Chloride Abstraction from Ruthenium Alkyl *Bis*-diphosphine Dichlorides

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Sections of this work have been presented at scientific conferences:

A. Tronoff, *Chloride Abstraction from Ruthenium* bis-*Diphosphine Dichlorides with Thallium, and Reactions Thereof* (talk), 3rd Australian Organometallic Conference (OZOM3), Monash (Gippsland), Churchill, VIC, 8th – 11th January 2006.

L. Field, H. Li and A. Tronoff, *Towards the Formation of Dinitrogen Complexes of* [$RuCl_2(DMPE)_2$] (poster), Pacifichem 2005, Honolulu, Hawaii, 15th – 20th December 2005.

Leslie D. Field and Ashley Tronoff, *Chloride Abstraction from Ruthenium Diphosphine Dichlorides with Thallium, and Reactions Thereof* (talk), 8th Reactive Organometallics Symposium, UNSW, Sydney, NSW, 5th August 2005.

Leslie D Field and Ashley Tronoff, *Towards the Formation of Dinitrogen Complexes of* [$RuCl_2(DMPE)_2$] (poster), The 12th Royal Australian Chemical Institute Convention (RACI Connect 2005), Sydney Convention and Exhibition Centre, Sydney, NSW, 3rd – 7th July 2005.

-Leslie D. Field, Hsiu Lin Li, and Ashley Tronoff, A *Story of Stability*: *The Attempt to Form a Dinitrogen Complex of* [$RuCl_2(DMPE)_2$] (talk), 7th Reactive Organometallics Symposium, ANU, Canberra, ACT, 11th February 2005.

Leslie D. Field, Nilay Hazari, Ashley Tronoff, *Tetratertiary Tripodal Phosphine Complexes of Tungsten* (poster), 2nd Australia and New Zealand Symposium on Organometallic Chemistry OZOM2, Adelaide University, Adelaide, SA, 11th – 14th January 2004.

Ashley Tronoff, *Tungsten Complexes with Tripodal Phosphine Ligands* (talk), 5th Reactive Organometallics Symposium, ANU, Canberra, ACT, 21st November 2003.

Abstract

Despite their early discovery, relatively few classes of ruthenium dinitrogen complexes are known. This work describes the successful coordination of dinitrogen to the electron-rich alkylphosphine cores $[RuCl(dmpe)_2]^+$ and $[RuCl(depe)_2]^+$ by chloride abstraction from both the *cis* and *trans* dichloro derivatives. One such complex, *trans*-$[RuCl(N_2)(dmpe)_2](BArF_{24})$, possesses the most activated ruthenium ν_{NN} reported to date.

A variety of chloride abstraction agents were tested on the *cis* and *trans* isomers of $[RuCl_2(P\text{-}P)_2]$ (P-P = dmpe, depe) with the choice of abstracting agent, anion and solvent all found to significantly affect the outcome. Reaction with silver triflate and trimethylsilyl triflate was found to give dichlororuthenium(III) products, which could be readily reduced to the ruthenium(II) starting materials with common reducing agents, as well as by alcohols and hydrazine.

The use of thallium triflate avoided oxidation and led to the formation of the crystallographically characterised polymeric incorporation product, $[\{$*trans*-$[RuCl_2(dmpe)_2]\cdot Tl(OTf)\}_n]$ from *trans*-$[RuCl_2(dmpe)_2]$ and the interesting chloride-bridged ruthenium dimer *cis*-$[\{Ru(depe)_2\}_2(\mu\text{-}Cl)_2](OTf)_2$ from *trans*-$[RuCl_2(depe)_2]$. Anion exchange of the complex $[\{$*trans*-$[RuCl_2(dmpe)_2]\cdot Tl(OTf)\}_n]$ with the non-coordinating anion *tetrakis*(3,5-*bis*(trifluoromethyl)phenyl)borate resulted in removal of thallium from the system and coordination of dinitrogen to give *trans*-$[RuCl(N_2)(dmpe)_2](BArF_{24})$. C*is*-$[\{Ru(depe)_2\}_2(\mu\text{-}Cl)_2](OTf)_2$ was found to readily react with a variety of small ligands and gave products such as *cis*-$[RuCl(CO)(depe)_2](OTf)$, *cis*-$[RuCl(NCMe)(depe)_2](OTf)$, *cis*-$[RuCl(CN^tBu)(depe)_2](OTf)$, *cis*-$[RuCl(NH_3)(depe)_2](OTf)$, *cis*-$[RuCl(N_3)(depe)_2]$, and *trans*-$[RuCl(\eta^2\text{-}H_2)(depe)_2](OTf)$. A preliminary X-ray single crystal structure analysis was conducted on the complex *cis*-$[RuCl(CN^tBu)(depe)_2](OTf)$.

