BIS(DIMETHYLPHOSPHINO)ETHANE AND RELATED COMPLEXES OF TRANSITION METALS

A thesis submitted by

VAHÉ HACOOB-SABOONCHIAN, B.Sc., A. R. C. S.

for the

DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF LONDON

AND

THE DIPLOMA OF IMPERIAL COLLEGE

Department of Chemistry

Imperial College of Science, Technology and Medicine

London SW7 2AY

January 1991

ABSTRACT

The reduction of $WCl_4(THF)_2$ by sodium naphthalenide in the presence of DMPE in THF affords *trans*-$WCl_2(DMPE)_2$. Interaction of this complex with $NaBPh_4$ in refluxing MeCN gives $[WCl(\eta^2\text{-MeCN})(DMPE)_2]BPh_4$, and with $SbCl_5$ the tungsten-(V) complex $[WCl_4(DMPE)_2]SbCl_6$. The X-ray crystal structure of the latter shows the cation to have dodecahedral geometry with equatorial chlorine atoms. Interaction of *trans*-$MCl_2(DMPE)_2$, where M = Mo or W, with $LiAlH_4$ in Et_2O gives the hydrido-aluminohydrides, $[MH(AlH_4)(DMPE)_2]_2$. The X-ray crystal structure of the molybdenum complex has been determined. Methanolysis of the tungsten complex gives $WH_4(DMPE)_2$.

The interaction of AgO_3SCF_3 and DMPE in MeCN in presence of $NaBPh_4$ gives the dimeric complex $[Ag_2(DMPE)_4][BPh_4]_2$. The X-ray crystal structure of the cation shows that each silver atom is four-coordinate with one chelating diphosphine and two phosphorus atoms from the two bridging DMPE ligands.

Interactions of $Re(NBu^t)_3Cl$ or $Re(NBu^t)_3(OSiMe_3)$ with LiX [X = NMe_2, NPh_2, PPh_2, $P(SiMe_3)_2$, PH(mes) and $N{=}PPh_3$] give complexes of the type $Re(NBu^t)_3X$. The chloride reacts with the sodium salt of pyrazole giving $Re(NBu^t)_3(C_3H_3N_2)$. Interaction of $Re(NBu^t)_3Cl$ with $SbCl_5$ in refluxing MeCN gives the salt $[Re(NBu^t)_2Cl_2(MeCN)_2]SbCl_6$, and with $Co_2(CO)_8$ the cluster complex $ReCo_3(\mu_3\text{-}NBu^t)_2(\mu\text{-}CO)_2(CO)_8$. Interaction of $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}OReO_3)$ with $AgCF_3CO_2$ gives $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}O_2CCF_3)$. If $Re(NBu^t)_3(OSiMe_3)$ is used as the starting material then $[Re(NBu^t)_2]_2(\mu\text{-}OSiMe_3)(\mu\text{-}O_2CCF_3)$ is isolated from the reaction. The X-ray crystal structures of $Re(NBu^t)_3PPh_2$, $[Re(NBu^t)_2Cl_2(MeCN)_2]SbCl_6$, $ReCo_3(\mu_3\text{-}NBu^t)_2(\mu\text{-}CO)_2(CO)_8$ and $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}O_2CCF_3)$ have been determined.

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LIST OF ABBREVIATIONS

Å	Angstrom, 10^{-10} m
Ar	aryl
B. M.	Bohr Magneton (0.927×10^{-23} Am^2)
bipy	2,2'-bipyridyl
Bu	butyl (*n* or *t* : normal or tertiary)
cm^{-1}	wavenumber
Cp	cyclopentadienyl (η^5-C_5H_5)
Cy	cyclohexyl
depe	1,2-bis(diethylphosphino)ethane
DMPE	1,2-bis(dimethylphosphino)ethane
dppe	1,2-bis(diphenylphosphino)ethane
Δ	separation between asymmetric and symmetric stretching vibrations of the OCO moiety in carboxylate complexes.
EPR	electron paramagnetic resonance
Et	ethyl
Hz	Hertz
IR	infrared
J	coupling constant (in Hz)
Λ_M	molar conductivity
Me	methyl
mes	mesityl (2,4,6-trimethylphenyl)
μ_{eff}	effective magnetic moment
NMR	nuclear magnetic resonance
Ph	phenyl
ppm	parts per million
Pr	propyl
py	pyridine

R	alkyl or aryl group
THF	tetrahydrofuran
TMED	N, N, N', N'-tetramethylethylenediamine
$w_{1/2}$	peak width at 1/2 height
xylyl	2,6-dimethylphenyl

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ACKNOWLEDGMENTS

Firstly, I would like to thank Professor Sir Geoffrey Wilkinson for his enthusiastic supervision and constant encouragement throughout the course of this work.

