added as a solution to $Me_2P(S)CH_2CH_2PH_2$ (**228**). This limits the accurate control of the amount of chlorinating agent which is added to the reaction. It was also difficult to purify the phosphorus pentachloride before use. Although it was possible to make $Me_2P(S)CH_2CH_2PCl_2$ (**229**) in reasonable yield using phosphorus pentachloride, a reagent which was soluble in organic solvents was desired for this conversion. Triphosgene (**227**) was found to be the reagent of choice for the conversion of the primary phosphine $Me_2P(S)CH_2CH_2PH_2$ (**228**) to 2-(dimethylphosphinesulfide)ethyldichlorophosphine (**229**).

4.2.8.2 Chlorination of $Me_2P(S)CH_2CH_2PH_2$ using triphosgene

Triphosgene (**227**) is soluble in organic solvents and is commercially available as a white crystalline solid in 99% purity. The chlorination of $Me_2P(S)CH_2CH_2PH_2$ (**228**) was carried out by adding a solution of triphosgene (**227**) in toluene to the starting material, thereby ensuring that the chlorinating agent was never in excess (Scheme 4.21).

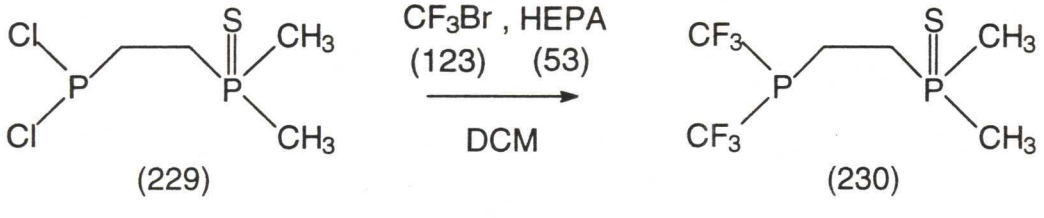


Scheme 4.21

Two-thirds of an equivalent of triphosgene (**227**) in toluene was added dropwise to a solution of 2-(dimethylphosphinesulfide)ethylphosphine (**228**) in toluene, and the solution was stirred at room temperature. $^{31}P\{^{1}H\}$ NMR analysis of the crude reaction mixture after 4 h showed that all starting material had reacted to form the required dichloride (**229**). Toluene was removed under reduced pressure, and the residue was washed with hexane to give 2-(dimethylphosphinesulfide)ethyldichlorophosphine (**229**) as a white solid in 70% yield. The NMR data obtained for this compound was identical to that obtained for the chlorination of 2-(dimethylphosphinesulfide)ethylphosphine (**228**) by phosphorus pentachloride (**224**).

4.2.9 Preparation of $Me_2P(S)CH_2CH_2P(CF_3)_2$

The methodology developed for the conversion of a dichlorophosphino group to a bis(trifluoromethyl)phosphino group in the synthesis of dfmpe (**50**) was applied to the synthesis of the mixed bisphosphine, bife (**222**). The low temperature reaction of hexaethylphosphorus triamide (**53**) and trifluoromethyl bromide (**123**) with $Me_2P(S)CH_2CH_2PCl_2$ (**229**) in dichloromethane was examined in an attempt to synthesise $Me_2P(S)CH_2CH_2P(CF_3)_2$ (**230**) (Scheme 4.22).



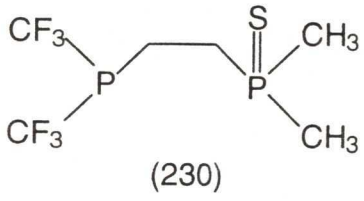
Scheme 4.22

Ten equivalents of trifluoromethyl bromide (**123**) were condensed into a flask at liquid nitrogen temperature and a solution of 2-(dimethylphosphinesulfide)-ethyldichlorophosphine (**229**) in dichloromethane (50 ml) was added. The reaction mixture was allowed to warm to -60°C, and four equivalents of hexaethylphosphorus triamide (**53**) in dichloromethane (20 ml) were added over a period of 1 h while the temperature was maintained between -60°C and -55°C. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. The mixture was eluted through flash silica with dichloromethane, to give 2-(dimethylphosphinesulfide)ethyl(*bis*-trifluoro-methyl)phosphine (**230**) as an air-stable white powder in 20% yield.

The $^{31}P\{^{1}H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2P(CF_3)_2$ (**230**) in $CDCl_3$ shows a doublet at δ 37.9 ppm due to the dimethylphosphine(sulfide) group, and a doublet of septets at δ 1.6 ppm arising from the bis(trifluoromethyl)phosphino group ($^{2}J_{P\text{-}F}$ = 69.6 Hz) (Figure 4.4). The P-P coupling between these two ^{31}P nuclei is 46 Hz. The ^{1}H NMR spectrum of $Me_2P(S)CH_2CH_2P(CF_3)_2$ (**230**) in $CDCl_3$ shows a phosphorus-coupled resonance arising from the two equivalent methyl groups at δ 1.83 ppm, and the two pairs of methylene protons at δ 2.45 ppm ($-C\mathbf{H}_2P(CF_3)_2$) and δ 2.10 ppm ($-C\mathbf{H}_2P(S)(CH_3)_2$).

The ^{19}F NMR of (**230**) consists of a phosphorus-coupled doublet at δ -50.8 ppm, with a phosphorus coupling of 69.6 Hz. The $^{13}C\{^{1}H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2P(CF_3)_2$ (**230**) in $CDCl_3$ shows a resonance at δ 129.4 ppm which is a doublet due to coupling to phosphorus ($^{2}J_{C\text{-}P}$ = 30 Hz) and a quartet due to fluorine coupling ($^{1}J_{C\text{-}F}$ = 319 Hz). The methylene carbon nucleus α to the phosphinesulfide group shows a resonance at δ 29.7 ppm, with couplings of 51 and 17 Hz to the α- and β-phosphorus nuclei. The methylene carbon adjacent to the $-P(CF_3)_2$ group resonates at δ 13.3 ppm, and exhibits

coupling to the two phosphorus nuclei of 1 Hz and 17 Hz. The resonance due to the two equivalent methyl carbon nuclei occurs as a phosphorus-coupled doublet at δ 21.5 ppm ($^1J_{C\text{-}P}$ = 55 Hz).



(230)

Figure 4.4 : $^{31}P\{^1H\}$ NMR spectrum of $Me_2P(S)CH_2CH_2P(CF_3)_2$ (**230**) in $CDCl_3$ at 300K

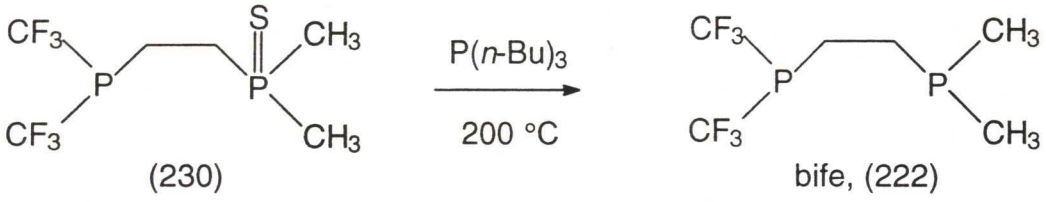
$Me_2P(S)CH_2CH_2P(CF_3)_2$ (**230**) was found to be thermally stable at room temperature in the presence of air , and is a convenient precursor for $Me_2PCH_2CH_2P(CF_3)_2$, bife (**222**).

4.2.10 Preparation of $Me_2PCH_2CH_2P(CF_3)_2$ (bife)

Desulfurisation of the mono-sulfide $Me_2P(S)CH_2CH_2P(CF_3)_2$ (**230**) was effected using *n*-butylphosphine. 2-(Dimethylphosphinesulfide)ethyl(*bis*-trifluoromethyl)-phosphine (**230**) was mixed with an excess of *n*-butylphosphine and the reaction mixture was

heated to 200°C for 1 h (Scheme 4.23). The vessel was cooled, and attached to a high-vacuum line, and all volatiles were removed at 5×10^{-5} Torr at 70°C.

2-(Dimethylphosphino)ethyl(bis-(trifluoromethyl))phosphine (**222**) was obtained as a colourless, air-sensitive liquid.



Scheme 4.23

The $^{31}P\{^{1}H\}$ NMR spectrum of $Me_2PCH_2CH_2P(CF_3)_2$ (**222**) in C_6D_6 shows a doublet of septets at δ 2.1 ppm arising from the bis(trifluoromethyl)phosphino group ($^{2}J_{P\text{-}F}$ = 68 Hz), and a doublet at δ -46.8 ppm due to the dimethylphosphino group. The P-P coupling between these two ^{31}P nuclei is 38 Hz (Figure 4.5). The ^{1}H NMR spectrum of $Me_2PCH_2CH_2P(CF_3)_2$ (**222**) in C_6D_6 shows a phosphorus-coupled resonance arising from the two equivalent methyl groups at δ 0.84 ppm, and the two pairs of methylene protons at δ 2.04 ppm (-C**H**$_2$P(CF$_3$)$_2$) and δ 1.33 ppm (-C**H**$_2$P(CH$_3$)$_2$). The ^{19}F NMR of (**222**) consists of a phosphorus-coupled doublet at δ -50.8 ppm, with a phosphorus coupling of 67 Hz.

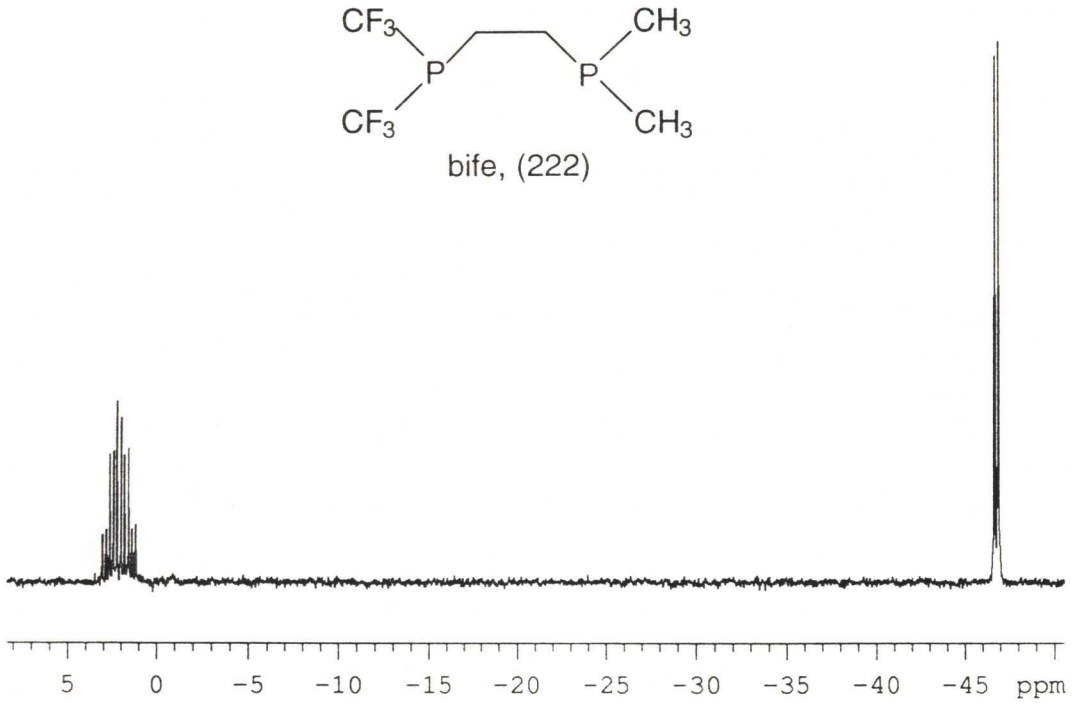


Figure 4.5 : $^{31}P\{^{1}H\}$ NMR spectrum of $Me_2PCH_2CH_2P(CF_3)_2$, bife (**222**) in C_6D_6 at 300K

Due to the low yields obtained for the trifluoromethylation step in this synthesis, only quantities of bife (**222**) sufficient for characterisation and identification were obtained. In this work, sufficient quantities of bife (**222**) were not available for the formation of organometallic complexes containing this ligand.

Table 4.1 summarises the $^{31}P\{^{1}H\}$ NMR data for the series of compounds leading to bife (**222**).

Table 4.1 : ^{31}P NMR data of unsymmetrical bisphosphines

Compound	δ (ppm)	$^{3}J_{P\text{-}P}$ (Hz)
$BrCH_2CH_2P(O)(OEt)_2$ **(207)**	25.3	-
$CH_2CHP(O)(OEt)_2$ **(208)**	16.3	-
$Me_2PCH_2CH_2P(O)(OEt)_2$ **(209)**	30.9, -47.3	52
$Me_2PCH_2CH_2PH_2$ **(202)**	-49.7, -130.8	15
$Me_2P(S)CH_2CH_2PH_2$ **(228)**	34.1, -129.7	17
$Me_2P(S)CH_2CH_2P(S)H_2$ **(233)**	38.0, -12.2	58
$Me_2P(S)CH_2CH_2PCl_2$ **(229)**	193.2, 36.2	22
$Me_2P(S)CH_2CH_2P(CF_3)_2$ **(230)**	37.9, 1.6	46
$Me_2PCH_2CH_2P(CF_3)_2$ **(222)**	2.1, -46.8	38

The application of $^{31}P\{^{1}H\}$ NMR spectroscopy to the identification of compounds of this class is illustrated by the range of chemical shifts observed for the bisphosphines shown in Table 4.1. Detailed structural information about unsymmetrical bisphosphines can be obtained from the chemical shift of the resonances obtained in the $^{31}P\{^{1}H\}$ NMR spectrum. The size of the $^{3}J_{P\text{-}P}$ coupling constant is also sensitive to both the oxidation state of each phosphorus atom in the unsymmetrical bisphosphine, and to the substituents bound to each phosphorus atom, and may well provide structural information about unsymmetrical bisphosphines.

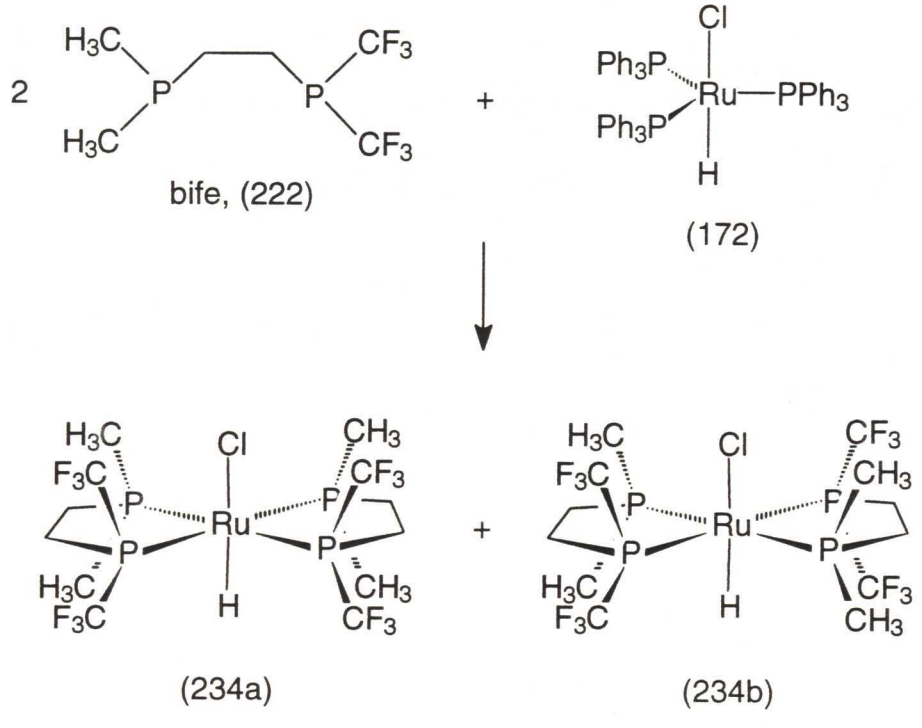
4.3 Coordination properties of bife

The coordination properties of dfmpe (**50**) have given some information concerning the coordination properties of the bis(trifluoromethyl)phosphino group, and the coordination properties of the dimethylphosphino group are well known. While the synthesis of iron

complexes containing dfmpe (**50**) proved difficult, this was partly due to the restriction of reaction conditions imposed by the difficulties in isolating dfmpe (**50**). Isolation of bife (**222**) faces no such problems.

Precursors enabling the formation of ruthenium complexes of dfmpe (**50**) were found, and high-yielding methods were developed for the synthesis of ruthenium complexes containing fluorinated phosphines. It is anticipated that the application of these methods to the synthesis of ruthenium complexes containing bife (**222**) be straightforward.

The synthesis of metal complexes containing two bife (**222**) ligands opens up the possibility of coordination isomers. The reaction of two equivalents of bife (**222**) with $RuHCl(PPh_3)_3$ (**172**) is likely to produce a mixture of compounds (**234a**) and (**234b**), with the bis(trifluoromethyl)phosphino groups adopting either a *cis* or *trans* orientation across the metal centre (Scheme 4.24).



Scheme 4.24

Intuitively, an approximately statistical ratio of **(234a)** and **(234b)** is expected, although one isomer may well predominate due to steric or electronic reasons.

4.4 Summary of synthesis of bife

The synthesis of bife **(222)** was achieved by the proposed multi-step procedure. (2-(Dimethylphosphino)ethyl)phosphine **(202)** was synthesised by the method developed by Bampos and Field, and was protected as the monosulfide, $Me_2P(S)CH_2CH_2PH_2$ **(228)** by reaction with sulfur at room temperature. Conversion of $Me_2P(S)CH_2CH_2PH_2$ **(228)** to the corresponding dichloride, $Me_2P(S)CH_2CH_2PCl_2$ **(229)** was carried out efficiently using triphosgene **(227)**. $Me_2P(S)CH_2CH_2P(CF_3)_2$ **(230)** was synthesised by the reaction of $Me_2P(S)CH_2CH_2PCl_2$ **(229)** with hepa **(53)** and trifluoromethyl bromide **(123)** at low temperature, the trifluoromethylation method developed in this work. The synthesis of $Me_2P(S)CH_2CH_2P(CF_3)_2$ **(230)** by this method demonstrates the general nature of this method for the trifluoromethylation of chlorophosphines.

Bife **(222)** was carried out by the desulfurisation of $Me_2P(S)CH_2CH_2P(CF_3)_2$ using *n*-butylphosphine, and characterised by NMR spectroscopy. Sufficient (bife) **(222)** was synthesised to allow characterisation and identification of this ligand, however an investigation of the coordination properties of bife **(222)** was not undertaken.

CHAPTER 5 : CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

5.1 Conclusions and suggestions for further work

A new route to the synthesis of trifluoromethylated phosphines was developed, which involved the low temperature addition of hepa (**53**) to a mixture of trifluoromethyl bromide (**123**) and the appropriate chlorophosphine. The method was applied to the synthesis of 1,2-bis(bis(trifluoromethyl)phosphino)ethane (**50**), resulting in the synthesis of this ligand in 20% yield. This synthesis is a significant improvement in the literature preparation of this compound, and a general approach to the synthesis of trifluoromethylated phosphines.