The thallium(I) salt $Tl(BArF_{24})$ was found to be an efficient chloride abstraction agent under mild conditions. Reactions with *cis*- and *trans*-$[RuCl_2(depe)_2]$ and *cis*-$[RuCl_2(dmpe)_2]$ furnished dinitrogen complexes of the form *cis*-$[\{RuCl(P\text{-}P)_2\}_2(\mu\text{-}N_2)](BArF_{24})_2$, whilst reaction of *trans*-$[RuCl_2(dmpe)_2]$ with $Tl(BArF_{24})$ led to the stable five-coordinate complex *trans*-$[RuCl(dmpe)_2](BArF_{24})$. Vapour diffusion techniques applied to a solution of *cis*-$[\{RuCl(depe)_2\}_2(\mu\text{-}N_2)](BArF_{24})_2$ gave rise to crystals of

trans-[RuCl(N_2)(depe)$_2$](BArF_{24}), on which preliminary X-ray molecular structure analysis was performed.

Reactions of both *cis*-[{Ru(depe)$_2$}$_2$(μ-Cl)$_2$](OTf)$_2$ and *trans*-[RuCl$_2$(dmpe)$_2$] with high pressure (140 psi) dinitrogen at 140-150°C in methanol or tetrahydrofuran resulted in solvent carbonyl abstraction to afford *trans*-[RuCl(CO)(depe)$_2$](OTf) and *trans*-[RuCl(CO)(dmpe)$_2$](Cl) from the depe and dmpe complexes respectively. The molecular structure of *trans*-[RuCl(CO)(dmpe)$_2$](Cl) was determined *via* single crystal X-ray structure analysis.

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16-TMC	1,5,9,13-tetramethyl-1,5,9,13-tetraazacyclohexadecane
2D	two dimensional (NMR)
3D	three dimensional (NMR)
acac	acetylacetonato
AMU	atomic mass units
APCI	atmospheric pressure chemical ionisation
app.	apparent (NMR)
Ar	aromatic ring
ATP	adenosine triphosphate
ATR	attenuated total reflection IR spectroscopy
b	broad (IR, NMR)
$BArF_{24}$	*tetrakis*(3,5-*bis*(trifluoromethyl)phenyl)borate
COSY	correlation spectroscopy (NMR)
cyttp	$PhP(CH_2CH_2CH_2PCy_2)_2$
δ	chemical shift (NMR)
d	deutero
d	doublet (NMR)
dd; dt	doublet of doublets; doublet of triplets, etc. (NMR)
dce	1,2-dichloroethane
dcm	dichloromethane
dcypb	1,4-*bis*(dicyclohexylphosphino)butane
depe	1,2-*bis*(diethylphosphino)ethane

dippae	1,2-*bis*((diisopropylphosphino)amino)ethane
dippe	1,2-*bis*(diisopropylphosphino)ethane
dmf	N,N-dimethylformamide
dmpe	1,2-*bis*(dimethylphosphino)ethane
DPB	diporphyrinatobiphenylene^{4-}
dppa	$Ph_2PCCPPh_2$
dppa	$Ph_2PCCPPh_2$
dppb	1,4-*bis*(diphenylphosphino)butane
dppe	1,2-*bis*(diphenylphosphino)ethane
dppen	$(Ph_2P)_2CCH_2$
dppen	$CH_2=C(PPh_2)_2$
edta	ethylenediaminetetraacetic acid
en	$H_2NCH_2CH_2NH_2$
EPR	electron paramagnetic resonance
ESI	electrospray ionisation
EXAFS	Extended X-ray Absorption Fine Structure
EXSY	exchange spectroscopy (NMR)
FID	recorded free induction decay signal (NMR)
FTIR	fourier transfer infrared
GB	gaussian broadening factor (NMR)
GM	Gaussian multiplication window function (NMR)
hex.	hexet (NMR)
HIPT	hexaisopropylterphenyl
HMQC	heteronuclear multiple-quantum coherence (NMR)