The S. E. R. C. is gratefully acknowledged for their financial support.

I would also like to express my gratitude to all members of the GW group, residents of the 6-th floor, and all my friends at college over the past three years, particularly, Andreas, Stefan, Danny, Robyn, Carl, Angel, Tony, Cindy, Simon A., John, Vic, Phil, Chih, Caroline, Niki, Jon, Peter, Dave, Pan Yi, Mike, Steve H., Hussein, Brent, Simon D., Dennis, Penny, Edie, Colin and Roger.

A special mention must go out to the "Losers Club", Brian, Robin and especially my lab partner Greg. Their friendship at college over the past three years has certainly made all the difference to the time I've spent as a postgraduate.

I am extremely grateful to Dick, Sue and Paul for all their NMR assistance, Bilquis, Mike and Dave for the determination of X-ray structures, and Geoff and John for the mass spectra.

Thanks to all my friends outside college, particularly Emil, Razmik, Armond, Narbé, Robert and Alenoush who made my life outside college much more entertaining and cosmopolitan than it otherwise would have been.

I am forever indebted to my three dearest and best friends - Paula, Parastoo and Carineh - for all their support and understanding during the most difficult times of the last three years, and for always being there and making all the difference-Thank you .

Finally I must thank my parents, Yervand and Elo, and my brothers Armen and Arby for all their moral and financial support.

CHAPTER 1

THE SYNTHESIS AND REACTIVITY OF *trans*-$WCl_2(DMPE)_2$

CHAPTER 1

Introduction

Among the elements of Group 6, the synthesis and reactions of DMPE complexes, *trans*-$MCl_2(DMPE)_2$, M = Cr[1] and Mo[2] , have been studied in recent years.

The chromium complex reacts with MeCN in presence of 1 or 2 equivalents of $NaBPh_4$ to give *trans*-$[CrCl(MeCN)(DMPE)_2]BPh_4$ and *trans*-$[Cr(MeCN)_2(DMPE)_2][BPh_4]_2$ respectively[3,4]. In attempting to exchange the anion of the above complexes in MeOH solution, it was found that the coordinated MeCN is rapidly attacked by MeOH[4]. It was proposed that these reactions proceeded *via* an intermediate with an η^2-MeCN group, and oxidative addition of MeOH as H and OMe followed by hydride transfer leading to NEt and N=CHMe groups. The reactions are summarised in Schemes 1.1 and 1.2 .

Later, it was found that *trans*-$MoCl_2(DMPE)_2$ undergoes similar reactions with MeCN in presence of $NaBPh_4$ [5]. However, for molybdenum, the monosubstituted complex has isomers with either η^1 or η^2 MeCN groups, depending on the solvent of crystallisation. The X-ray crystallographic characterisation of *trans*-$[MoCl(\eta^2\text{-MeCN})(DMPE)_2]BPh_4$ provided good support for the proposals concerning reactions of the chromium complexes with MeOH.

The hydridoaluminohydrido complex of chromium, $[(DMPE)_2HCr(\mu\text{-}H)_2Al(H)(\mu\text{-}H)]_2$, and for molybdenum and tungsten the similar PMe_3 complexes $[(PMe_3)_4HM(\mu\text{-}H)_2Al(H)(\mu\text{-}H)]_2$ have been prepared by the interaction of the *trans*-MCl_2L_4 complexes (L = PMe_3 ; L_2 = DMPE) with an excess of $LiAlH_4$ in Et_2O[6].