Difficulties were encountered in the isolation of dfmpe (**50**) from the by-products formed in its synthesis, and dfmpe was only obtained easily as a solution in dichloromethane. Use of dfmpe (**50**) as a solution in dichloromethane limited the reaction conditions that could be used in subsequent attempts to form metal complexes containing dfmpe (**50**). An improvement in the method of isolation of dfmpe (**50**) could facilitate the formation of complexes containing this ligand. A possible approach to this problem is the extraction of the reaction mixture with a perfluoroalkane such as perfluorohexane. The limited solubility of many organic compounds in perfluoroalkanes, and the high solubility a highly fluorinated compound such as dfmpe (**50**) is expected to have in solvents of this class, may provide a simple and effective method for the separation of dfmpe (**50**) from by-products formed in its synthesis.

The mechanism of the reaction of hexaethylphosphorus triamide (**53**) and trifluoromethyl bromide (**123**) with chlorophosphines is as yet unknown. Further work on the mechanism of this reaction could involve low temperature studies on reaction intermediates, or low temperature trapping experiments which may help to distinguish between ionic and radical

mechanisms. An investigation of the application of this reaction to a wider variety of phosphorus-containing compounds could also give information about the general applicability of this reaction to the synthesis of trifluoromethylated phosphines, phosphine oxides and other related compounds. Extension of the method of synthesis of trifluoromethylated phosphines to more sophisticated phosphine ligands may also be possible.

The improved synthesis of dfmpe (**50**) enabled a study of the properties of dfmpe (**50**) as an ancillary ligand for organometallic complexes to be performed. The coordination properties of dfmpe (**50**), were found to be dramatically different to those of dmpe (**6**) (dmpe = 1,2-bis(dimethylphosphino)ethane). In contrast to the extensive coordination chemistry dmpe (**6**) exhibits with iron, no iron complexes containing dfmpe (**50**) were isolated, or even observed. It may be possible to synthesise iron complexes containing dfmpe (**50**) if more forcing reaction conditions could be used. This could be possible if dfmpe (**50**) could be easily separated from dichloromethane.

In the search for a convenient synthesis of $RuH_2(dfmpe)_2$ (**113**), several ruthenium complexes containing dfmpe (**50**) were synthesised and characterised. Further work in this area could consist of a study of the reactions of $RuHCl(CO)(PPh_3)(dfmpe)$ (**155**) and $RuH_2(CO)(PPh_3)(dfmpe)$ (**170**) in the presence of organic substrates. Similar ruthenium complexes containing alkylated phosphines have been reported to carry out a wide range of organic transformations.

The efficient synthesis of $RuH_2(dfmpe)_2$ (**113**) by reduction of $RuHCl(dfmpe)_2$ (**172**) using sodium borohydride in 2-propanol was developed. $RuH_2(dfmpe)_2$ (**113**) is very different in properties to its alkyl analogue, $RuH_2(dmpe)_2$ (**143**). $RuH_2(dfmpe)_2$ (**113**) loses dihydrogen

reversibly under photochemical conditions, but does not form NMR-observable intermediates when photolysed in the presence of alkanes, alkenes or arenes. Preliminary laser flash photolysis experiments indicate that the intermediate formed upon irradiation of $RuH_2(dfmpe)_2$ **(113)** reacts extremely rapidly with hydrogen, too fast to allow competitive activation of C-H bonds of organic substrates.

Experiments in which the photolysis of $RuH_2(dfmpe)_2$ **(113)** takes place in the presence of a "hydrogen scavenger" could be envisaged, that is, in the presence of a compound that removes hydrogen from solution once it is liberated, could be envisaged. A hydrogen scavenger could promote the C-H activation reactions of $Ru(dfmpe)_2$ with organic substrates. No suitable compound has yet been found for this purpose.

The use of trifluoromethylated phosphines has been shown to dramatically alter the physical and chemical properties of organometallic complexes. Although the ruthenium complexes containing dfmpe **(50)** are more robust and stable (even in air), the use of dfmpe **(50)** in ruthenium complexes used to carry out the activation of C-H bonds of organic substrates has resulted in reduced reactivity.

The synthesis of bife **(222)** was achieved by a multi-step procedure, involving the synthesis of the unsymmetrical bisphosphines $Me_2P(S)CH_2CH_2PH_2$ **(228)**, $Me_2P(S)CH_2CH_2PCl_2$ **(229)** and $Me_2P(S)CH_2CH_2P(CF_3)_2$ **(230)** as precursors to bife **(222)**. These unsymmetrical phosphines show promise as synthetically useful precursors to the synthesis of other unsymmetrical bisphosphines. Through the development of this synthetic scheme, the application of the trifluoromethylation method used to synthesise dfmpe **(50)** was applied to the trifluoromethylation of $Me_2P(S)CH_2CH_2PCl_2$ **(229)**, and triphosgene was used to

efficiently carry out the chlorination of the primary phosphine, $Me_2P(S)CH_2CH_2PH_2$ (**228**).

Further work in this area involves an investigation of the coordination properties of bife (**222**) with transition metals. Application of the synthetic methods used to synthesis $RuH_2(dfmpe)_2$ (**113**) are expected to be directly applicable to bife (**222**), although the possibility of formation of coordination isomers must be considered.

CHAPTER 6 : EXPERIMENTAL

6.1 General Procedures

All manipulations involved in this work were carried out using standard Schlenk or vacuum-line methods, or in a dry-box equipped with a continuous slow nitrogen purge, unless otherwise stated.

Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. Microanalyses were not carried out on organometallic complexes containing fluorinated ligands, due to the high fluorine content of these compounds. I.R. spectra were run as Nujol mulls using NaBr plates, using a Perkin Elmer 1600 Series F.T.I.R. spectrometer. Samples for UV/Visible spectrophotometric analysis were prepared and analysed as KBr disks, and were recorded on a Hitachi 150-20 spectrophotometer.

General NMR samples were prepared in Wilmad 5 mm high precision pyrex NMR tubes, and were sealed with Wilmad natural rubber serum caps wrapped with parafilm.

NMR spectra were recorded on Bruker AMX400, AC200 and AMX600 spectrometers. Probe temperatures quoted are approximate (± 5K) and were obtained from the uncalibrated spectrometer variable temperature unit. Resonant frequencies for ^{1}H NMR, ^{2}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR are 400.13 MHz, 61.42 MHz, 100.62 MHz, 161.98 MHz, and 376.43 MHz, unless otherwise stated in the text. Pulse sequence listings and relevant acquisition parameters for non-standard experiments are provided in Appendix A1.

In the presentation of NMR data, chemical shifts (δ) are in ppm, with the lowfield region being positive. ^{1}H NMR, ^{2}H NMR and ^{13}C NMR shifts are referenced to internal solvent resonances. ^{31}P NMR chemical shifts are referenced to external, neat trimethyl

phosphite, taken as δ 140.85 ppm at the temperature quoted. ^{19}F NMR chemical shifts are referenced to external, neat hexafluorobenzene, taken as δ -163.0 ppm at the temperature quoted. Uncertainties in chemical shifts are typically ± 0.01 ppm for ^{1}H, ^{2}H and ^{19}F, and ± 0.1 for ^{13}C and ^{31}P. The following abbreviations for multiplicity of signals are used : s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; sep, septet; dd, doublet of doublets, etc.; m, multiplet. Coupling constants (*J*) are given in Hertz.

NMR data processing was done using ASPECTX32 and SUN SPARC station processing facilities using standard Bruker software. Baseline distortions were removed using a polynomial fit of order 4 for most ^{19}F NMR spectra. NMR simulations were carried out using the program PANIC.

Nitrogen (>99.5 %), hydrogen (>99.9 %), deuterium (>99.8 %) and carbon monoxide (>99.0 %) were purchased from BOC gases and used without further purification. All non-deuterated commercial solvents were distilled prior to use. Dichloromethane and benzonitrile used in ligand syntheses were distilled over P_2O_5 under a nitrogen atmosphere immediately prior to use. Pentane, THF, benzene, toluene, diethyl ether and hexane were stored over sodium benzophenone ketyl radical under a dry atmosphere and distilled under nitrogen prior to use. Deuterated solvents chloroform-d_1, dichloromethane-d_2, benzene-d_6, toluene-d_8, acetone-d_6 and methanol-d_4 were purchased from Merck and used without further purification.

Dichlorophenylphosphine, dichlorophenylphosphine oxide, triphosgene, phosphorus pentachloride, methyl fluorosulphonyldifluoroacetate, trifluoromethyl bromide (>99%) and tetra-*n*-butylammonium fluoride were purchased commercially (Aldrich) and were used without further purification. Anhydrous $FeCl_2$ was obtained by heating commercially available iron dichloride under vacuum for several hours. $RuCl_3.3H_2O$ was purchased from Johnson-

Matthey and used without further purification. Sodium borohydride was dried under vacuum overnight, then stored in a vacuum desiccator until required for use. Lithium aluminium hydride was purchased from Aldrich and stored under nitrogen until required for use. Tetramethyldiphosphine disulfide was synthesised using the preparation described in the literature.[130] Alternatively, tetramethyldiphosphine disulfide was purchased from Strem Chemical Co., and used without further purification.

1,2-Bis(dichlorophosphino)ethane, dcpe was synthesised according to the procedure of Chatt and co-workers.[18] Alternatively, dcpe was purchased from Aldrich and used without further purification.

Photolysis experiments were carried out by suspending samples in a vacuum jacketed pyrex dewar containing ethanol cooled with a Lauda ETK 50 refrigeration coil. The apparatus was positioned approximately 10 cm from a Oriel 66033 high pressure mercury lamp.

6.2 Reaction of trifluoromethylating reagents with phosphorus compounds

6.2.1 Reaction of FSO_2CF_2COOMe (119) with dcpe (12)

1,2-Bis(dichlorophosphino)ethane **(12)** (60 µl, 0.4 mmol) was added to a mixture of methyl fluorosulphonyldifluoroacetate **(119)** (0.20 ml, 1.7 mmol) and copper(I) iodide (10 mg, 50 µmol) in DMF (5 ml). The reaction mixture was heated at 70°C for 1h, during which time the colour of the reaction mixture changed from colourless to dark orange. ^{31}P NMR analysis of the crude reaction mixture showed the formation of $F_2P(O)CH_2CH_2P(O)F_2$ **(121)** as the sole product. ^{31}P NMR δ 24.5 ppm. Literature[81] : ^{31}P NMR (CD_3CN) 20.2 ppm. The $^{31}P\{^1H\}$ NMR spectrum of **(121)** was simulated using a molecular simulation program

(PANIC), and the experimental spectrum found to correspond closely to the experimental spectrum obtained. The coupling constants used in the simulation are listed in Appendix A2, and agree with those reported in the literature for **(121)**.[81]

A mixture of dcpe **(12)** (60 µl, 0.4 mmol) and methyl fluorosulphonyl-difluoroacetate **(119)** (0.20 ml, 1.7 mmol) in DMF (5 ml) (in the absence of copper iodide) was heated at 70°C for 1h. The colour of the reaction mixture changed to dark orange as the reaction proceeded. The reaction mixture was analysed by ^{31}P NMR and found to contain a complex mixture of products which were not investigated further.

A mixture of dcpe **(12)** (60 µl, 0.4 mmol), methyl fluorosulphonyldifluoroacetate **(119)** (0.20 ml, 1.7 mmol) and copper(I) iodide (10 mg, 50 µmol) in 2 ml THF was heated at 70°C for 1h. ^{31}P NMR analysis of the crude reaction mixture showed dcpe **(12)** was the sole phosphorus-containing compound in the reaction mixture, and that no trifluoromethylated phosphines were formed.

6.2.2 Reaction of CF_3TMS (122) with phosphorus compounds

6.2.2.1 Preparation of CF_3TMS (122)

(Trifluoromethyl)trimethylsilane **(122)** was synthesised by the method of Prakash *et al.*[84]

Chlorotrimethylsilane **(124)** (24.9 g, 0.24 mol) in benzonitrile (30 ml) was placed in a three-necked flask fitted with an efficient dry-ice condensor and was cooled to liquid nitrogen temperature. Trifluoromethyl bromide **(123)** (75 g, 0.5 mol) was precondensed into a flask, weighed, and then allowed to evaporate into the reaction vessel. The reaction mixture was

allowed to warm to -60°C, and hexaethylphosphorus triamide (**53**) (61.0 g, 0.25 mol) in benzonitrile (50 ml) was added over a period of 1 hr while maintaining the temperature between -60°C and -55°C. The reaction vessel was allowed to warm slowly to room temperature, and the reaction mixture was stirred overnight. The reaction flask was connected to a dry-ice/acetone cooled trap and subjected to aspirator vacuum (20 mmHg) with mild warming to remove all volatile material. The liquid in the trap was washed rapidly with cold water (3 × 50 ml), the top layer was separated and dried over MgSO4 and the dry liquid was decanted into a 50 ml flask. The product was analysed by NMR, found to be > 95% pure by ^{1}H NMR spectroscopy and used in subsequent reactions without further purification. The NMR data obtained for (trifluoromethyl)trimethylsilane (**122**) was consistent with that reported in the literature.[84] ^{1}H NMR (C_6D_6) : δ 0.68 (9H, s, -(C**H**$_3$)$_3$) ppm. ^{13}C{^{1}H} NMR (C_6D_6) : δ 132.0 (1C, q, -**C**F$_3$, $^{1}J_{C\text{-}F}$ = 321.5 Hz), -5.2 (3C, s, -(**C**H$_3$)$_3$) ppm. ^{19}F NMR (C_6D_6) : δ -66.1 (3F, s, -C**F**$_3$) ppm.

6.2.2.2 Reaction of $PPhCl_2$ (125) with CF_3TMS (122)

(Trifluoromethyl)trimethylsilane (**122**) (2.4 ml, 12 mmol) was added to dichlorophenylphosphine (**125**) (1.3 ml, 10 mmol) in THF (10 ml). The solution was cooled to 0°C and tetra-*n*-butylammonium fluoride (**126**) (20 mg, 0.08 mmol) was added. The reaction mixture was kept at 0°C for 30 min and allowed to warm to room temperature. Analysis of the reaction mixture by ^{31}P{^{1}H} NMR spectroscopy showed that unreacted dichlorophenylphosphine (**125**) was the major compound present, amongst minor amounts of decomposition products. There were no resonances arising from trifluoromethylation of phosphorus. Stirring the reaction mixture at room temperature for several days gave no

additional products. The volatility of (trifluoromethyl)trimethylsilane **(122)** precluded the use of higher temperatures in this reaction.

(Trifluoromethyl)trimethylsilane **(122)** (0.25 ml, 1.3 mmol) was added to dichlorophenylphosphine **(125)** (0.1 ml, 0.8 mmol) in THF (2 ml). The solution was cooled to 0°C and tetra-*n*-butylammonium fluoride **(126)** (0.26 g, 1.0 mmol) was added. The reaction mixture was kept at 0°C for 30 min and was then allowed to warm to room temperature. Analysis of the crude reaction mixture by ^{31}P NMR spectroscopy showed that no trifluoromethylated phosphines were formed, but that significant decomposition of dichlorophenylphosphine **(125)** had occurred.

(Trifluoromethyl)trimethylsilane **(122)** (0.25 ml, 1.3 mmol) was added to dichlorophenylphosphine **(125)** (0.1 ml, 0.8 mmol) in THF (2 ml). The solution was cooled to 0°C, and potassium fluoride (0.1 g, 1.7 mmol) was added. The reaction mixture was allowed to warm to room temperature, and stirred for 3 h at room temperature. Analysis of the reaction mixture by ^{31}P NMR spectroscopy showed the presence of dichlorophenylphosphine **(125)** at δ 161 ppm, and a small resonance at δ 30.5 ppm, arising from fluorochlorophenylphosphine **(127)**. ^{31}P NMR : δ 30.5 (d, $^{1}J_{F\text{-}P}$ = 1000 Hz) ppm. (Literature[87] : d, $^{1}J_{F\text{-}P}$ = 1050 Hz, no chemical shift reported.)

Potassium fluoride (0.2 g, 3.4 mmol) was added to a solution of dichlorophenylphosphine **(125)** (0.1 ml,) in THF (1 ml), and the reaction mixture was stirred at room temperature for 3 h. A small amount of dichlorophenylphosphine **(125)** had reacted to form fluorochlorophenylphosphine **(127)**. ^{31}P NMR : δ 30.5 (d, $^{1}J_{F\text{-}P}$ = 1000 Hz) ppm.

6.2.2.3 Reaction of $P(O)PhCl_2$ (128) with CF_3TMS (122)

A solution of dichlorophenylphosphine oxide **(128)** (0.1 ml) and (trifluoromethyl)-trimethylsilane **(122)** (0.25 ml, 1.3 mmol) in THF was cooled to 0°C, and tetra-*n*-butylammonium fluoride **(126)** (20 mg, 0.08 mmol) was added. The solution was stirred at 0°C for 1 h, and allowed to warm to room temperature. Analysis of the crude reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy showed the presence of a large peak at δ 33.5 ppm arising from dichlorophenylphosphine oxide **(128)**, and small resonances due to hydrolysis of **(128)**.

A solution of dichlorophenylphosphine oxide **(128)** (0.1 ml, 0.7 mmol) and (trifluoromethyl)trimethylsilane **(122)** (0.25 ml, 1.3 mmol) in THF was cooled to 0°C, and tetra-*n*-butylammonium fluoride **(126)** (0.1 g, 0.4 mmol) was added. The solution was stirred at 0°C for 1 h, and allowed to warm to room temperature. Analysis of the crude reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy showed that all dichlorophenylphosphine oxide **(128)** had reacted to form a mixture of phosphorus-containing compounds.

Distilled water (1 ml) was added to a sample of dichlorophenylphosphine oxide **(128)** (0.1 ml), and heat was evolved. $^{31}P\{^1H\}$ NMR analysis of the sample showed identical peaks to those formed in the reaction of dichlorophenylphosphine oxide **(128)** with (trifluoromethyl)trimethylsilane **(122)** in the presence of tetra-*n*-butylammonium fluoride **(126)**.

A solution of dichlorophenylphosphine oxide **(128)** (0.1 ml, 0.7 mmol) and (trifluoromethyl)trimethylsilane **(122)** (0.25 ml, 1.3 mmol) in THF was cooled to 0°C, and potassium fluoride (0.2 g, 3.4 mmol) was added. The solution was stirred at 0°C for 1 hour,

then allowed to warm to room temperature. Analysis of the crude reaction mixture by $^{31}P\{^{1}H\}$ NMR spectroscopy showed the formation of chlorofluorophenylphosphine oxide **(129)** and difluorophenylphosphine oxide **(130)**.$^{31}P\{^{1}H\}$ NMR for **(129)** : δ 13.5 (d, $^{1}J_{P\text{-}F}$ = 985 Hz) ppm. Literature[88] : δ 30.4 (t, $^{1}J_{P\text{-}F}$ = 1140 Hz) ppm. $^{31}P\{^{1}H\}$ NMR data for **(130)** : δ 11.4 (t, $^{1}J_{P\text{-}F}$ = 1100 Hz) ppm; Literature[88] : δ 11.5 (t, $^{1}J_{P\text{-}F}$ = 1100 Hz) ppm.

After 7 days at room temperature, $^{31}P\{^{1}H\}$ NMR analysis of this reaction mixture showed the appearance of a quartet, indicating the presence of a trifluoromethyl group. ^{31}P NMR (THF) : δ 8.2 (q, $^{2}J_{P\text{-}F}$ = 90 Hz) ppm. No further reaction was observed.