HSQC	heteronuclear single-quantum coherence (NMR)
I	nuclear spin number (NMR)
*Im	1-*tert*-butyl-5-phenylimidazole
IR	infrared
J	coupling constant (NMR)
κ	denticity
LB	line broadening factor (NMR)
m	medium (IR), or multiplet (NMR)
m/*z*	mass to charge ratio
MALDI	matrix assisted laser desorption and ionisation
MS	mass spectroscopy
'$N_2Me_2S_2$'	1,2-ethanediamine-N,N'-dimethyl-N,N'-*bis*(2-benzenethiolate)$^{2-}$
NMR	nuclear magnetic resonance
NN'N	2,6-*bis*[(dimethylamino)methyl]pyridine
NNNN	2,5,9,12-tetramethyl-2,5,9,12-tetraazatridecane
OEP	2,3,7,8,12,13,17,18-octaethylporphyrin^{2-}
ORTEP	Oak Ridge thermal ellipsoid plot program
OTf	$CF_3SO_3^-$
p	pentet (NMR)
P^2P_3	*tris*(2-diphenylphosphinoethyl)phosphine
$P^2P^3P'_2$	2-dimethylphosphinoethyl-*bis*-(3-dimethylphosphinopropyl)-phosphine
$P^3P^2P'_2$	*bis*(3-dimethylphosphinoproyl)(2-dimethylphosphinoethyl)-phosphine

P_c	central phosphorus atom in molecules containing axial symmetry (NMR)
P_t	terminal phosphorus atom in molecules containing axial symmetry (NMR)
PCP-^{t}Bu	2,6-$(CH_2P^tBu_2)_2C_6H_3^-$
pn	$Ph_2PCH_2CH_2NMe_2$
PNP-^{t}Bu	2,6-*bis*-(di-*tert*-butylphosphinomethyl)pyridine
P-O	(1,3-dioxan-2-ylmethyl)diphenylphosphine
POP-^{i}Pr	$(^iPr_2PCH_2CH_2)_2O$
POP-^{t}Bu	$(^tBu_2PCH_2CH_2)_2O$
P-P	any *bis*-diphosphine
PP_3	*tris*(2-diphenylphosphinoethyl)phosphine
ppm	parts per million
$py^{bu}S_4$	2,6-*bis*[(3,5-di-*tert*-butyl-2-sulfanulphenyl)thiomethyl]- pyridine^{2-}
pz	pyrazol-1-yl
q	quartet (NMR)
R,R'-dippach	(R,R')-1,2-*bis*((diisopropylphosphino)amino)cyclohexane
R,R'-Me-DuPHOS	1,2-*bis*((2R,5R)-2,5-dimethylphospholano)benzene
R,R-CHIRAPHOS	(R,R)-2,3-*bis*(diphenylphosphine)butane
R_f	retention factor
R_x^n	reaction
s	singlet (NMR)
sept.	septet (NMR)
sh	sharp

st	strong
t	triplet (NMR)
T_1	longitudinal relaxation time (NMR)
thf	tetrahydrofuran
TMP	5,10,15,20-tetramesitylporphyrin
TMS	trimethylsilyl
TOF	time-of-flight
Tp	$[HB(pz_3)]^-$ = hydrotris(pyrazol-1-yl)borate
trien	$H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
triflate	trifluoromethylsufonate
triphos**	2,2'-(phenylphosphinediyl)*bis*(2,1-phenylene)*bis*-(diphenylphosphine)
UV	ultraviolet
VT	variable temperature (NMR)
w	weak (IR)
η	hapticity
κ^4-PNP_{Si}-^{t}Bu	κ^4-H**N**$^+$($SiMe_2CH_2$**P**^{t}Bu_2)($SiMe_2CH_2$**P**^{t}Bu(CMe_2**C**$^-$$H_2$))
ν	vibrational stretch (IR)