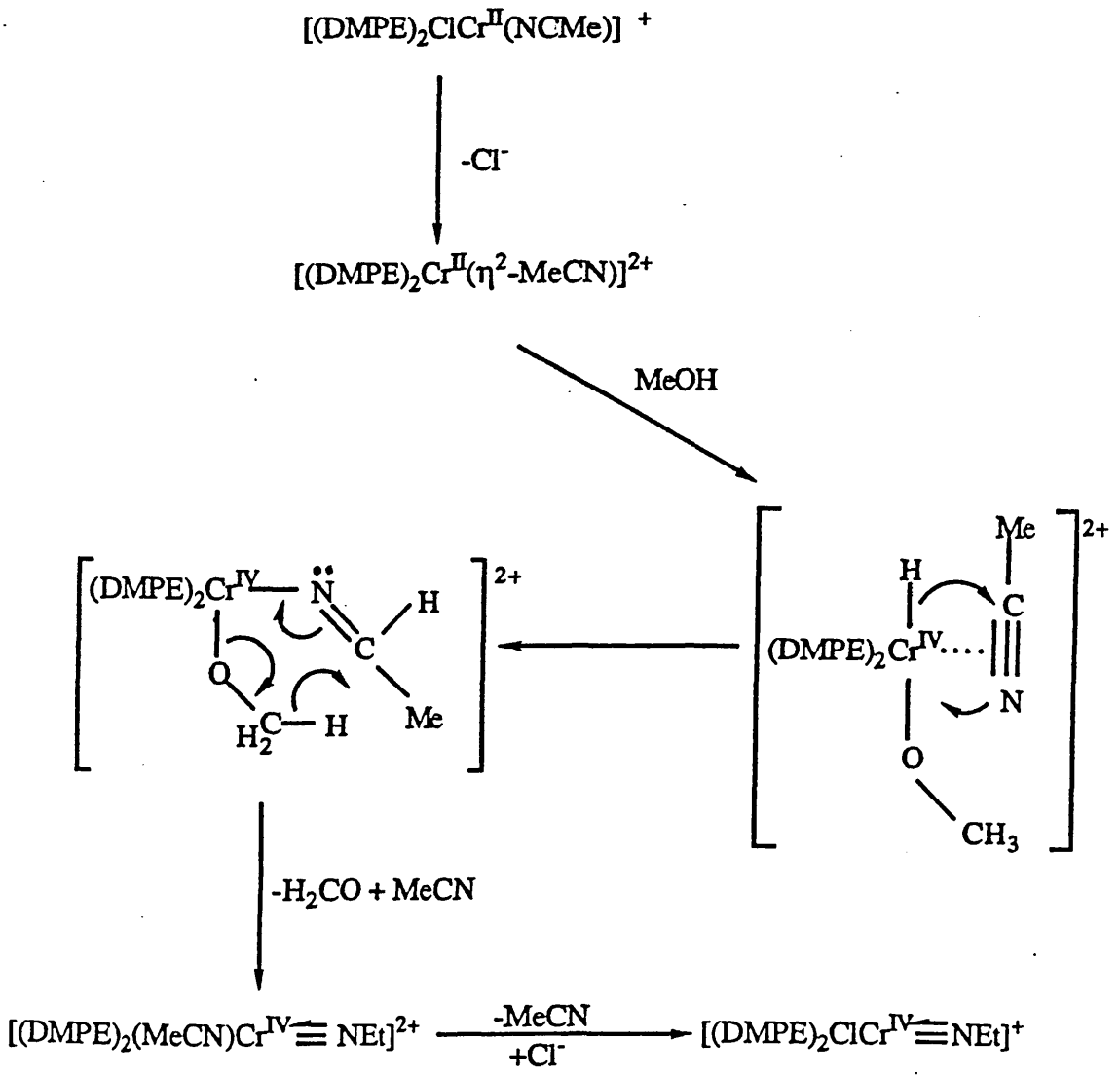
The tetrahydrides, $MH_4(DMPE)_2$, have also been prepared. The chromium complex[7] was obtained by the reaction of *trans*- $CrCl_2(DMPE)_2$ with Bu^nLi under hydrogen, or by the photolysis of $Cr(N_2)_2(DMPE)_2$ under hydrogen. The molybdenum analogue[8] was prepared by sodium-amalgam reduction of *trans*-$MoCl_2(DMPE)_2$ under hydrogen.