6.2.2.4 Reaction of dcpe (12) with CF_3TMS (122)

A solution of 1,2-bis(dichlorophosphino)ethane **(12)** (60 µl, 0.4 mmol) in THF (2 ml) was cooled to 0°C, and (trifluoromethyl)trimethylsilane **(122)** (0.35 ml, 1.7 mmol) and potassium fluoride (10 mg, 0.2 mmol) were added. The solution was stirred at 0°C for 1 h, then allowed to warm to room temperature and stirred overnight at room temperature. Analysis of the reaction mixture by $^{31}P\{^{1}H\}$ NMR spectroscopy showed that dcpe **(12)** was the only phosphorus-containing compound present.

6.3 Synthesis and reactions of hepa, $P(NEt_2)_3$ (53)

6.3.1 Preparation of hepa, $P(NEt_2)_3$ (53)

Hexaethylphosphorus triamide **(53)** was synthesised using a modification of the method of Stuebe and Lankelma.[90]

Phosphorus trichloride (23 ml, 0.26 mol) in ether (100 ml) was added to diethylamine

(156 g, 2.1 mol) in ether (300 ml) over 4 hours, while maintaining the temperature between 5°C and 10°C. During addition, a white precipitate formed, requiring the use of a mechanical stirrer to ensure solution homogeneity. The reaction mixture was allowed to warm to room temperature and stirred for 16 h at room temperature. The resulting white precipitate was filtered off and washed well with ether. The combined filtrate and washings were freed of volatile material under vacuum, and the crude product was purified by distillation under reduced pressure. Hexaethylphosphorus triamide **(53)** (61g, 95%) distilled as a colourless, viscous liquid at 105°C at 10 mmHg. The NMR data for hepa **(53)** is identical to that described in the literature.[90] $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) : δ 117.0 (s) ppm. ^{1}H NMR ($CDCl_3$) : δ 2.89 (12H, dq, -NC**H**$_2$-, $^{3}J_{P-H}$ = 9 Hz, $^{3}J_{H-H}$ = 7 Hz), 0.99 (18H, t, -C**H**$_3$, $^{3}J_{H-H}$ = 7 Hz). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) : δ 39.7 (6C, d, -NC**H**$_2$-, $^{2}J_{C-P}$ = 19 Hz), 14.4 (6C, s, -**C**H$_3$) ppm.

6.3.2 Preparation of $P(S)(NEt_2)_3$ (137)

Hexaethylphosphorus triamide **(53)** was sulfurised following the method described by Lankelma and Stuebe.[90]

Sulfur powder (44 mg, 1.4 mmol) was added to a solution of hepa **(53)** (340 mg, 1.4 mmol) in THF (2 ml) and stirred for 10 min at room temperature. The sulfur powder dissolved instantly, and the reaction mixture became homogeneous. The solvent was removed under vacuum to give hexaethylphosphorothioic triamide **(137)** as a viscous, colourless oil in almost quantitative yield (365 mg, 1.4 mmol, 95 %). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) : δ 78.1 (1P, s) ppm. ^{1}H NMR ($CDCl_3$) : δ 3.14 (12H, dq, -NC**H**$_2$-, $^{3}J_{P-H}$ = 12 Hz, $^{3}J_{H-H}$ = 7 Hz), 1.12 (18H, t, -C**H**$_3$, $^{3}J_{H-H}$ = 7 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) : δ 40.5 (6C, d, -NC**H**$_2$-, $^{2}J_{C-P}$ = 4 Hz), 14.3 (6C, d, -C**H**$_3$, $^{3}J_{C-P}$ = 3 Hz) ppm.

6.3.3 Chlorination of hepa (53)

A solution of hepa (**53**) (30 mg, 0.12 mmol) in $CDCl_3$ (0.5 ml) in a 5 mm NMR tube was left in the probe of a high field NMR spectrometer at 300K. A $^{31}P\{^1H\}$ NMR spectrum was run at 30 min intervals.[132] The ^{31}P NMR spectrum acquired after 90 min at 300K showed that all hepa (**53**) had reacted to form two products (**140**) and (**141**), the spectra of which are described below.

Major product (**140**) : $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 51.5 (1P, s). ^1H NMR ($CDCl_3$) : δ 3.12 (12H, dq, -NC**H**$_2$-, $^3J_{P\text{-}H}$ = 7 Hz, $^3J_{H\text{-}H}$ = 7 Hz), 1.10 (18H, t, -C**H**$_3$, $^3J_{H\text{-}H}$ = 7 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 39.9 (6C, d, -NC**H**$_2$-, $^2J_{C\text{-}P}$ = 19 Hz), 12.1 (6C, s, -**C**H$_3$) ppm.

Minor product (**141**) : $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 50.5 (1P, s). ^1H NMR ($CDCl_3$) : δ 3.05 (12H, dq, -NC**H**$_2$-, $^3J_{P\text{-}H}$ = 11 Hz, $^3J_{H\text{-}H}$ = 7 Hz), 1.05 (18H, t, -C**H**$_3$, $^3J_{H\text{-}H}$ = 7 Hz) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) : δ 38.8 (6C, d, -NC**H**$_2$-, $^2J_{C\text{-}P}$ = 19 Hz), 12.4 (6C, s, -**C**H$_3$) ppm.

A solution of hepa (**53**) (30 mg, 0.12 mmol) in CD_2Cl_2 (0.5 ml) in a 5 mm NMR tube was left in the probe of a high field NMR spectrometer at 300K. A $^{31}P\{^1H\}$ NMR spectrum was run on this sample at 30 min intervals.[132] The ^{31}P NMR spectrum acquired after 20 h showed that only slight decomposition of hepa (**53**) had occurred, to a product with a ^{31}P NMR shift of 51.5 ppm.

6.4 Reaction of dcpe (12) and CF_3Br (123) with hepa (53) : Synthesis of dfmpe (50)

In a typical reaction, trifluoromethyl bromide (**123**) (36.0 g, 240 mmol) was condensed into a flask and allowed to evaporate into a three-necked flask cooled to liquid nitrogen

temperature and fitted with a dry-ice condenser. The reaction mixture was allowed to warm to -60°C, and dcpe (**12**) (4.0 g, 17 mmol) was added to the reaction mixture using an air-tight syringe. Dichloromethane (20 ml) was added, and a solution of hexaethylphosphorus triamide (**53**) (34.0 g, 140 mmol) in dichloromethane (20 ml) was added over a period of 1 h while the temperature was maintained between -60°C and -55°C. The colour of the reaction was pale yellow after all the hepa (**53**) had been added. Sulfur powder (2.0 g, 62 mmol) was added, and the reaction mixture was allowed to warm slowly to room temperature. Dichloromethane and dfmpe (**50**) were distilled from the reaction mixture under vacuum and collected at liquid nitrogen temperature. The dichloromethane solution obtained contained dfmpe (**50**) (1.2 g, 3.3 mmol, 20%) as the sole component (>95%, 0.03 g/ml) and was used directly for most applications. $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) : δ 0.2 (2P, m, -**P**$(CF_3)_2$) ppm. ^{1}H NMR (CD_2Cl_2) : δ 2.29 (4H, apparent triplet, PC**H**$_2$-, $^{2}J_{P\text{-}H}$ = 4 Hz) ppm. ^{19}F NMR (CD_2Cl_2) : δ -51.5 (12F, m, -P(C**F**$_3)_2$) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) : δ 14.9 (-**C**H_2-), 128.4 ppm (4C, m, -**C**F_3, $^{1}J_{C\text{-}F}$ = 325 Hz) ppm. Mass Spectrum (EI) *m/e* M+ 366(0.5), 347(5), 297(100), 247(27), 197(23), 131(5), 119(10), 69(90).

$(CF_3)_2PCH_2P(CF_3)_2$ (**138**) : $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) : δ -7.0 (m, -**P**$(CF_3)_2$) ppm. ^{1}H NMR (CD_2Cl_2) : δ 2.62 ppm (t, PC**H**$_2$-, $^{2}J_{P\text{-}H}$ = 2.5 Hz) ppm. ^{19}F NMR (CD_2Cl_2) : δ -52.1 (m, -P(C**F**$_3)_2$) ppm. Mass spectrum (EI) : 69(100), 229(95), 131(23), 179(20), 270(5), 352(1). These values are identical to literature reports for this compound.[61]

6.5 Attempted sulfurisation of dfmpe (50)

A solution of dfmpe (**50**) in dichloromethane (8 ml, 0.011 g/ml, 0.23 mmol) was added to sulfur powder (0.015 g, 0.64 mmol) and stirred at room temperature for 16 h. Analysis of

the resulting solution by $^{31}P\{^{1}H\}$ NMR spectroscopy showed no sulfurised products present, and that dfmpe **(50)** was the only compound present. THF (3 ml) was added to the reaction mixture, and the solution was stirred for a further 2 h. Analysis of the solution by $^{31}P\{^{1}H\}$ NMR spectrsocopy again showed no sulfurised products and only dfmpe **(50)** present. More sulfur powder (0.15 g, 6.4 mmol) was added and the solution stirred for a further 48 h, but no sulfurised products were observed by $^{31}P\{^{1}H\}$ NMR spectroscopy. Heating the reaction to 45°C for 48 h also produced no sulfurised products, only dfmpe **(50)** itself. A small amount of $AlCl_3$ was added to the solution, and the solution was heated to reflux, but again no new products were observed in the $^{31}P\{^{1}H\}$ NMR spectrum.

6.6 Reactions of dfmpe (50) with iron complexes

6.6.1 Reaction of dfmpe (50) with anhydrous $FeCl_2$

A solution of dfmpe **(50)** in dichloromethane (8 ml, 0.011 g/ml, 0.23 mmol) was added to anhydrous $FeCl_2$ (0.10 g, 0.8 mmol) and stirred at room temperature for 24 h. Analysis of the resulting solution by ^{19}F NMR showed no products had formed and that dfmpe **(50)** was the only fluorinated product present. The reaction mixture was heated at 50°C for 12 h, and ^{19}F NMR analysis of the reaction mixture showed only dfmpe **(50)** present.

A solution of dfmpe **(50)** in dichloromethane (3 ml, 0.011 g/ml, 0.10 mmol) was added to anhydrous $FeCl_2$ (0.01 g, 0.08 mmol) in THF (2.5 ml) and stirred at room temperature at 7500 atm for 24h. Analysis of the resulting solution by ^{19}F NMR showed the formation of no products and that dfmpe **(50)** was the sole fluorine-containing compound present. The reaction mixture was heated to 100°C at 7500 atm for a further 48 h, but again no products were observed by ^{19}F NMR spectroscopy.

6.6.2 Reaction of dfmpe (50) with $FeCl_2(depe)_2$ (147)

A solution of dfmpe (**50**) in dichloromethane (8 ml, 0.011 g/ml, 0.23 mmol) was added to $FeCl_2(depe)_2$ (**147**) (0.063 g, 0.12 mmol) and stirred at room temperature for 1 h. Analysis of the resulting solution by $^{31}P\{^1H\}$ NMR showed no indication of displacement of depe (**14**) and only dfmpe (**50**) present, and a ^{19}F NMR spectrum of the reaction mixture showed that dfmpe (**50**) was the only fluorine-containing compound present. The reaction mixture was stirred at room temperature for 7 days, but again no products were observed by $^{31}P\{^1H\}$ NMR and ^{19}F NMR spectroscopy.

6.6.3 Reaction of dfmpe (50) $FeCl_2(dprpe)_2$ (148)

A solution of dfmpe (**50**) in dichloromethane (8 ml, 0.011 g/ml, 0.23 mmol) was added to $FeCl_2(dprpe)_2$ (**148**) (0.075 g, 0.12 mmol) and stirred at room temperature for 1 h. Analysis of the resulting solution by $^{31}P\{^1H\}$ NMR showed no indication of displacement of dprpe (**15**) and only dfmpe (**50**) present, and a ^{19}F NMR spectrum of the reaction mixture showed that dfmpe (**50**) was the only fluorine-containing compound present. The reaction mixture was stirred at room temperature for 7 days, but again no products were observed by $^{31}P\{^1H\}$ NMR and ^{19}F NMR spectroscopy.

6.6.4 Reaction of dfmpe (50) with $Fe(CO)_5$ (64)

Iron pentacarbonyl (**64**) (80 mg, 0.4 mmol) was added to a solution of dfmpe (**50**) (0.15 g, 0.4 mmol) in dichloromethane (10 ml) and stirred at room temperature for 24 h. Analysis of the resulting solution by $^{31}P\{^1H\}$ NMR showed dfmpe (**50**) as the only fluorine-containing product. The mixture was heated at 40°C for 24 h, however $^{31}P\{^1H\}$ NMR analysis again showed no trace of complexed dfmpe, and only free dfmpe (**50**) present.

6.7 Reactions of dfmpe (50) with ruthenium complexes

6.7.1 Reaction of dfmpe (50) with $RuCl_3.3H_2O$

A solution of dfmpe (**50**) (180 mg, 0.50 mmol) in dichloromethane (30 ml) was added to ruthenim trichloride trihydrate (50 mg, 0.24 mmol) in ethanol (10 ml), and the mixture was refluxed for 1 h. The solution was filtered, the solvent was removed under vacuum, and the solution was eluted through flash silica using ethyl acetate. The product obtained was a mixture of two compounds (**150**) and (**151**). (**150**) is assigned as $RuCl_2(dfmpe)_2$, and (**151**) has yet to be identified.

Major product, (**151**): $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$) : δ 118.6 (m) ppm. ^1H NMR ($CDCl_3$) : δ 2.7-2.9 (m, PC**H**$_2$-) ppm. ^{19}F NMR ($(CD_3)_2CO$) : δ -50.3 (12F, d, P(C**F**$_3)_2$, $^2J_{F\text{-}P}$ = 62 Hz), -53.3 (12F, d, P(C**F**$_3)_2$, $^2J_{F\text{-}P}$ = 66 Hz) ppm. $^{13}C\{^1H, ^{31}P\}$ NMR ($(CD_3)_2CO$) : δ 126.0 (q, -P(**C**F$_3)_2$, $^1J_{F\text{-}C}$ = 320 Hz), 124.9 (4C, m, -P(**C**F$_3)_2$, $^1J_{F\text{-}C}$ = 320 Hz), 22.1 (s, -**C**H$_2$P(CF$_3)_2$) ppm. m.p. >320°C. Mass Spectrum (CI) *m/e* M+ : 1099 (100), 1116 (58), 1133 (18), 1080 (12), 1063 (11).

Minor product, $RuCl_2(dfmpe)_2$ (**150**) : $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$) : δ 90.5 (m) ppm. ^1H NMR ($CDCl_3$) : δ 2.7-2.9 (m, PC**H**$_2$-) ppm. ^{19}F NMR ($(CD_3)_2CO$) : δ -47.1 (m, P(C**F**$_3)_2$) ppm. m.p. >320°C. Mass Spectrum (CI) *m/e* M+ : 871 (100), 887 (22), 834 (13), 815 (7), 906 (6).

6.7.2 Reaction of dfmpe (50) with $RuCl_2(PPh_3)_3$ (152)

The synthesis of tris(triphenylphosphine)dichlororuthenium (II) (**152**) was carried out following the general method of Hallman, Stephenson and Wilkinson.[102]

Ruthenium trichloride trihydrate (1.0 g, 3.8 mmol) was dissolved in methanol (250 ml) and refluxed under nitrogen for 5 minutes. The solution was cooled and triphenylphosphine (**44**) (6.0 g, 22.9 mmol) was added. The solution was refluxed under nitrogen for 3 h, allowed to cool and the precipitate that formed was filtered. The brown residue was washed with ether and dried under vacuum to give $RuCl_2(PPh_3)_3$ (**152**) (3.04 g, 3.2 mmol, 83%) as a fine brown powder.

A solution of dfmpe (**50**) in dichloromethane (4 ml, 0.011 g/ml, 0.11 mmol) was added to $RuCl_2(PPh_3)_3$ (**152**) (0.053 g, 0.06 mmol) and stirred at room temperature for 1 h. The colour of the solution changed from colourless to bright yellow immediately on addition of dfmpe (**50**), and the starting complex dissolved. Analysis of the resulting solution by $^{31}P\{^1H\}$ NMR spectroscopy showed displacement of triphenylphosphine (**44**) had occurred (free triphenylphosphine), and the presence of fluorine-coupled multiplets at 118.6 ppm and 90.5 ppm, amongst a number of other products. The ^{19}F NMR spectrum showed the formation of several fluorine-containing compounds, among them the resonances at δ -47.1 and -50.3 and -53.3 ppm arising from the formation of (**150**) and (**151**). Attempts to separate the components of this mixture were again unsuccessful.

6.7.3 Reaction of dfmpe (50) with $RuH_2(CO)(PPh_3)_3$ (153)

Carbonyldihydridotris(triphenylphosphine) ruthenium(II), $RuH_2CO(PPh_3)_3$, (**153**) was synthesised using the general method of Ahmad, Levison, Robinson and Uttley.[103]

A solution of dfmpe (**50**) (16 mg, 0.04 mmol) in dichloromethane (3 ml) was added to $RuH_2CO(PPh_3)_3$ (**153**) (20 mg, 0.02 mmol) and stirred at room temperature for 48 h. Analysis of the crude reaction mixture by ^{19}F NMR spectroscopy showed dfmpe (**50**) as the only

fluorine-containing product present. Attempts to use higher temperatures or extended reaction periods resulted only in the decomposition of dfmpe (**50**).

6.7.4 Reaction of dfmpe (50) with $RuHCl(CO)(PPh_3)_3$ (154)

6.7.4.1 Synthesis of $RuHCl(CO)(PPh_3)$(dfmpe) (155)

Carbonylchlorohydridotris(triphenylphosphine) ruthenium(II) (**154**) was prepared using the genral method of Ahmad, Levison, Robinson and Uttley.[103]

Hydrated ruthenium trichloride (0.52 g, 2.0 mmol) in 2-methoxyethanol (40 ml) and aqueous formaldehyde (40 ml, 40% w/v) were added quickly and successively to a vigorously refluxing solution of triphenylphosphine (**44**) (3.16 g, 12 mmol) in 2-methoxyethanol (120 ml). The mixture was refluxed for 10 min and allowed to cool. The precipitate that formed was filtered, washed successively with ethanol (20 ml), water (20 ml), ethanol (20 ml) and light petroleum (50 ml), and dried under vacuum to give carbonylchlorohydrido-tris(triphenylphosphine) ruthenium(II) (**154**) as a brown powder (1.49 g, 78% based on $RuCl_3.3H_2O$).

A solution of dfmpe (**50**) (0.15 g, 0.4 mmol) in dichloromethane (5 ml) was added to $RuHCl(CO)(PPh_3)_3$ (**154**) (0.39 g, 0.4 mmol) and the solution was stirred overnight at room temperature. The resulting yellow solution was filtered, and purified by column chromatography on flash silica, using a 1:1 mixture of dichloromethane and light petroleum as eluant. The fractions containing the required compound were identified by t.l.c., combined and washed with light petroleum (3 × 10 ml) to remove traces of triphenylphosphine (**44**).

1,2-(*Bis*(*bis*(trifluoromethyl)phosphino)ethane)carbonylchlorohydrido(triphenylphosphine) ruthenium(II) **(155)** was obtained as an air-stable white powder, which was recrystallised from light petroleum to afford colourless prisms (140 mg, 43%).