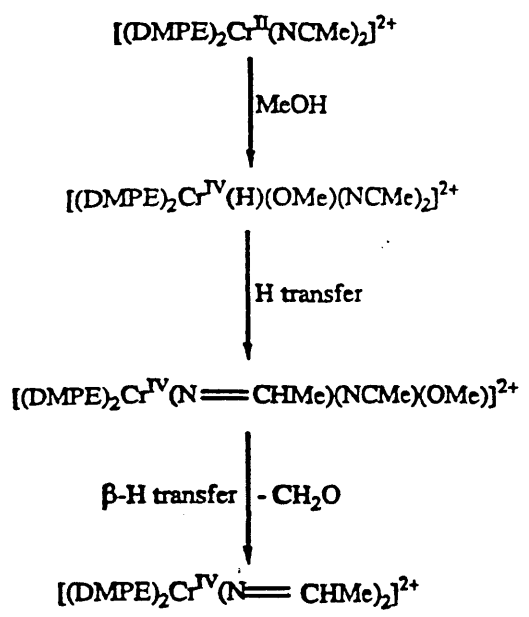
Although a number of molybdenum(IV) tetrahydrido tetraphosphane complexes are known[9-14], $CrH_4(DMPE)_2$ was the first chromium(IV) hydrido complex and the

first example of 8-coordinate chromium(IV) complex to be characterised by X-ray crystallography.

In order to extend the series of DMPE complexes of Group 6 elements, different routes to the synthesis of $WCl_2(DMPE)_2$ were investigated, and some of its reactions were studied.

Scheme 1.1





Scheme 1.2

Results and Discussion

Trans-bis[1,2-bis(dimethylphosphino)ethane]dichlorotungsten(II).

The interaction of $WCl_4(THF)_2$ with 2 equivalents of sodium naphthalenide in THF , containing excess DMPE, gives *trans*-$WCl_2(DMPE)_2$ in *ca.* 35% yield. On a small scale Na / Hg can be used as the reductant. Using WCl_4 instead of $WCl_4(THF)_2$ gives similar results, but the product is obtained in smaller yields. The compound crystallises from hexane as large, deep red crystals, that are soluble in toluene, THF, CH_2Cl_2 and MeCN but sparingly soluble in Et_2O and hexane. In addition to DMPE bands, the IR spectrum shows a single band at 324 cm^{-1} that can be assigned as the W-Cl stretch of the *trans*-ClWCl moiety. Although paramagnetic with the magnetic moment, $\mu_{eff} = 2.20$ BM , implying a low spin d^4 configuration with 2 unpaired electrons [*cf.* $MoCl_2$-$(DMPE)_2$, $\mu_{eff} = 2.65$ BM[2]], the compound is EPR silent at both 293 and 77K. As for the molybdenum compound[2] NMR spectra can be obtained for this and other tungsten(II) complexes ; the CH_2 and CH_3 resonances of DMPE are however shifted compared to diamagnetic species (19.55 and -3.99 ppm respectively).

The $^{31}P\{^1H\}$ NMR spectrum of this compound shows a sharp singlet centred at 16.93 ppm having ^{183}W satellites ($^1J_{W-P} = 157.29$ Hz.).

trans-$WCl_2(DMPE)_2$ can also be prepared by a 2-step process, as with *trans*-$WCl_2(PMe_3)_4$ [15]. Addition of excess DMPE to a suspension of WCl_4 in THF gives a green precipitate which is washed a few times with THF and crystallised from CH_2Cl_2 / hexane. This powder analyses as $WCl_4(DMPE)_2$. Sodium amalgam reduction of this compound, in THF, in presence of excess DMPE yields *trans*-$WCl_2(DMPE)_2$. However, for this method the yield is considerably smaller and a larger excess of DMPE is required .

Trans-(η^2-acetonitrile)(chloro)bis[1,2-bis(dimethylphosphino)ethane] tungsten(II)-tetraphenylborate .

Upon refluxing in MeCN, in the presence of $NaBPh_4$, *trans*-$WCl_2(DMPE)_2$ reacts to give a green solution from which the monosubstituted complex $[WCl(\eta^2\text{-MeCN})(DMPE)_2]BPh_4$, similar to its molybdenum analogue[5], can be isolated, as a pale green powder in *ca.* 70% yield. It is readily soluble in MeCN, THF and CH_2Cl_2 . Whereas *trans*-$MoCl_2(DMPE)_2$ and *trans*-$CrCl_2(DMPE)_2$ react with MeCN in presence of 2 equivalents of $NaBPh_4$ to give *trans*-$[M(MeCN)_2(DMPE)_2][BPh_4]_2$, the only product formed for tungsten is the monosubstituted complex, even when a large excess of $NaBPh_4$ is used .

The ^1H NMR spectrum of this compound shows the methyl resonance of MeCN at 3.42 ppm which is close to the value for similar η^2-MeCN species[5]. The $^{31}P\{^1H\}$ NMR spectrum has a sharp singlet at 14.92 ppm, showing ^{183}W satellites ($^1J_{W\text{-}P}$ = 118.52 HZ.).