NMR data: $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) : δ 102.1 (1P, ddsep, $\mathbf{P_A}$, $^{2}J_{P\text{-}F}$ = 70 Hz, $^{2}J_{PA\text{-}PB}$ = 22 Hz, $^{2}J_{PA\text{-}PC}$ = 310 Hz), 65.9 (1P, ddsep, $\mathbf{P_B}$, $^{2}J_{P\text{-}F}$ = 63 Hz, $^{2}J_{PB\text{-}PA}$ = 22 Hz, $^{2}J_{PB\text{-}PC}$ = 20 Hz) 36.2 (1P, dd, $\mathbf{P_C}$, $^{2}J_{PC\text{-}PA}$ = 310 Hz, $^{2}J_{PC\text{-}PB}$ = 20 Hz) ppm. ^{1}H NMR ($CDCl_3$) : δ 7.3-7.7 (15H, m, $P(C_6\mathbf{H}_5)_3$), 2.3-2.9 (4H, m, -$PC\mathbf{H}_2C\mathbf{H}_2P$-), -5.19 (1H, ddd, $^{2}J_{H\text{-}PA}$ = 19 Hz, $^{2}J_{H\text{-}PB}$ = 150 Hz, $^{2}J_{H\text{-}PC}$ = 19 Hz, Ru**H**) ppm. ^{19}F NMR ($CDCl_3$) : δ -48.8 - -49.2 (6F, two overlapping doublets, 2 × P-$C\mathbf{F}_3$), -53.3 (3F, d, P-$C\mathbf{F}_3$, $^{2}J_{F\text{-}P}$ = 66 Hz), -55.2 (3F, dm, P-$C\mathbf{F}_3$, $^{2}J_{F\text{-}P}$ = 73 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) : δ 195.3 (1C, s, **C**O), 134.9 (6C, d, $^{1}J_{C\text{-}P}$ = 11 Hz, 3 × P-C(**C**HCH-)$_2$CH), 133.8 (3C, d, $^{1}J_{C\text{-}P}$ = 47 Hz, 3 × P-**C**(CHCH-)$_2$CH), 131.1 (3C, s, 3 × P-C(CHCH-)$_2$**C**H), 128.9 (6C, d, $^{1}J_{C\text{-}P}$ = 10 Hz, 3 × P-C(CH**C**H-)$_2$CH), 21.1(1C, m, -$\mathbf{C}H_2P(CF_3)_2$), 19.2 (1C, m, -$\mathbf{C}H_2P(CF_3)_2$) ppm. M.p. 193-194°C (dec.). I.R. (Nujol Mull) : 1992.2 cm^{-1} (m, C≡O), 1978.0 cm^{-1} (w, Ru-H). Mass Spectrum (CI) *m/e* M^+ 793(100), 775(14), 759(57), 739(8), 731(10), 719(8).

6.7.4.2 Synthesis of $RuH_2(CO)(PPh_3)$(dfmpe) (170)

A solution of sodium borohydride (15 mg, 0.4 mmol) in THF (10 ml) was added to a solution of $RuHCl(CO)(PPh_3)$(dfmpe) **(150)** (50 mg, 63 μmol) in tetrahydrofuran (10 ml) and stirred at room temperature for 20 h. The solvent was removed under vacuum, and the residue was extracted with light petroleum (3 × 20 ml). Removal of the solvent from the combined extracts afforded $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** as a white powder (43 mg, 90%) which was >95% pure by ^{1}H and ^{19}F NMR spectroscopy. NMR data: $^{31}P\{^{1}H\}$ NMR (C_6D_6) : δ 118.8

(1P, ddsep, $\mathbf{P_A}$, $^2J_{P\text{-}F}$ = 75 Hz, $^2J_{PA\text{-}PB}$ = 20 Hz, $^2J_{PA\text{-}PC}$ = 247 Hz), 89.6 (1P, ddsep, $\mathbf{P_B}$, $^2J_{P\text{-}F}$ = 63 Hz, $^2J_{PB\text{-}PA}$ = 20 Hz, $^2J_{PB\text{-}PC}$ = 21 Hz), 51.8 (1P, dd, $\mathbf{P_C}$, $^2J_{PC\text{-}PA}$ = 247 Hz, $^2J_{PC\text{-}PB}$ = 21 Hz) ppm. ^{1}H NMR ($CDCl_3$) : δ 7.3-7.7 (15H, m, P($C_6\mathbf{H}_5$)$_3$), 2.3-2.9 (4H, m, -PC$\mathbf{H}_2$C$\mathbf{H}_2$P-), -6.55 (1H, ddd, $^2J_{H\text{-}P}$ = 22, 102, 23 Hz, Ru**H**), -9.31 (1H, ddd, $^2J_{H\text{-}P}$ = 20, 25, 20 Hz, Ru**H**) ppm. ^{19}F NMR ($CDCl_3$) : δ -56.9 (3F, d, P-C$\mathbf{F}_3$, $^2J_{F\text{-}P}$ = 67 Hz), -57.2 (3F, dq, P-C$\mathbf{F}_3$, $^2J_{F\text{-}P}$ = 68 Hz, $^4J_{F\text{-}F}$ = 7 Hz), -59.1 (3F, d, P-C$\mathbf{F}_3$, $^2J_{F\text{-}P}$ = 76 Hz), -60.2 (3F, d, P-C$\mathbf{F}_3$, $^2J_{F\text{-}P}$ = 77 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6) : δ 199.2 (1C, s, **C**O), 137.6 (3C, d, $^1J_{C\text{-}P}$ = 47 Hz, 3 × P-**C**(CHCH-)$_2$CH), 134.3 (6C, d, $^1J_{C\text{-}P}$ = 12 Hz, 3 × P-C(**C**HCH-)$_2$CH), 130.8 (3C, s, 3 × P-C(CHCH-)$_2$**C**H), 129.8 (6C, d, $^1J_{C\text{-}P}$ = 12 Hz, 3 × P-C(CH**C**H-)$_2$CH), 23.7 (1C, m, -$\mathbf{C}$H$_2$P(CF$_3$)$_2$), 20.6 (1C, m, -**C**H$_2$P(CF$_3$)$_2$) ppm. M.p. 119-120°C (dec.). I.R. (Nujol Mull) : 2005.4 cm^{-1} (m, C≡O), stretches for Ru-H not observed. Mass Spectrum (CI) *m/e* M$^+$ 759(100), 739(42).

6.7.4.3 Attempted synthesis of $RuH_2(dfmpe)_2$ (113) via $RuH_2(CO)(PPh_3)(dfmpe)$ (170)

A solution of dfmpe (**50**) (10 mg, 30 μmol) in dichloromethane (1 ml) was added to ($RuH_2(CO)(PPh_3)$(dfmpe) (**170**) (10 mg, 13 μmol), and the solution was stirred at room temperature for 24 h. Analysis of the reaction mixture by ^{19}F NMR spectroscopy showed only the presence of the starting dihydride complex (**170**) and dfmpe (**50**). Attempts to heat this solution resulted only in decomposition of the starting dihydride complex (**170**).

6.7.4.4 Reaction of $RuH_2(CO)(PPh_3)$(dfmpe) (170) with chloroform : Synthesis of $RuCl_2(CO)(PPh_3)$(dfmpe) (171)

A solution of $RuH_2(CO)(PPh_3)$(dfmpe) (**170**) in $CDCl_3$ was kept at room temperature in an NMR tube overnight. After 16 h, analysis by ^{19}F NMR spectroscopy showed 50% of the

starting complex had reacted to form a new product. The reaction mixture was left at room temperature for 2 weeks, after which time ^{19}F NMR spectroscopy showed complete conversion of the starting complex $RuH_2(CO)(PPh_3)$(dfmpe) **(170)** to a single clean product, found to be $RuCl_2(CO)(PPh_3)$(dfmpe) **(171)**. **(171)** was purified by extraction into methanol and subsequent column chromatography using ethyl acetate as eluant. The compound was found to be pure by ^1H NMR, ^{31}P NMR and ^{19}F NMR spectroscopy. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 93.7 (1P, dsep, $\mathbf{P_B}$, $^2J_{P\text{-}F}$ = 66 Hz, $^2J_{PB\text{-}PC}$ = 23 Hz), 88.1 (1P, dsep, $\mathbf{P_A}$, $^2J_{P\text{-}F}$ = 63 Hz, $^2J_{PA\text{-}PC}$ = 390 Hz), 21.3 (1P, dd, $\mathbf{P_C}$, $^2J_{PC\text{-}PA}$ = 390 Hz, $^2J_{PC\text{-}PB}$ = 23 Hz) ppm. ^1H NMR ($CDCl_3$) : δ 7.3-7.7 (15H, m, $P(C_6\mathbf{H}_5)_3$), 3.05, 2.90, 2.75, 2.30 (4 × 1H, m, $-PC\mathbf{H}_2C\mathbf{H}_2P-$) ppm. ^{19}F NMR ($CDCl_3$) : δ -44.2 (3F, d, P-$C\mathbf{F}_3$, $^2J_{F\text{-}P}$ = 60 Hz), -47.6 (3F, d, P-$C\mathbf{F}_3$, $^2J_{F\text{-}P}$ = 66 Hz), -53.3 (3F, d, P-$C\mathbf{F}_3$, $^2J_{F\text{-}P}$ = 69 Hz), -53.9 (3F, d, P-$C\mathbf{F}_3$, $^2J_{F\text{-}P}$ = 65 Hz) ppm. $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$) : δ 193.0 (1C, s, **C**O), 135.4, 132.8, 131.4, 128.9 ($P(\mathbf{C}_6H_6)_3$ peaks), 21.1 (1C, s, -$\mathbf{C}H_2P(CF_3)_2$), 19.2 (1C, s, -$\mathbf{C}H_2P(CF_3)_2$) ppm. I.R. (Nujol Mull) : 2008.4 cm^{-1} (m, C≡O). Mass Spectrum (CI) *m/e* M^+ 795(100), 759(12).

A solution of sodium tetraphenylborate in methanol was added to a solution of **(171)** in methanol, and no precipitate was observed.

6.7.5 Reaction of dfmpe with Ru(COD)(COT) (93): Preparation of $RuH_2(dfmpe)_2$ (113)

The preparation of (η^4-cyclo-octa-1,5-diene)(η^6-cyclo-octa-1,3,5-triene)ruthenium (0), Ru(COD)(COT) (**93**), was based on the synthesis described by Pertici and co-workers in 1980.[109]

1,5-Cyclooctadiene (8.8 g, 81 mmol) was added to a solution of ruthenium trichloride

trihydrate (0.34 g, 1.3 mmol) in ethanol (10 ml). Zinc dust (3.5 g) was added and the mixture was heated under reflux with magnetic stirring for 3 hours. The solvent was removed under vacuum, and the residue was extracted into hexane (30 ml). This solution was calibrated by ^{1}H NMR spectroscopy by integration against an internal standard (trinitrotoluene) and found to contain Ru(COD)(COT) **(93)** (0.95 mmol, 73%). This solution was used in subsequent reactions without further purification.

A solution of Ru(COD)(COT) **(93)** (0.21 g, 0.65 mmol) in hexane (20 ml) was added to a reaction vessel and the solvent removed under vacuum. A solution of dfmpe **(50)** (0.48 g, 1.3 mmol) in dichloromethane (15 ml) was added to this residue. The vessel was evacuated and filled with 1 atm H_2 gas, and stirred overnight at room temperature. Flash silica was added, and the solvent was removed under vacuum. The resulting dry powder was packed onto the top of a flash silica column, and flushed with light petroleum. $RuH_2(dfmpe)_2$ **(113)** was obtained as a white air-stable solid which was purified by recrystallisation from hexane to form white needles (0.15 g, 27%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) : δ 108.2 (2P, m), 90.0 (2P, m) ppm. ^{1}H NMR ($CDCl_3$) : δ 2.58 (4H, m, PCH_2-), 2.09 (4H, m, PCH_2-), -9.94 (2H, m, RuH_2) ppm. ^{19}F NMR ($CDCl_3$) : δ -56.9 (6F, d, $P(CF_3)_2$, $^{2}J_{F\text{-}P}$ = 70 Hz), -57.3 (6F, d, $P(CF_3)_2$, $^{2}J_{F\text{-}P}$ = 75 Hz), -58.0 (6F, m, $P(CF_3)_2$), -60.0 (6F, m, $P(CF_3)_2$) ppm. $^{13}C\{^{1}H, ^{31}P\}$ NMR ($CDCl_3$) : δ 127.1 (4C, m, $P(CF_3)_2$), 123.9 (4C, m, $P(CF_3)_2$), 23.5 (2C, s, $-CH_2P(CF_3)_2$), 22.2 (2C, s, $-CH_2P(CF_3)_2$) ppm. M.p. 155-156°C U.V./vis (hexane) : 253.7 nm ($\varepsilon = 5.274 \times 10^3$, br shoulder), 222.3 nm ($\varepsilon = 1.117 \times 10^4$, broad) and 190.9 nm ($\varepsilon = 2.016 \times 10^4$). I.R. (KBr disk) : 1931.4 cm^{-1} (weak) Ru-H. Mass Spectrum M/Z : (M^+-1) 834 (50), 715 (40), 468 (53), 418 (30), 297 (37), 247 (10), 197 (20), 77 (28), 69 (100), 47 (32), 28(80). High Resolution Mass Spectrum (M^+-H_2) : Experimental 833.82230 a.m.u.; expected 833.82368 a.m.u..

6.7.6 Reaction of dfmpe (50) with $RuHCl(PPh_3)_3$ (172)

6.7.6.1 Synthesis of $RuHCl(dfmpe)_2$ (175)

$RuHCl(PPh_3)_3$ **(172)** was synthesised following a modification of the method of Hallman, McGarvey and Wilkinson.[110]

Sodium borohydride (0.2 g, 5.3 mmol) in water (2 ml) was added to a solution of $RuCl_2(PPh_3)_3$ **(172)** (1.0 g, 1.0 mmol) in benzene (150 ml). The solution was refluxed for 30 min, during which time the colour of the solution changed to deep purple. The solution was filtered and the solvent was removed under vacuum to give tris(triphenylphosphine)-hydrochlororuthenium (II) **(172)** (0.89 g, 0.96 mmol, 96%) as a fine purple solid. The NMR spectra of this compound were identical to those reported in the literature.[110]

A solution of dfmpe **(50)** (0.22 g, 0.61 mmol) in dichloromethane (50 ml) was added to a solution of $RuHCl(PPh_3)_3$ **(172)** (0.33 g, 0.36 mmol) in benzene (20 ml) and stirred at room temperature for 1 h. The deep purple colour of the reaction mixture faded after this time, and the reaction mixture became yellow. The resulting solution was flushed through a small plug of vacuum-dried flash silica with dichloromethane (50 ml), and stripped of solvent under vacuum. The residue was washed with light petroleum (3 × 10 ml), dried under vacuum and was found to contain pure $RuHCl(dfmpe)_2$ **(175)** as an air-stable white powder (0.15 g, 56 %). NMR data: $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 96.2 (4P, m) ppm. ^1H NMR ($CDCl_3$) : δ 2.75 (4H, m, 2× -PC**H**H′-C**H**H′P-), 2.56 (4H, m, 2× -PCH**H′**-CH**H′**P-), -17.21 (1H, quin, $^2J_{H\text{-}P}$ = 21 Hz, Ru**H**) ppm. ^{19}F NMR ($CDCl_3$) : δ -50.3 (12F, m, 4 × **F**$_3$C-P-CF′$_3$), -55.6 (12F, m, 4 × F$_3$C-P-C**F′**$_3$)ppm. $^{13}C\{^1H, ^{31}P\}$ NMR ($CDCl_3$) : δ 126.0 (2 × 4C, q, 4 × F$_3$**C**-P-**C**F′$_3$, $^1J_{C\text{-}F}$ = 320 Hz), 21.1(4C, s, -**C**H$_2$P-) ppm. M.p. 217-218°C (dec.). I.r. (Nujol mull) 1978.8(w) cm^{-1}, Ru-H. Mass Spectrum (CI) *m/e* M^++2 871(12), 835(100), 803(7).

6.7.6.2 Reduction of $RuHCl(dfmpe)_2$ (175) with sodium borohydride

Sodium borohydride (20 mg, 0.5 mmol) was added to a solution of $RuHCl(dfmpe)_2$ **(175)** (100 mg, 0.1 mmol) in isopropanol (20 ml) and the solution was stirred at room temperature for 16 h. The solvent was removed under vacuum, and the residue was extracted exhaustively with light petroleum. The combined extracts were stripped of solvent and the residue sublimed onto a water-cooled cold-finger at 70°C at 4×10^{-5} Torr to afford $RuH_2(dfmpe)_2$ **(113)** (56 mg, 70 μmol, 67%) as a white air-stable solid. The NMR data and physical data found for this compound were identical to that described previously (Section 6.7.5).

6.7.6.3 Reaction of $RuHCl(dfmpe)_2$ (175) with MeOD

$RuHCl(dfmpe)_2$ **(175)** (30 mg, 34 μmol) was dissolved in CD_3OD (0.5 ml) in an NMR tube, and the sample was kept at room temperature for 30 min. Subsequent analysis by ^{19}F NMR spectroscopy showed the presence of resonances due only to the starting complex, $RuHCl(dfmpe)_2$ **(113)**.

6.7.6.4 Reaction of $RuHCl(dfmpe)_2$ (175) with MeOD and phenylacetylene

Two drops of phenylacetylene were added to a sample of $RuHCl(dfmpe)_2$ **(175)** (30 mg, 34 μmol) in CD_3OD (0.5 ml). Analysis of the sample by ^{19}F NMR spectroscopy showed the presence of resonances due only to the starting complex, $RuHCl(dfmpe)_2$ **(175)**. The sample was heated to 90°C for 45 min, and analysis of the sample by $^{31}P\{^1H\}$ NMR spectroscopy showed almost complete decomposition of the starting complex **(175)** had occurred. No new complexes containing phenylacetylene were observed.

6.8 Reactions of $RuH_2(dfmpe)_2$ (113)

6.8.1 Photolysis of $RuH_2(dfmpe)_2$ (113) in the presence of D_2 gas

$RuH_2(dfmpe)_2$ **(113)** (5 mg, 6 μmol) was dissolved in pentane (0.3 ml) in an NMR tube equipped with a concentric teflon valve, and the solution was degassed by three freeze-pump-thaw cycles on a high-vacuum line. The NMR tube was back-filled with 1 atm D_2 gas, and the sample was irradiated with ultraviolet light at 0°C for 16 h. A ^2H NMR spectrum of the sample showed a broad signal at -9.9 ppm, and a ^1H NMR spectrum showed no hydride present at -9.9 ppm.

$RuH_2(dfmpe)_2$ **(113)** (5 mg, 6 μmol) was dissolved in pentane (0.3 ml) in an NMR tube equipped with a concentric teflon valve, and the solution was degassed by three freeze-pump-thaw cycles on a high-vacuum line. The NMR tube was back-filled with 1 atm D_2 gas, and the sample was kept at room temperature in the dark for 43 h. A ^2H NMR spectrum of the sample showed no signal at -9.9 ppm, and a ^1H NMR spectrum showed a resonance present at -9.9 ppm.

6.8.2 Photolysis of $RuH_2(dfmpe)_2$ (113) in the presence of organic substrates

In a typical reaction, $RuH_2(dfmpe)_2$ **(113)** (5 mg, 6 μmol) was dissolved in the organic substrate (0.3 ml) in an NMR tube equipped with a concentric teflon valve, and the solution was degassed by three freeze-pump-thaw cycles on a high-vacuum line, then back-filled with nitrogen. The sample was irradiated at room temperature for 16 h. The reaction was monitored in all cases by ^{19}F NMR spectroscopy.

6.8.3 Reaction of $RuH_2(dfmpe)_2$ (113) with organic acids

In a typical reaction, $RuH_2(dfmpe)_2$ **(113)** (5 mg, 6 μmol) was dissolved in the organic acid (0.3 ml) in an NMR tube, and the sample was kept at room temperature for 30 min. Subsequent analysis by ^{19}F NMR spectroscopy showed the presence of resonances due only to the starting complex, $RuH_2(dfmpe)_2$ **(113)**, and in the case of triflic acid and trifluoroacetic acid, resonances due to these acids. No new resonances were observed.

$RuH_2(dfmpe)_2$ **(113)** (5 mg, 6 μmol) was dissolved in CD_3OD (0.5 ml), and the solvent was removed under vacuum. This procedure was repeated twice more, and the residue was dissolved in THF. Analysis of the sample by ^2H NMR spectroscopy showed no resonance in the hydride region of this spectrum.

6.9 Synthesis of bife (222)

6.9.1 Preparation of $BrCH_2CH_2P(O)(OEt)_2$ (207)

A solution of triethyl phosphite **(206)** (41.7 g, 0.25 mol) in 1,2-dibromoethane (1400 g, 7.5 mol) was refluxed for 8 h. Excess dibromoethane was removed by distillation and the residue was fractionally distilled under reduced pressure. Diethyl 2-bromoethyl-phosphonate **(207)** (55.4 g, 0.23 mol, 90%) was collected as a colourless liquid at 60-110°C /0.35 mmHg. $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 25.1 (s) ppm (lit.[117] $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 25.3 (s) ppm).

6.9.2 Preparation of CH_2=CHP(O)$(OEt)_2$ (208)

Triethylamine (101 g, 1.0 mol) was added to a solution of diethyl 2-bromoethyl-phosphonate **(207)** (55.4 g, 0.23 mol) in benzene (200 ml) and the mixture was refluxed for 12 h. The reaction mixture was filtered to remove precipitated salts, and excess triethylamine and benzene were removed under vacuum. The residue was distilled at 60-70°C /0.1-0.2 mmHg to afford diethyl vinylphosphonate **(208)** as a colourless liquid (34.2 g, 0.18 mol, 80%). $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 16.5 (s) ppm (lit.[117] $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ 16.3 (s) ppm).

6.9.3 Preparation of Me_2PH (197)

Tetramethyldiphosphine disulfide **(231)** (60.0 g, 0.32 mol), tri-*n*-butylphosphine (130.0 g, 0.64 mol) and water (6.0 g, 0.33 mol) were added to a three-necked round-bottom flask. The flask was fitted with a short fractionating column connected to a condenser and a receiving vessel cooled to 0°C fitted with a dry-ice condenser. The reaction mixture was slowly heated to 140°C using an oil bath until the reaction mixture became homogeneous (approximately 3h). The temperature of the reaction mixture was raised to 210°C and dimethylphosphine **(197)** was collected under nitrogen as it distilled from the reaction mixture (26.0 g, 0.42 mol, 66%) b.p. 24°C (lit.[131] b.p. 21°C). $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ -99.0 (s) ppm (lit.[131] $^{31}P\{^1H\}$ NMR ($CDCl_3$) : δ -99.2 (s) ppm).

6.9.4 Preparation of $Me_2PCH_2CH_2P(O)(OEt)_2$ (209)

Dimethylphosphine **(197)** (8.8 g, 0.14 mol) was added to a solution of diethyl vinylphosphonate **(208)** (19.3 g, 0.12 mol) in benzene (200 ml). The solution was irradiated

for 2.5 h at room temperature with a high pressure Mercury lamp in a quartz flask fitted with a dry-ice condenser. Benzene and excess dimethylphosphine (**197**) were removed under vacuum (0.1-0.2 mmHg), and the crude oil remaining was distilled at 80-95°C at 0.4 mmHg to afford diethyl 2-(dimethylphosphino)ethylphosphonate (**209**) as a colourless, air-sensitive oil (13.1 g, 0.058 mol, 48%). $^{31}P\{^{1}H\}$ NMR (d_8-THF) : δ 30.9 (1P, d, $^{3}J_{P\text{-}P}$ = 52 Hz, -**P**(O)$(OEt)_2$) -47.3 (1P, d, -**P**Me_2 ,$^{3}J_{P\text{-}P}$ = 52 Hz) ppm (lit.[117] $^{31}P\{^{1}H\}$ NMR (C_6D_6) : δ -48.1 (d, $^{3}J_{P\text{-}P}$ = 50.4 Hz) 30.8 (1P, d) ppm).

6.9.5 Preparation of $Me_2PCH_2CH_2PH_2$ (202)

A solution of diethyl 2-(dimethylphosphino)ethylphosphonate (**209**) (22.0 g, 0.10 mol) in dry ether (100 ml) was added dropwise to a suspension of powdered lithium aluminium hydride (14 g, 0.24 mol) in ether (400 ml) while maintaining the temperature of the solution between 0°C and 10°C. The mixture was stirred at room temperature for 48 h, and the solution was filtered under nitrogen. The filtrate was hydrolysed by the succesive addition of deaerated water (5 ml), deaerated aqueous sodium hydroxide solution (10%, 5 ml) and deaerated water (5 ml). The solution was filtered under nitrogen, the ether layer was separated, and the water layer was extracted with ether (2 × 50 ml). The ether layers were combined and were found to contain 2-(dimethylphosphino)ethylphosphine (**202**) by $^{31}P\{^{1}H\}$ NMR spectroscopy. The ether solution was used in subsequent reactions without further purification. The concentration of the ether solution was determined by integration against a known amount of $PhP(O)(OMe)_2$ in the ^{31}P NMR spectrum. The concentration of 2-(dimethylphosphino)ethylphosphine (**202**) in ether was calculated to be 0.24 $mmol.ml^{-1}$ (9.8 g, 0.08 mol, 80%). $^{31}P\{^{1}H\}$ NMR (ether) : δ -49.7 (1P, d, $(CH_3)_2$**P**-), -130.8 (1P, d, -**P**H_2, $^{3}J_{P\text{-}P}$ = 15 Hz, $^{1}J_{P\text{-}H}$ = 180 Hz) ppm (lit.[117] : $^{31}P\{^{1}H\}$ NMR (ether) : δ -49.7 (1P, d,

$(CH_3)_2$**P**-), -130.5 (1P, d, -**P**H_2, $^3J_{P\text{-}P}$ = 15.0 Hz, $^1J_{P\text{-}H}$ = 180 Hz) ppm.

6.9.6 Preparation of $Me_2P(S)CH_2CH_2PH_2$ (228)

A solution of 2-(dimethylphosphino)ethylphosphine (**202**) (7.8 g, 0.064 mol) in ether (400 ml) was added with stirring to a suspension of sulfur powder (3.0 g, 0.094 mol) in ether (100 ml) at room temperature. The solution was stirred for 30 min, filtered, and the ether was removed under reduced pressure to give 2-(dimethylphosphinesulfide)ethylphosphine (**228**) as a white powder (8.7 g, 88%). $^{31}P\{^1H\}$ NMR (C_6D_6) : δ 34.1 (1P, d, $(CH_3)_2$**P**(S)-), -129.7 (1P, d, -**P**H_2, $^3J_{P\text{-}P}$ = 17 Hz, $^1J_{P\text{-}H}$ = 192 Hz) ppm. ^1H NMR (C_6D_6) : δ 1.22 (6H, d, (CH_3)$_2$P(S)-, $^2J_{P\text{-}H}$ = 12.7 Hz), 1.70-1.52 (4H, m, -PCH_2CH_2P-), 2.54 (1H, m, -PH_2), 3.02 (1H, m, PH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6) : δ 38.7 (1C, dd, $(CH_3)_2$P(S)CH_2-, $^1J_{C\text{-}P}$ = 49.2 Hz, $^2J_{C\text{-}P}$ = 4.2 Hz), 21.0 (2C, d, (CH_3)$_2$P(S)-, $^1J_{C\text{-}P}$ = 53.4 Hz), 7.7 (1C, dd, -CH_2PH_2, $^1J_{C\text{-}P}$ = 11.0 Hz, $^2J_{C\text{-}P}$ = 5.1 Hz) ppm.

$^{31}P\{^1H\}$ NMR analysis of the small quantity of ether-insoluble by-product of this reaction showed the formation of $Me_2P(S)CH_2CH_2P(S)H_2$ (**233**). $^{31}P\{^1H\}$ NMR δ 38.0 (1P, d, $(CH_3)_2$**P**(S)-, $^3J_{P\text{-}P}$ = 58 Hz), -12.2 (1P, d, -**P**(S)H_2, $^1J_{P\text{-}H}$ = 453 Hz) ppm.

6.9.7 Preparation of $Me_2P(S)CH_2CH_2PCl_2$ (229) using phosphorus pentachloride (224)

A solution of 2-(dimethylphosphinesulfide)ethylphosphine (**228**) (0.30 g, 1.9 mmol) in toluene (10 ml) was added to a suspension of phosphorus pentachloride (**224**) (0.81 g, 3.9 mmol) in toluene (10 ml) at a rate governed by the evolution of hydrochloric acid. The reaction mixture warmed to 70°C during addition of $Me_2P(S)CH_2CH_2PH_2$ (**228**). The solution

was filtered and the toluene removed under reduced pressure to give 2-(dimethylphosphinesulfide)ethyldichlorophosphine **(229)** as a yellow-green solid (0.22 g, 52%) $^{31}P\{^{1}H\}$ NMR (C_6D_6) : δ 193.2 (1P, d, -**P**Cl_2), 36.2 (1P, d, $(CH_3)_2$**P**(S)-), $^{3}J_{P\text{-}P}$ = 22 Hz) ppm. ^{1}H NMR (C_6D_6) : δ 2.54-2.43 (2H, m, -C**H**$_2$PCl_2), 1.96-1.87 (2H, m, $(CH_3)_2$P(S)C**H**$_2$-), 1.32 (6H, d, (C**H**$_3)_2$P(S)-, $^{2}J_{P\text{-}H}$ = 12.7 Hz) ppm. $^{13}C\{^{1}H\}$ NMR (C_6D_6) : δ 35.4 (1C, dd, $(CH_3)_2$P(S)**C**H_2-, $^{1}J_{C\text{-}P}$ = 49 Hz, $^{2}J_{C\text{-}P}$ = 4 Hz), 27.8 (1C, dd, -**C**H_2PCl_2, $^{1}J_{C\text{-}P}$ = 51 Hz, $^{2}J_{C\text{-}P}$ = 10 Hz), 20.5 (2C, d, (**C**$H_3)_2$P(S)-, $^{1}J_{C\text{-}P}$ = 55 Hz) ppm.

6.9.8 Preparation of $Me_2P(S)CH_2CH_2PCl_2$ (229) using triphosgene (227)

A solution of triphosgene **(227)** (2.6 g, 8.7 mmol) in toluene (50 ml) was added dropwise to a solution of 2-(dimethylphosphinesulfide)ethylphosphine **(228)** (2.0 g, 13 mmol) in toluene (100 ml). The reaction mixture was stirred for 4 h and the solvent was removed under reduced pressure. The residue was washed with hexane (2 × 10 ml) to afford 2-(dimethylphosphinesulfide)ethylphosphinedichloride **(229)** as a white powder (2.0 g, 70 %) with identical NMR data as described previously.

6.9.9 Preparation of $Me_2P(S)CH_2CH_2P(CF_3)_2$ (230)

Trifluoromethyl bromide **(123)** (6.8 g, 46 mmol) was condensed into a flask and allowed to evaporate into a three-necked flask cooled to liquid nitrogen temperature and fitted with a dry-ice condenser. A solution of 2-(dimethylphosphinesulfide)ethyl-dichlorophosphine **(229)** (0.80 g, 3.6 mmol) in dichloromethane (20ml) was added and the reaction mixture was allowed to warm to -60°C. A solution of hexaethylphosphorus triamide **(53)** (3.4 g, 14 mmol) in dichloromethane (20 ml) was added over a period of 1 h while the temperature was maintained between -60°C and -55°C. The reaction mixture was

allowed to warm slowly to room temperature and was stirred overnight. The crude reaction mixture was eluted through flash silica with dichloromethane, to give 2-(dimethylphosphinesulfide)ethyl(bis(trifluoromethyl))phosphine (**230**) as a white, air-stable powder (0.19 g, 20%). $^{31}P\{^{1}H\}$ NMR ($CDCl_3$) : δ 37.9 (1P, d, $(CH_3)_2$**P**(S)-), $^{3}J_{P\text{-}P}$ = 46 Hz), 1.6 (1P, dsept, **P**$(CF_3)_2$, $^{3}J_{P\text{-}P}$ = 46 Hz, $^{2}J_{P\text{-}F}$ = 70 Hz) ppm. ^{1}H NMR ($CDCl_3$) : δ 2.45 (2H, m, -**C**$\mathbf{H}_2$P$(CF_3)_2$), 2.10 (2H, m, $(CH_3)_2$P(S)**C**$\mathbf{H}_2$-), 1.83 (6H, d, $(\mathbf{C}H_3)_2$P(S)-, $^{2}J_{P\text{-}H}$ = 12.9 Hz) ppm. ^{19}F NMR ($CDCl_3$) : δ -50.8 (6F, d, -P$(\mathbf{C}F_3)_2$, $^{2}J_{F\text{-}P}$ = 70 Hz) ppm. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) : δ 129.4 (2C, dq, -P$(\mathbf{C}F_3)_2$, $^{1}J_{C\text{-}F}$ = 319 Hz, $^{2}J_{C\text{-}P}$ = 30 Hz), 29.7 (1C, dd, $(CH_3)_2$P(S)**C**H_2-, $^{1}J_{C\text{-}P}$ = 51 Hz, $^{2}J_{C\text{-}P}$ = 17 Hz), 21.5 (2C, d, $(\mathbf{C}H_3)_2$P(S)-, $^{1}J_{C\text{-}P}$ = 55 Hz), 13.3 (1C, dd, -**C**H_2P$(CF_3)_2$, $^{1}J_{C\text{-}P}$ = 1 Hz, $^{2}J_{C\text{-}P}$ = 17 Hz) ppm. M.p. 58-60°C. Mass Spectrum (CI) *m/e* 221(100), 189(7), 171(55), 152(19), 93(40), 69(17), 32(38).

6.9.10 Preparation of $Me_2PCH_2CH_2P(CF_3)_2$ (222) (bife)

2-(Dimethylphosphinesulfide)ethyl(bis(trifluoromethyl))phosphine, $Me_2P(S)CH_2CH_2P(CF_3)_2$ (**230**) (100 mg, 0.4 mmol) and tri(*n*-butyl)phosphine (0.5 ml, 2.0 mmol) were added to an NMR tube fitted with a concentric teflon valve. The sample was heated at 200°C for 1 h, allowed to cool, and all volatiles were condensed from the reaction vessel at 5×10^{-5} Torr while the reaction mixture was heated at 70°C. Analysis of the volatile component of the sample showed the presence of 2-(dimethylphosphino)ethyl-(bis(trifluoromethyl))phosphine, $Me_2PCH_2CH_2P(CF_3)_2$ (**222**). $^{31}P\{^{1}H\}$ NMR (C_6D_6) : δ 2.1 (1P, dsep, **P**$(CF_3)_2$, $^{3}J_{P\text{-}P}$ = 38 Hz, $^{2}J_{P\text{-}F}$ = 68 Hz), -46.8 (1P, d, $(CH_3)_2$**P**-), $^{3}J_{P\text{-}P}$ = 38 Hz) ppm. ^{1}H NMR ($CDCl_3$) : δ 2.04 (2H, m, -**C**$\mathbf{H}_2$P$(CF_3)_2$), 1.33 (2H, m, $(CH_3)_2$PC$\mathbf{H}_2$-), 0.84 (6H, d, $(\mathbf{C}H_3)_2$P(S)-, $^{2}J_{P\text{-}H}$ = 2.9 Hz) ppm. ^{19}F NMR ($CDCl_3$) : δ -50.8 (6F, d, -P$(\mathbf{C}F_3)_2$, $^{2}J_{F\text{-}P}$ = 67 Hz) ppm.

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APPENDIX A1

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132. Spectra were run at 30 min intervals using the automatic program **timecourse** and the pulse program **tcourse_mpw**. Parameters and program lists are given in Appendix A1.

NMR spectra were recorded on an Bruker AMX400 spectrometer. The following pulse program and automatic programs are provided in standard format for use with UXNMR acquisition software. Relevant parameters are given in comment statements.

Automatic program "**timecourse**"

```
/* (Program sufficient for a kinetic series where all acquisitions have identical parameter sets)
*/

getdataset
times(160)                              /* vary as required : delays between
                                * experiments can best be handled at a pulse
                        * program level */

        zg
        iexpno

end
quit
```

Pulse program "**tcourse_MPW**"

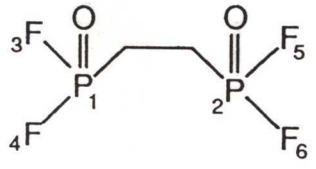
```
; timecourse program for running identical spectra at intervals
; with decoupling of specified heteronucleus
;
; NOTE: do not specify CPD in decstat, it is turned on and off
; automatically here.

10 ze
20 d1 hl1 cpd                   ; d1   delay between scans
     (p1 ph1) :t
30 go=20 ph2
40 wr #0
d2                              ; d2   delay between spectra
    do
50 exit

ph1=0 0 1 1 2 2 3 3
ph2=0 0 1 1 2 2 3 3
```

APPENDIX A2

The values and signs of the coupling constants used to simulate the spectrum of $F_2P(O)CH_2CH_2P(O)F_2$ (**121**) in reference 81 are tabulated below.