The IR spectrum shows no bands attributable to MeCN, a phenomenon not un - common[16]. The complex is a 1:1 electrolyte in MeCN (Λ_M = 90 ohm^{-1} cm^2 mol^{-1}). Unlike the chromium[4] and molybdenum[5] species the MeCN ligand is not attacked by MeOH even under forcing conditions.

Trans-bis[1,2-bis(dimethylphosphino)ethane]tetrachlorotungsten(V)-hexachloroantimonate(V).

In an attempt to remove both chlorides from *trans*-$WCl_2(DMPE)_2$ and form the bis-acetonitrile complex, *trans*-$[W(MeCN)_2(DMPE)_2]^{2+}$, it was treated with 2 equivalents of $SbCl_5$ in refluxing MeCN. This led, however, to chlorination by $SbCl_5$ and the isolation in high yield (73%) of the unusual tungsten(V) salt, $[WCl_4(DMPE)_2]SbCl_6$. *Trans*-$MoCl_2(DMPE)_2$ is reported to be oxidised only to the molybdenum(III) cation, $[MoCl_2(DMPE)_2]^+$, upon treatment with $SnCl_2$[2]. The magnetic moments for d^1 tungsten (V) compounds are reported to be very low[17-19] and no shift in the MeCN solution of the salt , by Evans' NMR method, was observed. In CH_2Cl_2 solution at 293K, the X-band EPR spectrum shows a single sharp resonance with g = 1.90. Due to its paramagnetism, NMR spectra were not obtained for this compound.

Cationic tungsten(V) species are not well known. Most nitrogen containing ligands are known to reduce tungsten(VI) and(V) halides to tungsten(IV) complexes[20-22]. However some substitution products of WX_5 (W = Cl or Br) do exist. These complexes are poorely characterised and are considered to be of the type $[WX_4L_2]X$ (L = Me_3py, py, PhCN, bipy and dppe)[17-19] . Apart from compounds containing oxo, sulphido, η^5-cyclopentadienyl, etc. groups, established tungsten(V) compounds are the halides and alkoxides[19], octahedral WX_6^- and 8-coordinate $[W(CN)_8]^{3-}$ anions[19,23]. Recently, aryloxides, notably the Et_4N^+ and Li^+ salts of the octahedral $[W(OC_6H_5)_6]^-$ ion and the aryloxohalides with bulky OAr groups, $WCl_3(OC_6H_3\text{-}2,6\text{-}Ph_2)L_2$ (L = THF, PMe_2Ph)[24] and $W(OC_6H_3\text{-}2,6\text{-}Cl_2)_4Cl(Et_2O)$[25] have been characterised by X-ray crystallography. The $[WCl_4(DMPE)_2]^+$ cation has a dodecahedral structure with the four chlorines occupying the equatorial, B, sites and the phosphorus atoms the A sites. A diagram of the crystal structure, which also contains two independent centrosymmetric $SbCl_6^-$ anions, is shown in Figure 1.1, the cation in Figure 1.2 . Bond lengths and angles are given in Table 1.1 .

The dodecahedral geometry is analogous to that found in the chromium(IV) complex $CrH_4(DMPE)_2$[7] in which the anionic ligands, the hydrides, are also equatorial. Dodecahedral geometry also almost certainly occurs in tungsten(IV) phosphine hydride and aluminohydride complexes[26,27], but in these structures the monodentate phosphines

occupy both types of site. It is pertinent to note that the W-P bonds in the present tungsten(V) complex are longer than any of those in the tungsten(IV) complexes and also longer than the W-CL bonds. This feature is a reflection of the weakness of the W-P interactions in the absence of any W-P π-back bonding.