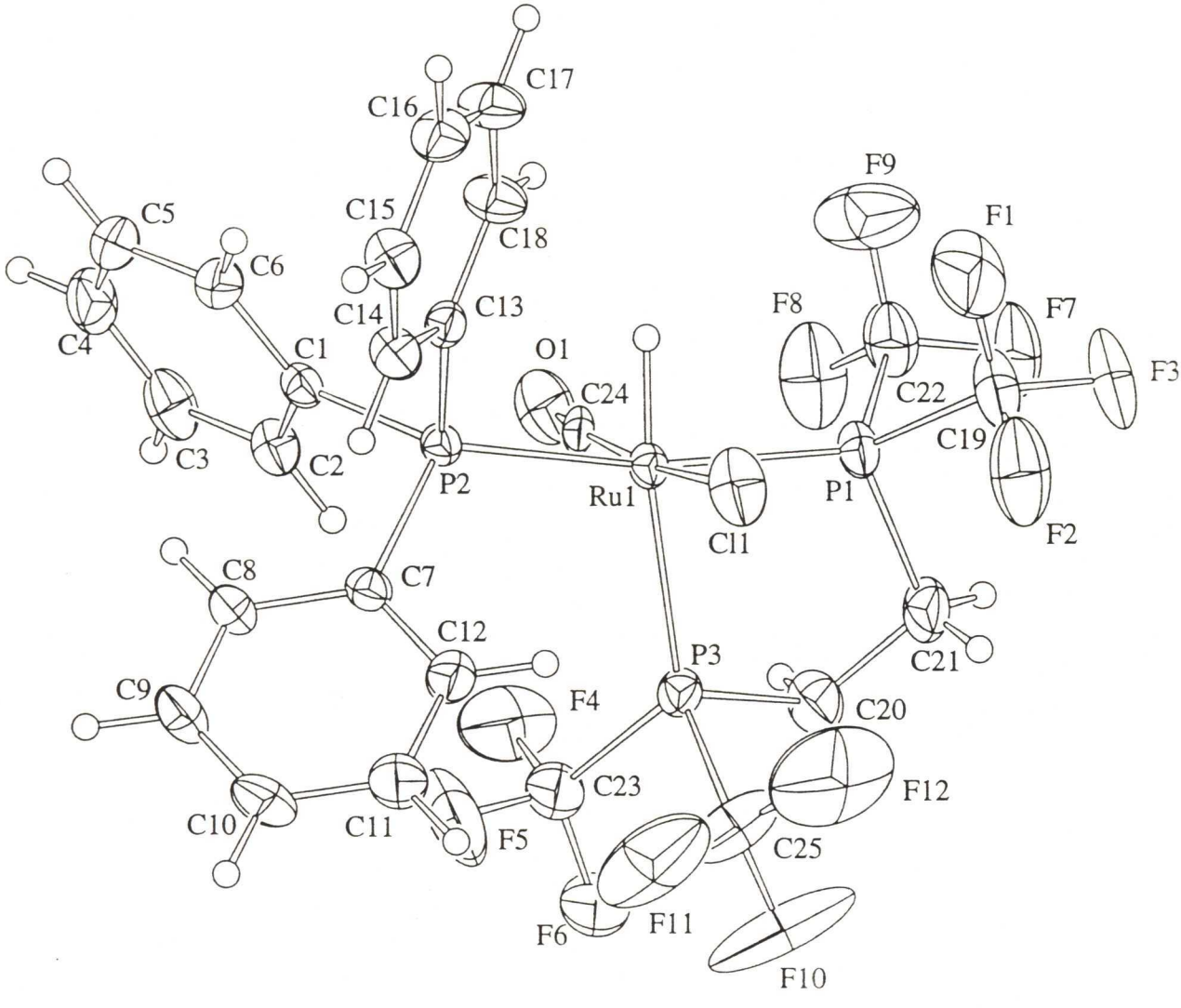


Coupling constants used to simulate $F_2P(O)CH_2CH_2P(O)F_2$ (**121**)

J(1,2)	96.2	J(2,6)	-1129.8
J(1,3)	-1129.8	J(3,4)	0
J(1,4)	-1129.8	J(3,5)	0
J(1,5)	3.8	J(3,6)	0
J(1,6)	3.8	J(4,5)	0
J(2,3)	3.8	J(4,6)	0
J(2,4)	3.8	J(5,6)	0
J(2,5)	-1129.8		

APPENDIX A3

RuHCl(CO)(PPh_3)(dfmpe) **(155)**



Crystal data for $RuHCl(CO)(PPh_3)(dfmpe)$ (**155**) (LDF50)

Empirical formula :	$RuC_{25}H_{20}P_3OF_{12}Cl$	Formula weight	739.86
Crystal system	monoclinic	space group	$P2_1/c$
a	11.917(4)	α	90
b	14.631(9)	β	107.72(2)
c	17.744(5)	γ	90
V	2946.9	Z	4
D_{calc}	1.79	D_{obs}	-
F(000)	1568,00	μ	8.82 cm^{-1}
T	21°C	λ	0.71069
crystal habit	prism	crystal dimensions	$0.08 \times 0.32 \times 0.42$
crystal faces	**2**10, 2**1**0, **12**0, 120, 0**1**5, 10**5**	crystal colour	colourless
data collection range	$1 < \theta < 25$	% decomposition	2.74
scan width	$1.55 - 0.35\theta$	counter aperture	1.90 + 1.05
scan type	$\omega - \theta/3$	range of *hkl*	(-14,14), (0,17), (0,21)
data collected	5579	data after merging	5454
R_{merg}	0.02	maximum transmittance	0.992
absorption correction?	ANALYTICAL	total variables	388
minimum transmittance	0.973	R_w	0.0480
data with $I>2.5\sigma(I)$	4310	extinction correction	-
R	0.0417	max/min peaks	0.76, -0.71
maximum shift/esd	0.001	solution program	SHELXS
solution method	DIRECT	Disorder	In CF3 peaks. Also Cl_1 and $C_{24}=O_1$ appear to exchange positions. Hence very short C=O bond (0.88A) and very long Ru-Cl bond (2.42A)
treatment of H atoms	H1 refined others calc. groups		

Positional parameters

atom	x	y	z
Ru(1)	0.684553(30)	0.192581(24)	0.296832(21)
Cl(1)	0.58655(14)	0.32784(11)	0.22927(11)
P(1)	0.50906(11)	0.139404(89)	0.305163(83)
P(2)	0.863238(97)	0.271787(78)	0.303306(67)
P(3)	0.63419(10)	0.101864(86)	0.181550(75)
F(1)	0.42210(40)	0.28511(31)	0.35678(34)
F(2)	0.34977(34)	0.26303(31)	0.23441(32)
F(3)	0.29327(30)	0.18116(27)	0.31204(28)
F(4)	0.79895(46)	-0.02214(34)	0.22029(28)
F(5)	0.81973(41)	0.06987(35)	0.13479(37)
F(6)	0.69544(34)	-0.03834(27)	0.10315(24)
F(7)	0.40206(32)	0.03624(28)	0.38880(25)
F(8)	0.57646(36)	0.00205(31)	0.40257(29)
F(9)	0.53905(49)	0.12043(37)	0.45826(25)
F(10)	0.51128(64)	0.08256(34)	0.02865(27)
F(11)	0.62179(63)	0.19034(54)	0.04808(27)
F(12)	0.47677(68)	0.19905(51)	0.08139(37)
O(1)	0.80460(44)	0.04424(32)	0.39414(31)
C(1)	0.99876(38)	0.22436(31)	0.36989(26)
C(2)	1.02357(42)	0.13214(34)	0.36438(31)
C(3)	1.12636(52)	0.09572(41)	0.41384(39)
C(4)	1.20484(49)	0.14888(51)	0.46902(36)
C(5)	1.18282(46)	0.23840(49)	0.47334(33)
C(6)	1.08037(44)	0.27693(37)	0.42459(30)
C(7)	0.90250(39)	0.28918(30)	0.21281(26)
C(8)	1.01786(42)	0.28977(33)	0.21239(28)
C(9)	1.04513(49)	0.31117(39)	0.14417(34)
C(10)	0.95738(57)	0.32967(42)	0.07563(33)
C(11)	0.84291(52)	0.32942(46)	0.07519(31)
C(12)	0.81505(45)	0.30924(40)	0.14315(30)
C(13)	0.86297(36)	0.38921(30)	0.33933(26)
C(14)	0.89344(43)	0.46196(33)	0.30122(30)
C(15)	0.89944(46)	0.54945(33)	0.33174(34)
C(16)	0.87429(48)	0.56494(34)	0.40009(33)
C(17)	0.84199(54)	0.49410(41)	0.43792(32)
C(18)	0.83562(50)	0.40596(35)	0.40831(30)
C(19)	0.38766(54)	0.22175(46)	0.30287(52)
C(20)	0.52389(51)	0.01818(42)	0.19082(39)
C(21)	0.43566(46)	0.06177(40)	0.22385(37)
C(22)	0.50563(56)	0.07269(49)	0.39450(43)
C(23)	0.74083(56)	0.02182(47)	0.15839(42)
C(24)	0.76618(45)	0.08740(52)	0.36171(32)
C(25)	0.56100(85)	0.14188(49)	0.07801(46)
H(1)	0.701	0.228	0.366
H(2)	0.968	0.094	0.326
H(3)	1.143	0.031	0.408
H(4)	1.275	0.122	0.505
H(5)	1.239	0.277	0.511
H(6)	1.066	0.342	0.428
H(8)	1.080	0.275	0.260

Positional parameters

atom	x	y	z
H(9)	1.127	0.313	0.145
H(10)	0.977	0.343	0.028
H(11)	0.781	0.343	0.027
H(12)	0.734	0.309	0.142
H(14)	0.911	0.452	0.252
H(15)	0.923	0.600	0.305
H(16)	0.879	0.626	0.422
H(17)	0.823	0.506	0.486
H(18)	0.812	0.356	0.436
H(20B)	0.484	-0.007	0.140
H(20A)	0.564	-0.031	0.227
H(21A)	0.395	0.015	0.244
H(21B)	0.380	0.096	0.183

Positional parameters and B(eq)

atom	x	y	z	B(eq)
Ru(1)	0.684553(30)	0.192581(24)	0.296832(21)	2.63(1)
Cl(1)	0.58655(14)	0.32784(11)	0.22927(11)	6.29(8)
P(1)	0.50906(11)	0.139404(89)	0.305163(83)	3.53(5)
P(2)	0.863238(97)	0.271787(78)	0.303306(67)	2.58(4)
P(3)	0.63419(10)	0.101864(86)	0.181550(75)	3.23(5)
F(1)	0.42210(40)	0.28511(31)	0.35678(34)	10.4(3)
F(2)	0.34977(34)	0.26303(31)	0.23441(32)	9.3(3)
F(3)	0.29327(30)	0.18116(27)	0.31204(28)	8.4(2)
F(4)	0.79895(46)	-0.02214(34)	0.22029(28)	11.2(3)
F(5)	0.81973(41)	0.06987(35)	0.13479(37)	12.1(3)
F(6)	0.69544(34)	-0.03834(27)	0.10315(24)	8.1(2)
F(7)	0.40206(32)	0.03624(28)	0.38880(25)	8.2(2)
F(8)	0.57646(36)	0.00205(31)	0.40257(29)	9.3(2)
F(9)	0.53905(49)	0.12043(37)	0.45826(25)	11.2(3)
F(10)	0.51128(64)	0.08256(34)	0.02865(27)	16.1(4)
F(11)	0.62179(63)	0.19034(54)	0.04808(27)	15.2(4)
F(12)	0.47677(68)	0.19905(51)	0.08139(37)	16.7(5)
O(1)	0.80460(44)	0.04424(32)	0.39414(31)	6.0(3)
C(1)	0.99876(38)	0.22436(31)	0.36989(26)	2.9(2)
C(2)	1.02357(42)	0.13214(34)	0.36438(31)	3.8(2)
C(3)	1.12636(52)	0.09572(41)	0.41384(39)	5.2(3)
C(4)	1.20484(49)	0.14888(51)	0.46902(36)	5.5(3)
C(5)	1.18282(46)	0.23840(49)	0.47334(33)	5.2(3)
C(6)	1.08037(44)	0.27693(37)	0.42459(30)	4.1(2)
C(7)	0.90250(39)	0.28918(30)	0.21281(26)	2.9(2)
C(8)	1.01786(42)	0.28977(33)	0.21239(28)	3.5(2)
C(9)	1.04513(49)	0.31117(39)	0.14417(34)	4.6(2)
C(10)	0.95738(57)	0.32967(42)	0.07563(33)	5.2(3)
C(11)	0.84291(52)	0.32942(46)	0.07519(31)	5.4(3)
C(12)	0.81505(45)	0.30924(40)	0.14315(30)	4.4(2)
C(13)	0.86297(36)	0.38921(30)	0.33933(26)	2.9(2)
C(14)	0.89344(43)	0.46196(33)	0.30122(30)	3.7(2)
C(15)	0.89944(46)	0.54945(33)	0.33174(34)	4.2(2)
C(16)	0.87429(48)	0.56494(34)	0.40009(33)	4.3(2)
C(17)	0.84199(54)	0.49410(41)	0.43792(32)	5.1(3)
C(18)	0.83562(50)	0.40596(35)	0.40831(30)	4.3(2)
C(19)	0.38766(54)	0.22175(46)	0.30287(52)	6.2(3)
C(20)	0.52389(51)	0.01818(42)	0.19082(39)	5.8(3)
C(21)	0.43566(46)	0.06177(40)	0.22385(37)	5.3(3)
C(22)	0.50563(56)	0.07269(49)	0.39450(43)	5.9(3)
C(23)	0.74083(56)	0.02182(47)	0.15839(42)	5.8(3)
C(24)	0.76618(45)	0.08740(52)	0.36171(32)	4.2(3)
C(25)	0.56100(85)	0.14188(49)	0.07801(46)	7.8(4)
H(1)	0.701	0.228	0.366	5.0
H(2)	0.968	0.094	0.326	4.5
H(3)	1.143	0.031	0.408	6.2
H(4)	1.275	0.122	0.505	6.7
H(5)	1.239	0.277	0.511	6.3
H(6)	1.066	0.342	0.428	4.9
H(8)	1.080	0.275	0.260	4.2

Positional parameters and B(eq)

atom	x	y	z	B(eq)
H(9)	1.127	0.313	0.145	5.5
H(10)	0.977	0.343	0.028	6.2
H(11)	0.781	0.343	0.027	6.5
H(12)	0.734	0.309	0.142	5.3
H(14)	0.911	0.452	0.252	4.5
H(15)	0.923	0.600	0.305	5.1
H(16)	0.879	0.626	0.422	5.1
H(17)	0.823	0.506	0.486	6.1
H(18)	0.812	0.356	0.436	5.1
H(20B)	0.484	-0.007	0.140	6.9
H(20A)	0.564	-0.031	0.227	6.9
H(21A)	0.395	0.015	0.244	6.2
H(21B)	0.380	0.096	0.183	6.2

U values

atom	U11	U22	U33	U12	U13
Ru(1)	0.02921(20)	0.03102(21)	0.04130(22)	-0.00257(15)	0.01305(16)
Cl(1)	0.06341(97)	0.0694(10)	0.1123(14)	0.00494(79)	0.03553(96)
P(1)	0.03328(64)	0.04062(73)	0.06480(87)	-0.00330(55)	0.02168(61)
P(2)	0.03119(60)	0.03295(62)	0.03601(63)	-0.00352(48)	0.01360(50)
P(3)	0.03520(65)	0.03882(69)	0.04721(74)	-0.00322(53)	0.01055(56)
F(1)	0.1011(34)	0.1014(34)	0.2002(54)	0.0182(27)	0.0594(35)
F(2)	0.0682(26)	0.1089(35)	0.1797(47)	0.0330(25)	0.0425(29)
F(3)	0.0530(21)	0.1014(30)	0.1871(45)	0.0113(20)	0.0707(26)
F(4)	0.1545(45)	0.1319(42)	0.1113(36)	0.0965(37)	0.0010(33)
F(5)	0.1047(34)	0.1397(43)	0.2616(65)	-0.0434(32)	0.1273(42)
F(6)	0.0927(28)	0.0951(29)	0.1223(33)	-0.0041(23)	0.0376(25)
F(7)	0.0683(23)	0.1165(33)	0.1418(36)	-0.0190(23)	0.0539(24)
F(8)	0.0839(28)	0.1053(34)	0.1672(44)	0.0200(26)	0.0420(29)
F(9)	0.2041(56)	0.1567(47)	0.0753(30)	-0.0878(44)	0.0600(33)
F(10)	0.3271(84)	0.0920(36)	0.0889(34)	-0.0394(46)	-0.0929(44)
F(11)	0.2182(70)	0.2573(77)	0.0673(31)	-0.1290(64)	-0.0076(35)
F(12)	0.2302(77)	0.2022(69)	0.1362(51)	0.1188(63)	-0.0400(50)
O(1)	0.0756(36)	0.0672(32)	0.1008(42)	-0.0124(25)	0.0481(31)
C(1)	0.0338(24)	0.0430(26)	0.0369(25)	-0.0004(20)	0.0175(20)
C(2)	0.0448(28)	0.0428(29)	0.0618(33)	0.0014(23)	0.0225(25)
C(3)	0.0580(36)	0.0599(37)	0.0890(45)	0.0218(30)	0.0373(34)
C(4)	0.0440(33)	0.1016(53)	0.0637(39)	0.0242(35)	0.0149(29)
C(5)	0.0386(29)	0.1017(50)	0.0510(34)	0.0079(32)	0.0037(25)
C(6)	0.0418(29)	0.0598(34)	0.0509(31)	0.0028(25)	0.0109(24)
C(7)	0.0410(26)	0.0349(25)	0.0390(25)	-0.0053(20)	0.0180(21)
C(8)	0.0440(28)	0.0498(31)	0.0462(28)	0.0059(23)	0.0229(23)
C(9)	0.0566(34)	0.0709(38)	0.0609(35)	0.0105(30)	0.0361(29)
C(10)	0.0831(44)	0.0776(43)	0.0501(34)	0.0057(34)	0.0403(33)
C(11)	0.0613(37)	0.1041(51)	0.0407(31)	0.0031(34)	0.0160(28)
C(12)	0.0446(29)	0.0772(39)	0.0456(30)	-0.0103(28)	0.0130(24)
C(13)	0.0299(23)	0.0371(25)	0.0416(26)	-0.0028(20)	0.0094(20)
C(14)	0.0508(30)	0.0378(27)	0.0589(32)	-0.0058(23)	0.0254(25)
C(15)	0.0583(33)	0.0328(27)	0.0750(38)	-0.0081(24)	0.0293(29)
C(16)	0.0613(34)	0.0366(28)	0.0622(35)	-0.0026(25)	0.0150(28)
C(17)	0.0869(43)	0.0590(37)	0.0539(34)	-0.0058(32)	0.0283(31)
C(18)	0.0774(38)	0.0409(29)	0.0514(31)	-0.0051(27)	0.0304(29)

U values

atom	U11	U22	U33	U12	U13
C(19)	0.0464(36)	0.0649(42)	0.1340(67)	0.0004(31)	0.0443(41)
C(20)	0.0643(38)	0.0646(39)	0.1027(49)	-0.0320(31)	0.0423(36)
C(21)	0.0419(30)	0.0678(39)	0.0934(45)	-0.0188(28)	0.0259(30)
C(22)	0.0578(38)	0.0813(48)	0.0916(51)	-0.0071(36)	0.0339(37)
C(23)	0.0639(40)	0.0737(44)	0.0832(46)	-0.0005(35)	0.0256(36)
C(24)	0.0201(26)	0.1059(58)	0.0343(30)	-0.0109(30)	0.0086(22)
C(25)	0.1205(67)	0.0574(43)	0.0793(53)	-0.0113(46)	-0.0307(48)

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	atom	atom	distance
Ru(1)	Cl(1)	2.424(2)	F(10)	C(25)	1.246(7)
Ru(1)	P(1)	2.278(1)	F(11)	C(25)	1.24(1)
Ru(1)	P(2)	2.396(1)	F(12)	C(25)	1.32(1)
Ru(1)	P(3)	2.355(1)	O(1)	C(24)	0.884(6)
Ru(1)	C(24)	1.991(7)	C(1)	C(2)	1.391(6)
P(1)	C(19)	1.874(6)	C(1)	C(6)	1.379(6)
P(1)	C(21)	1.834(6)	C(2)	C(3)	1.379(7)
P(1)	C(22)	1.875(7)	C(3)	C(4)	1.370(8)
P(2)	C(1)	1.824(5)	C(4)	C(5)	1.342(9)
P(2)	C(7)	1.823(4)	C(5)	C(6)	1.384(7)
P(2)	C(13)	1.832(5)	C(7)	C(8)	1.377(6)
P(3)	C(20)	1.840(6)	C(7)	C(12)	1.385(6)
P(3)	C(23)	1.863(6)	C(8)	C(9)	1.382(7)
P(3)	C(25)	1.873(7)	C(9)	C(10)	1.369(8)
F(1)	C(19)	1.304(8)	C(10)	C(11)	1.362(8)
F(2)	C(19)	1.309(8)	C(11)	C(12)	1.378(7)
F(3)	C(19)	1.325(7)	C(13)	C(14)	1.369(6)
F(4)	C(23)	1.281(8)	C(13)	C(18)	1.381(6)
F(5)	C(23)	1.340(8)	C(14)	C(15)	1.382(7)
F(6)	C(23)	1.304(6)	C(15)	C(16)	1.354(7)
F(7)	C(22)	1.320(7)	C(16)	C(17)	1.354(7)
F(8)	C(22)	1.315(7)	C(17)	C(18)	1.385(7)
F(9)	C(22)	1.284(8)	C(20)	C(21)	1.493(8)

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Ru(1)	P(1)	89.88(5)	C(20)	P(3)	C(25)	99.5(4)
Cl(1)	Ru(1)	P(2)	85.17(5)	C(23)	P(3)	C(25)	97.3(4)
Cl(1)	Ru(1)	P(3)	94.16(6)	P(2)	C(1)	C(2)	119.3(4)
Cl(1)	Ru(1)	C(24)	174.7(2)	P(2)	C(1)	C(6)	122.6(4)
P(1)	Ru(1)	P(2)	169.15(5)	C(2)	C(1)	C(6)	118.0(4)
P(1)	Ru(1)	P(3)	82.42(5)	C(1)	C(2)	C(3)	119.9(5)
P(1)	Ru(1)	C(24)	89.7(2)	C(2)	C(3)	C(4)	121.1(5)
P(2)	Ru(1)	P(3)	107.52(4)	C(3)	C(4)	C(5)	119.4(5)
P(2)	Ru(1)	C(24)	94.4(2)	C(4)	C(5)	C(6)	120.9(6)
P(3)	Ru(1)	C(24)	91.0(2)	C(1)	C(6)	C(5)	120.8(5)
Ru(1)	P(1)	C(19)	119.8(2)	P(2)	C(7)	C(8)	122.0(4)
Ru(1)	P(1)	C(21)	112.8(2)	P(2)	C(7)	C(12)	119.4(4)
Ru(1)	P(1)	C(22)	119.4(2)	C(8)	C(7)	C(12)	118.4(4)
C(19)	P(1)	C(21)	101.5(3)	C(7)	C(8)	C(9)	120.5(5)
C(19)	P(1)	C(22)	98.0(3)	C(8)	C(9)	C(10)	120.3(5)
C(21)	P(1)	C(22)	102.4(3)	C(9)	C(10)	C(11)	119.9(5)
Ru(1)	P(2)	C(1)	116.4(1)	C(10)	C(11)	C(12)	120.2(5)
Ru(1)	P(2)	C(7)	119.3(1)	C(7)	C(12)	C(11)	120.7(5)
Ru(1)	P(2)	C(13)	112.0(1)	P(2)	C(13)	C(14)	121.9(3)
C(1)	P(2)	C(7)	102.2(2)	P(2)	C(13)	C(18)	120.0(4)
C(1)	P(2)	C(13)	103.1(2)	C(14)	C(13)	C(18)	118.1(4)
C(7)	P(2)	C(13)	101.7(2)	C(13)	C(14)	C(15)	121.1(5)
Ru(1)	P(3)	C(20)	107.2(2)	C(14)	C(15)	C(16)	120.3(5)
Ru(1)	P(3)	C(23)	122.3(2)	C(15)	C(16)	C(17)	119.4(5)
Ru(1)	P(3)	C(25)	126.5(2)	C(16)	C(17)	C(18)	121.1(5)
C(20)	P(3)	C(23)	98.9(3)	C(13)	C(18)	C(17)	120.0(5)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
P(1)	C(19)	F(1)	111.8(5)	F(11)	C(25)	F(12)	102.0(7)
P(1)	C(19)	F(2)	111.3(5)				
P(1)	C(19)	F(3)	112.8(5)				
F(1)	C(19)	F(2)	107.1(6)				
F(1)	C(19)	F(3)	108.5(6)				
F(2)	C(19)	F(3)	104.8(6)				
P(3)	C(20)	C(21)	111.0(4)				
P(1)	C(21)	C(20)	110.4(4)				
P(1)	C(22)	F(7)	114.0(5)				
P(1)	C(22)	F(8)	108.9(5)				
P(1)	C(22)	F(9)	112.4(5)				
F(7)	C(22)	F(8)	104.2(5)				
F(7)	C(22)	F(9)	108.6(6)				
F(8)	C(22)	F(9)	108.3(6)				
P(3)	C(23)	F(4)	110.8(5)				
P(3)	C(23)	F(5)	109.2(5)				
P(3)	C(23)	F(6)	115.7(4)				
F(4)	C(23)	F(5)	106.6(6)				
F(4)	C(23)	F(6)	107.3(6)				
F(5)	C(23)	F(6)	106.8(6)				
Ru(1)	C(24)	O(1)	174.8(8)				
P(3)	C(25)	F(10)	116.8(5)				
P(3)	C(25)	F(11)	116.2(6)				
P(3)	C(25)	F(12)	106.7(7)				
F(10)	C(25)	F(11)	108.1(9)				
F(10)	C(25)	F(12)	105.5(8)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Torsion or Conformation Angles

(1)	(2)	(3)	(4)	angle
Ru(1)	P(1)	C(19)	F(1)	-54.3(7)
Ru(1)	P(1)	C(19)	F(2)	65.5(6)
Ru(1)	P(1)	C(19)	F(3)	-177.0(4)
Ru(1)	P(1)	C(21)	C(20)	24.8(5)
Ru(1)	P(1)	C(22)	F(7)	-172.4(4)
Ru(1)	P(1)	C(22)	F(8)	-56.5(6)
Ru(1)	P(1)	C(22)	F(9)	63.5(6)
Ru(1)	P(2)	C(1)	C(2)	51.5(4)
Ru(1)	P(2)	C(1)	C(6)	-130.4(4)
Ru(1)	P(2)	C(7)	C(8)	-146.6(3)
Ru(1)	P(2)	C(7)	C(12)	38.3(5)
Ru(1)	P(2)	C(13)	C(14)	-131.4(4)
Ru(1)	P(2)	C(13)	C(18)	51.0(4)
Ru(1)	P(3)	C(20)	C(21)	42.0(5)
Ru(1)	P(3)	C(23)	F(4)	42.9(6)
Ru(1)	P(3)	C(23)	F(5)	-74.2(6)
Ru(1)	P(3)	C(23)	F(6)	165.3(4)
Ru(1)	P(3)	C(25)	F(10)	-159.9(7)
Ru(1)	P(3)	C(25)	F(11)	71(1)
Ru(1)	P(3)	C(25)	F(12)	-42.3(9)
Cl(1)	Ru(1)	P(1)	C(19)	-24.8(3)
Cl(1)	Ru(1)	P(1)	C(21)	94.6(2)
Cl(1)	Ru(1)	P(1)	C(22)	-145.2(3)
Cl(1)	Ru(1)	P(2)	C(1)	166.7(2)
Cl(1)	Ru(1)	P(2)	C(7)	-70.1(2)
Cl(1)	Ru(1)	P(2)	C(13)	48.4(2)
Cl(1)	Ru(1)	P(3)	C(20)	-109.4(2)
Cl(1)	Ru(1)	P(3)	C(23)	137.7(3)
Cl(1)	Ru(1)	P(3)	C(25)	6.9(4)
Cl(1)	Ru(1)	C(24)	O(1)	-19(9)
P(1)	Ru(1)	P(2)	C(1)	103.6(3)
P(1)	Ru(1)	P(2)	C(7)	-133.2(3)
P(1)	Ru(1)	P(2)	C(13)	-14.7(3)
P(1)	Ru(1)	P(3)	C(20)	-20.1(2)
P(1)	Ru(1)	P(3)	C(23)	-133.0(3)
P(1)	Ru(1)	P(3)	C(25)	96.3(4)
P(1)	Ru(1)	C(24)	O(1)	-104(8)
P(1)	C(21)	C(20)	P(3)	-42.2(6)
P(2)	Ru(1)	P(1)	C(19)	37.9(4)
P(2)	Ru(1)	P(1)	C(21)	157.3(3)
P(2)	Ru(1)	P(1)	C(22)	-82.5(4)
P(2)	Ru(1)	P(3)	C(20)	164.3(2)
P(2)	Ru(1)	P(3)	C(23)	51.5(3)
P(2)	Ru(1)	P(3)	C(25)	-79.3(4)
P(2)	Ru(1)	C(24)	O(1)	66(8)
P(2)	C(1)	C(2)	C(3)	179.3(4)
P(2)	C(1)	C(6)	C(5)	-179.2(4)
P(2)	C(7)	C(8)	C(9)	-174.2(4)
P(2)	C(7)	C(12)	C(11)	175.1(5)
P(2)	C(13)	C(14)	C(15)	-176.2(4)
P(2)	C(13)	C(18)	C(17)	176.3(4)
P(3)	Ru(1)	P(1)	C(19)	-119.0(3)

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Torsion or Conformation Angles cont

(1)	(2)	(3)	(4)	angle
P(3)	Ru(1)	P(1)	C(21)	0.4(2)
P(3)	Ru(1)	P(1)	C(22)	120.6(3)
P(3)	Ru(1)	P(2)	C(1)	-100.5(2)
P(3)	Ru(1)	P(2)	C(7)	22.8(2)
P(3)	Ru(1)	P(2)	C(13)	141.2(2)
P(3)	Ru(1)	C(24)	O(1)	173(8)
F(1)	C(19)	P(1)	C(21)	-179.3(5)
F(1)	C(19)	P(1)	C(22)	76.3(6)
F(2)	C(19)	P(1)	C(21)	-59.4(5)
F(2)	C(19)	P(1)	C(22)	-163.9(5)
F(3)	C(19)	P(1)	C(21)	58.1(6)
F(3)	C(19)	P(1)	C(22)	-46.4(6)
F(4)	C(23)	P(3)	C(20)	-74.1(6)
F(4)	C(23)	P(3)	C(25)	-175.0(5)
F(5)	C(23)	P(3)	C(20)	168.8(5)
F(5)	C(23)	P(3)	C(25)	67.9(6)
F(6)	C(23)	P(3)	C(20)	48.3(6)
F(6)	C(23)	P(3)	C(25)	-52.6(6)
F(7)	C(22)	P(1)	C(19)	56.7(6)
F(7)	C(22)	P(1)	C(21)	-47.0(6)
F(8)	C(22)	P(1)	C(19)	172.6(5)
F(8)	C(22)	P(1)	C(21)	68.9(5)
F(9)	C(22)	P(1)	C(19)	-67.4(6)
F(9)	C(22)	P(1)	C(21)	-171.1(5)
F(10)	C(25)	P(3)	C(20)	-40(1)
F(10)	C(25)	P(3)	C(23)	60.3(9)
F(11)	C(25)	P(3)	C(20)	-169.5(8)
F(11)	C(25)	P(3)	C(23)	-69.2(9)
F(12)	C(25)	P(3)	C(20)	77.6(7)
F(12)	C(25)	P(3)	C(23)	178.0(7)
C(1)	P(2)	Ru(1)	C(24)	-8.0(2)
C(1)	P(2)	C(7)	C(8)	-16.6(4)
C(1)	P(2)	C(7)	C(12)	168.3(4)
C(1)	P(2)	C(13)	C(14)	102.7(4)
C(1)	P(2)	C(13)	C(18)	-74.9(4)
C(1)	C(2)	C(3)	C(4)	0.4(8)
C(1)	C(6)	C(5)	C(4)	-0.5(9)
C(2)	C(1)	P(2)	C(7)	-80.2(4)
C(2)	C(1)	P(2)	C(13)	174.5(4)
C(2)	C(1)	C(6)	C(5)	-1.1(7)
C(2)	C(3)	C(4)	C(5)	-2.0(9)
C(3)	C(2)	C(1)	C(6)	1.1(7)
C(3)	C(4)	C(5)	C(6)	2.0(9)
C(6)	C(1)	P(2)	C(7)	97.9(4)
C(6)	C(1)	P(2)	C(13)	-7.4(4)
C(7)	P(2)	Ru(1)	C(24)	115.2(2)
C(7)	P(2)	C(13)	C(14)	-2.9(4)
C(7)	P(2)	C(13)	C(18)	179.5(4)
C(7)	C(8)	C(9)	C(10)	-1.7(8)
C(7)	C(12)	C(11)	C(10)	0(1)
C(8)	C(7)	P(2)	C(13)	89.7(4)
C(8)	C(7)	C(12)	C(11)	-0.1(8)

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

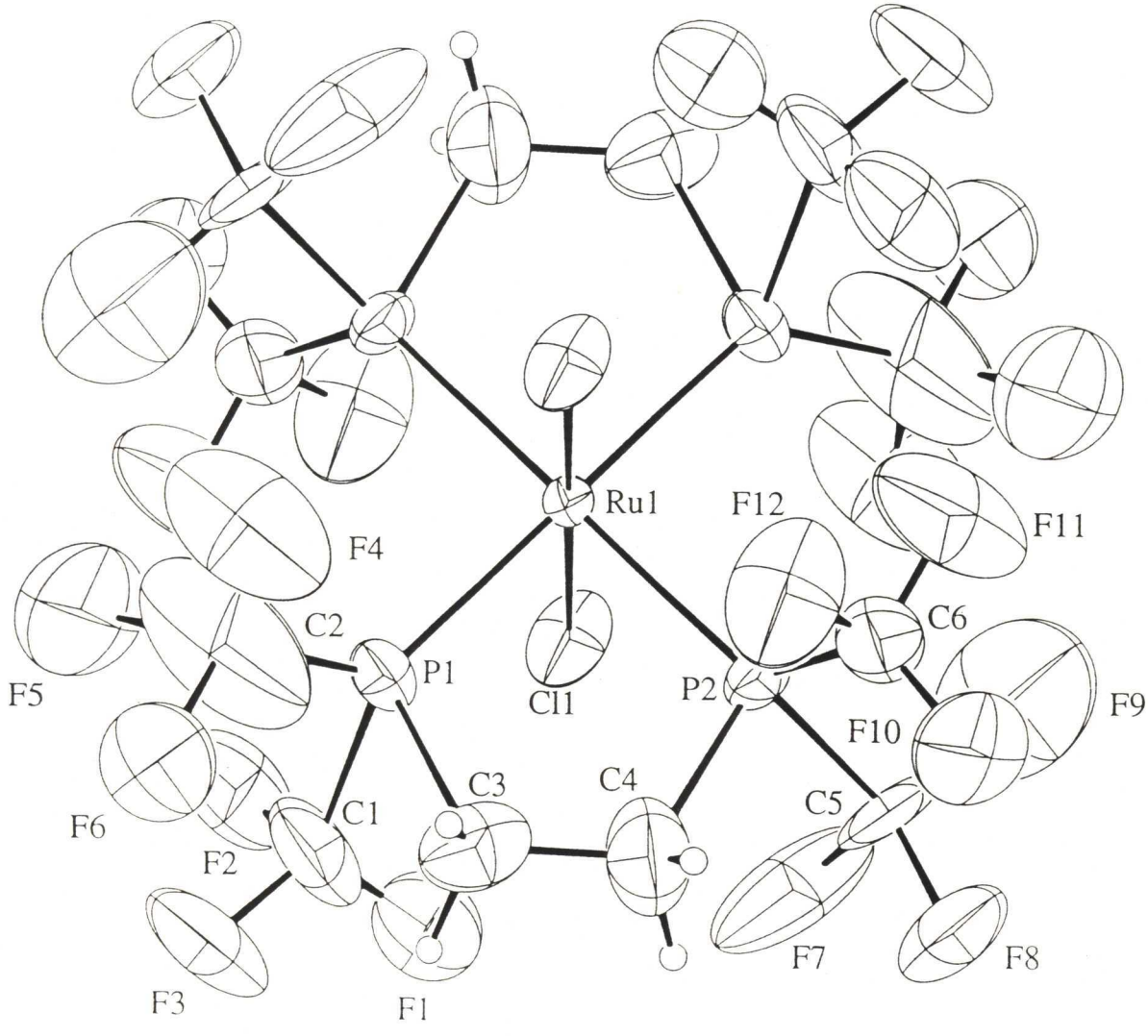
Torsion or Conformation Angles cont

(1)	(2)	(3)	(4)	angle	(1)	(2)	(3)	(4)	angle
C(8)	C(9)	C(10)	C(11)	2(1)					
C(9)	C(8)	C(7)	C(12)	0.9(7)					
C(9)	C(10)	C(11)	C(12)	-1(1)					
C(12)	C(7)	P(2)	C(13)	-85.3(4)					
C(13)	P(2)	Ru(1)	C(24)	-126.3(2)					
C(13)	C(14)	C(15)	C(16)	-0.5(8)					
C(13)	C(18)	C(17)	C(16)	0.3(9)					
C(14)	C(13)	C(18)	C(17)	-1.4(8)					
C(14)	C(15)	C(16)	C(17)	-0.7(9)					
C(15)	C(14)	C(13)	C(18)	1.5(7)					
C(15)	C(16)	C(17)	C(18)	0.8(9)					
C(19)	P(1)	Ru(1)	C(24)	149.9(4)					
C(19)	P(1)	C(21)	C(20)	154.3(5)					
C(20)	P(3)	Ru(1)	C(24)	69.4(3)					
C(20)	C(21)	P(1)	C(22)	-104.8(5)					
C(21)	P(1)	Ru(1)	C(24)	-90.7(3)					
C(21)	C(20)	P(3)	C(23)	169.9(5)					
C(21)	C(20)	P(3)	C(25)	-91.1(6)					
C(22)	P(1)	Ru(1)	C(24)	29.6(3)					
C(23)	P(3)	Ru(1)	C(24)	-43.4(3)					
C(24)	Ru(1)	P(3)	C(25)	-174.2(5)					

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

APPENDIX A4

RuHCl(dfmpe)$_2$ (**175**)



Crystal data for $RuHCl(dfmpe)_2$ (**175**) (LDF58)

Empirical formula :	$RuC_{12}H_8P_4F_{24}Cl$	Formula weight	868.58
Crystal system	monoclinic	space group	$P2_1/n$ (#14)
a	10.239(2)	α	90
b	8.747(4)	β	108.42(3)
c	14.077(6)	γ	90.01(3)
V	1333(1)	Z	2
D_{calc}	2.16	D_{obs}	-
F(000)	834	μ	11.01 cm^{-1}
T	21°C	λ	0.7093
crystal habit	plate	crystal dimensions	0.0275 × 0.275 × 0.075
crystal faces		crystal colour	clear
data collection range	$1 < \theta < 25$	% decomposition	1.81.5%
scan width	1.8 - 0.35θ	counter aperture	1.8
scan type	ω / θ	range of *hkl*	(-12,12), (-1,11), (-1,16)
data collected	3158	data after merging	2745
R_{merg}	4.8%	maximum transmittance	
absorption correction?	ANALYTICAL	total variables	186
minimum absorbance	0.785	R_w	0.0569
data with I>2.5σ(I)	1815	extinction correction	-
R	0.0694	max/min peaks	-0.52, 0.67
maximum shift/esd	0.00	solution program	SHELXS
solution method	DIRECT	Disorder	Inversion disorder No hydride detected, 50% Cl occupancy
treatment of H atoms	-		

Positional parameters for ldf58

atom	x	y	z	occupancy
Ru(1)	1/2	0	0	1/2
Cl(1)	0.6397(6)	0.1639(8)	0.1363(4)	1/2
P(1)	0.6802(2)	-0.1500(3)	0.0256(2)	
P(2)	0.4351(2)	-0.1322(3)	0.1121(2)	
F(1)	0.826(1)	-0.081(2)	0.215(1)	
F(2)	0.8986(8)	-0.004(1)	0.112(1)	
F(3)	0.9442(8)	-0.196(1)	0.144(1)	
F(4)	0.636(2)	-0.278(2)	-0.136(1)	
F(5)	0.849(1)	-0.126(2)	-0.072(1)	
F(6)	0.815(1)	-0.346(1)	-0.0247(9)	
F(7)	0.574(2)	-0.033(2)	0.2827(6)	
F(8)	0.441(1)	-0.183(1)	0.2984(6)	
F(9)	0.319(3)	-0.009(2)	0.216(1)	
F(10)	0.270(1)	-0.319(1)	0.144(1)	
F(11)	0.184(1)	-0.198(2)	0.030(2)	
F(12)	0.296(1)	-0.329(2)	0.005(1)	
C(1)	0.848(2)	-0.105(2)	0.137(2)	
C(2)	0.735(4)	-0.239(3)	-0.054(4)	
C(3)	0.666(2)	-0.310(2)	0.106(1)	
C(4)	0.561(2)	-0.291(2)	0.154(2)	
C(5)	0.452(2)	-0.060(2)	0.245(1)	
C(6)	0.291(2)	-0.242(2)	0.080(1)	
H(1)	0.64273	-0.38974	0.06239	
H(2)	0.75405	-0.32438	0.15681	
H(3)	0.60770	-0.28166	0.22549	
H(4)	0.50454	-0.37337	0.14182	

Positional parameters and B(eq) for ldf58

atom	x	y	z	B(eq)
Ru(1)	1/2	0	0	4.12(3)
Cl(1)	0.6397(6)	0.1639(8)	0.1363(4)	10.7(3)
P(1)	0.6802(2)	-0.1500(3)	0.0256(2)	6.8(1)
P(2)	0.4351(2)	-0.1322(3)	0.1121(2)	6.2(1)
F(1)	0.826(1)	-0.081(2)	0.215(1)	22(1)
F(2)	0.8986(8)	-0.004(1)	0.112(1)	18.6(7)
F(3)	0.9442(8)	-0.196(1)	0.144(1)	19.4(7)
F(4)	0.636(2)	-0.278(2)	-0.136(1)	29(1)
F(5)	0.849(1)	-0.126(2)	-0.072(1)	25(1)
F(6)	0.815(1)	-0.346(1)	-0.0247(9)	22.5(8)
F(7)	0.574(2)	-0.033(2)	0.2827(6)	25(1)
F(8)	0.441(1)	-0.183(1)	0.2984(6)	16.5(6)
F(9)	0.319(3)	-0.009(2)	0.216(1)	34(2)
F(10)	0.270(1)	-0.319(1)	0.144(1)	17.8(6)
F(11)	0.184(1)	-0.198(2)	0.030(2)	30(1)
F(12)	0.296(1)	-0.329(2)	0.005(1)	22(1)
C(1)	0.848(2)	-0.105(2)	0.137(2)	16(1)
C(2)	0.735(4)	-0.239(3)	-0.054(4)	35(3)
C(3)	0.666(2)	-0.310(2)	0.106(1)	14(1)
C(4)	0.561(2)	-0.291(2)	0.154(2)	17(1)
C(5)	0.452(2)	-0.060(2)	0.245(1)	15(1)
C(6)	0.291(2)	-0.242(2)	0.080(1)	11.4(9)
H(1)	0.64273	-0.38974	0.06239	16.9
H(2)	0.75405	-0.32438	0.15681	16.9
H(3)	0.60770	-0.28166	0.22549	20.0
H(4)	0.50454	-0.37337	0.14182	20.0

Torsion or Conformation Angles

(1)	(2)	(3)	(4)	angle
Ru(1)	P(1)	C(1)	F(1)	50(2)
Ru(1)	P(1)	C(1)	F(2)	-70(2)
Ru(1)	P(1)	C(1)	F(3)	-179(1)
Ru(1)	P(1)	C(2)	F(4)	-32(4)
Ru(1)	P(1)	C(2)	F(5)	91(2)
Ru(1)	P(1)	C(2)	F(6)	-161(2)
Ru(1)	P(1)	C(3)	C(4)	-13(1)
Ru(1)	P(1)	C(1)	F(1)	-50(2)
Ru(1)	P(1)	C(1)	F(2)	70(2)
Ru(1)	P(1)	C(1)	F(3)	179(1)
Ru(1)	P(1)	C(2)	F(4)	32(4)
Ru(1)	P(1)	C(2)	F(5)	-91(2)
Ru(1)	P(1)	C(2)	F(6)	161(2)
Ru(1)	P(1)	C(3)	C(4)	13(1)
Ru(1)	P(2)	C(4)	C(3)	-5(2)
Ru(1)	P(2)	C(5)	F(7)	-59(2)
Ru(1)	P(2)	C(5)	F(8)	-163.9(7)
Ru(1)	P(2)	C(5)	F(9)	92(1)
Ru(1)	P(2)	C(6)	F(10)	174(1)
Ru(1)	P(2)	C(6)	F(11)	-49(2)
Ru(1)	P(2)	C(6)	F(12)	53(1)
Ru(1)	P(2)	C(4)	C(3)	5(2)
Ru(1)	P(2)	C(5)	F(7)	59(2)
Ru(1)	P(2)	C(5)	F(8)	163.9(7)
Ru(1)	P(2)	C(5)	F(9)	-92(1)
Ru(1)	P(2)	C(6)	F(10)	-174(1)
Ru(1)	P(2)	C(6)	F(11)	49(2)
Ru(1)	P(2)	C(6)	F(12)	-53(1)
Cl(1)	Ru(1)	P(1)	C(1)	4.1(8)
Cl(1)	Ru(1)	P(1)	C(2)	-140(2)
Cl(1)	Ru(1)	P(1)	C(3)	100.8(5)
Cl(1)	Ru(1)	P(1)	C(1)	175.9(8)
Cl(1)	Ru(1)	P(1)	C(2)	-40(2)
Cl(1)	Ru(1)	P(1)	C(3)	79.2(5)
Cl(1)	Ru(1)	P(2)	C(4)	-95.5(7)
Cl(1)	Ru(1)	P(2)	C(5)	17.2(7)
Cl(1)	Ru(1)	P(2)	C(6)	158.9(7)
Cl(1)	Ru(1)	P(2)	C(4)	-84.5(7)
Cl(1)	Ru(1)	P(2)	C(5)	162.8(7)
Cl(1)	Ru(1)	P(2)	C(6)	21.1(7)
P(1)	Ru(1)	P(2)	C(4)	-2.9(7)
P(1)	Ru(1)	P(2)	C(5)	109.8(7)
P(1)	Ru(1)	P(2)	C(6)	-108.6(7)
P(1)	Ru(1)	P(2)	C(4)	-177.1(7)
P(1)	Ru(1)	P(2)	C(5)	70.2(7)
P(1)	Ru(1)	P(2)	C(6)	-71.4(7)
P(1)	C(3)	C(4)	P(2)	11(2)
P(2)	Ru(1)	P(1)	C(1)	-88.6(8)
P(2)	Ru(1)	P(1)	C(2)	127(2)
P(2)	Ru(1)	P(1)	C(3)	8.1(5)
P(2)	Ru(1)	P(1)	C(1)	-91.4(8)
P(2)	Ru(1)	P(1)	C(2)	53(2)

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

Torsion or Conformation Angles

cont

(1)	(2)	(3)	(4)	angle
P(2)	Ru(1)	P(1)	C(3)	171.9(5)
F(1)	C(1)	P(1)	C(2)	-157(2)
F(1)	C(1)	P(1)	C(3)	-64(2)
F(2)	C(1)	P(1)	C(2)	83(2)
F(2)	C(1)	P(1)	C(3)	176(2)
F(3)	C(1)	P(1)	C(2)	-27(2)
F(3)	C(1)	P(1)	C(3)	67(2)
F(4)	C(2)	P(1)	C(1)	-179(3)
F(4)	C(2)	P(1)	C(3)	94(3)
F(5)	C(2)	P(1)	C(1)	-56(2)
F(5)	C(2)	P(1)	C(3)	-142(2)
F(6)	C(2)	P(1)	C(1)	52(4)
F(6)	C(2)	P(1)	C(3)	-35(3)
F(7)	C(5)	P(2)	C(4)	60(2)
F(7)	C(5)	P(2)	C(6)	153(1)
F(8)	C(5)	P(2)	C(4)	-45(1)
F(8)	C(5)	P(2)	C(6)	48(1)
F(9)	C(5)	P(2)	C(4)	-149(1)
F(9)	C(5)	P(2)	C(6)	-55(1)
F(10)	C(6)	P(2)	C(4)	59(2)
F(10)	C(6)	P(2)	C(5)	-40(2)
F(11)	C(6)	P(2)	C(4)	-165(2)
F(11)	C(6)	P(2)	C(5)	97(2)
F(12)	C(6)	P(2)	C(4)	-62(1)
F(12)	C(6)	P(2)	C(5)	-161(1)
C(1)	P(1)	C(3)	C(4)	104(1)
C(2)	P(1)	C(3)	C(4)	-152(2)
C(3)	C(4)	P(2)	C(5)	-131(1)
C(3)	C(4)	P(2)	C(6)	123(2)

The sign is positive if when looking from atom 2 to atom 3 a clockwise motion of atom 1 would superimpose it on atom 4.

U values for ldf58

atom	U11	U22	U33	U12	U13	U23
Ru(1)	0.0469(4)	0.0655(5)	0.0440(4)	0.0013(5)	0.0142(3)	0.0045(6)
Cl(1)	0.127(4)	0.202(6)	0.069(3)	-0.090(4)	0.021(3)	-0.057(4)
P(1)	0.066(1)	0.086(2)	0.107(2)	0.015(1)	0.027(1)	0.003(2)
P(2)	0.082(2)	0.094(2)	0.064(1)	-0.013(1)	0.029(1)	0.017(1)
F(1)	0.145(8)	0.46(3)	0.20(1)	-0.01(1)	0.018(7)	0.03(1)
F(2)	0.103(6)	0.28(1)	0.29(1)	-0.030(8)	0.008(7)	-0.01(1)
F(3)	0.102(5)	0.22(1)	0.37(1)	0.052(6)	0.014(8)	0.08(1)
F(4)	0.31(1)	0.38(2)	0.31(1)	0.10(1)	-0.05(1)	-0.25(1)
F(5)	0.28(1)	0.35(2)	0.35(2)	-0.05(1)	0.13(1)	0.10(1)
F(6)	0.37(1)	0.25(1)	0.30(1)	0.213(9)	0.19(1)	0.07(1)
F(7)	0.47(2)	0.37(2)	0.084(5)	-0.26(1)	0.046(8)	-0.032(8)
F(8)	0.29(1)	0.24(1)	0.132(6)	-0.001(8)	0.106(6)	0.061(7)
F(9)	0.68(4)	0.26(2)	0.44(2)	0.17(2)	0.30(2)	0.02(2)
F(10)	0.197(8)	0.21(1)	0.27(1)	-0.086(7)	0.078(8)	0.084(9)
F(11)	0.125(7)	0.34(2)	0.61(2)	-0.058(8)	0.02(1)	0.29(2)
F(12)	0.28(1)	0.34(2)	0.23(1)	-0.14(1)	0.10(1)	-0.12(1)
C(1)	0.08(1)	0.20(2)	0.33(3)	0.02(1)	0.06(1)	0.09(2)
C(2)	0.41(3)	0.28(2)	0.61(7)	0.25(2)	0.11(4)	-0.13(3)
C(3)	0.21(2)	0.17(1)	0.14(1)	-0.02(1)	0.04(1)	0.03(1)
C(4)	0.20(1)	0.21(2)	0.27(2)	0.05(1)	0.14(1)	0.05(2)
C(5)	0.19(1)	0.33(3)	0.057(7)	-0.07(2)	0.035(8)	0.07(1)
C(6)	0.14(1)	0.13(1)	0.17(1)	0.02(1)	0.06(1)	0.05(1)

Intramolecular Bond Angles Involving the Nonhydrogen Atoms

atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Ru(1)	Cl(1)	180.00	C(5)	P(2)	C(6)	106.0(8)
Cl(1)	Ru(1)	P(1)	92.7(2)	P(1)	C(1)	F(1)	114(1)
Cl(1)	Ru(1)	P(1)	87.3(2)	P(1)	C(1)	F(2)	107(2)
Cl(1)	Ru(1)	P(2)	92.8(2)	P(1)	C(1)	F(3)	111(2)
Cl(1)	Ru(1)	P(2)	87.2(2)	F(1)	C(1)	F(2)	109(3)
Cl(1)	Ru(1)	P(1)	87.3(2)	F(1)	C(1)	F(3)	114(2)
Cl(1)	Ru(1)	P(1)	92.7(2)	F(2)	C(1)	F(3)	101(2)
Cl(1)	Ru(1)	P(2)	87.2(2)	P(1)	C(2)	F(4)	114(2)
Cl(1)	Ru(1)	P(2)	92.8(2)	P(1)	C(2)	F(5)	99(2)
P(1)	Ru(1)	P(1)	180.00	P(1)	C(2)	F(6)	121(4)
P(1)	Ru(1)	P(2)	85.7(1)	F(4)	C(2)	F(5)	116(4)
P(1)	Ru(1)	P(2)	94.3(1)	F(4)	C(2)	F(6)	106(2)
P(1)	Ru(1)	P(2)	94.3(1)	F(5)	C(2)	F(6)	100(2)
P(1)	Ru(1)	P(2)	85.7(1)	P(1)	C(3)	C(4)	112(1)
P(2)	Ru(1)	P(2)	180.0000(1	P(2)	C(4)	C(3)	118(1)
Ru(1)	P(1)	C(1)	116.2(7)	P(2)	C(5)	F(7)	105(1)
Ru(1)	P(1)	C(2)	131(1)	P(2)	C(5)	F(8)	102(1)
Ru(1)	P(1)	C(3)	113.4(6)	P(2)	C(5)	F(9)	94(1)
C(1)	P(1)	C(2)	105(2)	F(7)	C(5)	F(8)	101(1)
C(1)	P(1)	C(3)	85.5(8)	F(7)	C(5)	F(9)	146(2)
C(2)	P(1)	C(3)	94(2)	F(8)	C(5)	F(9)	103(1)
Ru(1)	P(2)	C(4)	110.2(5)	P(2)	C(6)	F(10)	120(1)
Ru(1)	P(2)	C(5)	120.0(6)	P(2)	C(6)	F(11)	118(1)
Ru(1)	P(2)	C(6)	124.6(6)	P(2)	C(6)	F(12)	110(1)
C(4)	P(2)	C(5)	98.1(9)	F(10)	C(6)	F(11)	109(2)
C(4)	P(2)	C(6)	90.8(8)	F(10)	C(6)	F(12)	105(1)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Angles Involving the Nonhydrogen Atoms cont

atom	atom	atom	angle	atom	atom	atom	angle
F(11)	C(6)	F(12)	91(2)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
Ru(1)	Cl(1)	2.554(5)	1	F(2)	C(1)	1.22(2)	1
Ru(1)	Cl(1)	2.554(5)	65503	F(3)	C(1)	1.31(2)	1
Ru(1)	P(1)	2.293(2)	1	F(4)	C(2)	1.33(4)	1
Ru(1)	P(1)	2.293(2)	65503	F(5)	C(2)	1.68(5)	1
Ru(1)	P(2)	2.295(2)	1	F(6)	C(2)	1.31(3)	1
Ru(1)	P(2)	2.295(2)	65503	F(7)	C(5)	1.22(2)	1
P(1)	C(1)	1.97(2)	1	F(8)	C(5)	1.44(2)	1
P(1)	C(2)	1.65(4)	1	F(9)	C(5)	1.38(2)	1
P(1)	C(3)	1.96(2)	1	F(10)	C(6)	1.24(2)	1
P(2)	C(4)	1.98(2)	1	F(11)	C(6)	1.18(2)	1
P(2)	C(5)	1.96(2)	1	F(12)	C(6)	1.36(2)	1
P(2)	C(6)	1.76(2)	1	C(3)	C(4)	1.46(2)	1
F(1)	C(1)	1.21(3)	1				

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Intermolecular Distances Involving the Nonhydrogen Atoms

atom	atom	distance	ADC(*)	atom	atom	distance	ADC(*)
Cl(1)	F(1)	3.20(2)	65502	F(4)	F(8)	3.55(2)	54404
Cl(1)	C(4)	3.54(2)	65502	F(4)	C(1)	3.77(2)	44404
Cl(1)	C(3)	3.56(2)	65502	F(5)	F(8)	2.96(2)	54404
Cl(1)	F(3)	3.71(1)	65502	F(5)	F(11)	3.35(2)	65501
F(1)	C(4)	3.37(3)	65502	F(6)	F(8)	3.15(1)	54404
F(1)	F(4)	3.49(2)	54504	F(6)	F(12)	3.41(2)	64503
F(1)	C(3)	3.63(2)	65502	F(6)	F(10)	3.65(2)	64503
F(2)	F(5)	3.09(2)	75503	F(6)	F(7)	3.72(1)	64502
F(2)	F(8)	3.58(2)	65502	F(7)	C(3)	3.41(2)	65502
F(3)	F(4)	3.11(2)	54504	F(7)	F(12)	3.51(2)	54504
F(3)	F(11)	3.34(2)	65501	F(8)	C(2)	3.48(4)	44504
F(3)	F(7)	3.46(2)	64502	F(8)	F(11)	3.62(2)	54504
F(3)	F(10)	3.54(1)	65501	F(9)	F(10)	3.04(2)	2

Contacts out to 3.80 angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

(*)footnote

The ADC (atom designator code) specifies the position of an atom in a crystal. The 5-digit number shown in the table is a composite of three one digit numbers and one two digit number: TA(1st digit) + TB(2nd digit) + TC(3rd digit) + SN(4th and 5th digit). TA, TB, & TC are the crystal lattice translation digits along cell edges a, b, and c. A translation digit of 5 indicates the origin unit cell. If TA=4, this indicates a translation of one unit cell length along the a axis in the negative direction. Each translation digit can range in value from 1 to 9 and thus (+/-)4 lattice translations from the origin (TA=5,TB=5,TC=5) can be represented.

The SN or symmetry operator number refers to the number of the symmetry operator used to generate the coordinates of the target atom. A list of the symmetry operators relevant to this structure are given below.

For a given intermolecular contact, the first atom (origin atom) is located in the origin unit cell (TA=5,TB=5,TC=5) and its position can be generated using the identity operator (SN=1). Thus, the ADC for an origin atom is always ADC=55501. The position of the second atom (target atom) can be generated using the ADC and the coordinates of that atom in the parameter table. For example, an ADC of 47502 refers to the target atom moved through operator two, then translated -1 cell translations along the a axis, +2 cell translations along the b axis, and 0 cell translations along the c axis.

An ADC of 1 indicates an intermolecular contact between two fragments (i.e.cation and anion) that reside in the same asymmetric unit.

Symmetry Operators:

(1)	+X	,	+Y	,	+Z	(2)	1/2-X	,1/2+Y	,1/2-Z
(3)	-X	,	-Y	,	-Z	(4)	1/2+X	,1/2-Y	,1/2+Z