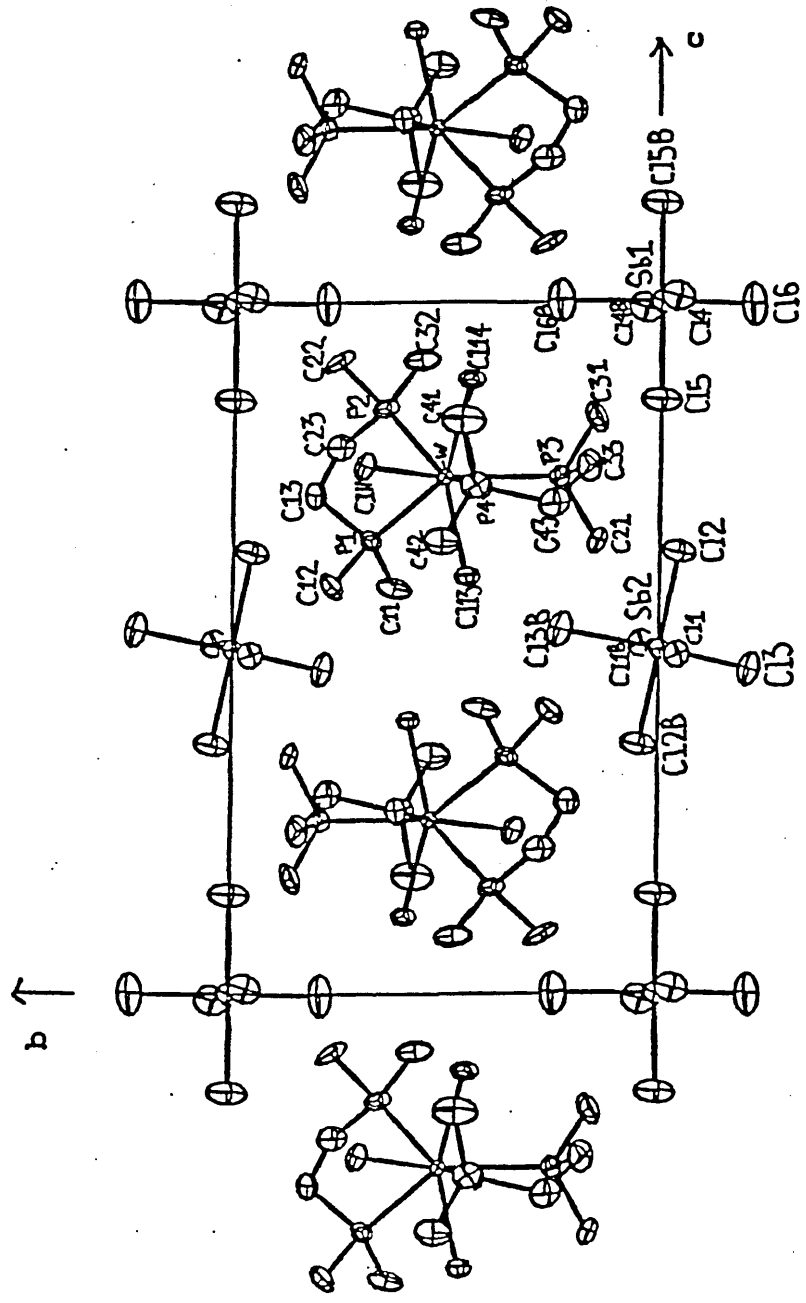


Figure 1.1 : The crystal structure of $[WCl_4(DMPE)_2]^+[SbCl_6]^-$.

Table 1.1 : Bond lengths (Å) and angles (°) for $[WCl_4(DMPE)_2]^+[SbCl_6]^-$.

Bond lengths

Cl(4)-Sb(1)	2.357(7)	Cl(5)-Sb(1)	2.352(7)
Cl(2)-Sb(2)	2.350(7)	Cl(3)-Sb(2)	2.352(6)
Cl(11)-W(1)	2.432(5)	Cl(12)-W(1)	2.432(5)
Cl(13)-W(1)	2.431(5)	Cl(14)-W(1)	2.421(5)
P(1)-W(1)	2.588(7)	P(2)-W(1)	2.575(7)
Cl(6)-Sb(1)	2.349(8)	Cl(1)-Sb(2)	2.374(6)
P(3)-W(1)	2.590(7)	P(4)-W(1)	2.581(7)
C(11)-P(1)	1.838(18)	C(12)-P(1)	1.833(20)
C(13)-P(1)	1.866(19)	C(22)-P(2)	1.865(20)
C(23)-P(2)	1.817(19)	C(32)-P(2)	1.814(22)
C(21)-P(3)	1.842(20)	C(31)-P(3)	1.839(20)
C(33)-P(3)	1.857(23)	C(41)-P(4)	1.820(22)
C(42)-P(4)	1.805(21)	C(43)-P(4)	1.803(22)
C(23)-C(13)	1.454(27)	C(43)-C(33)	1.466(30)

Bond angles.

Cl(12)-W(1)-Cl(11)	146.0(1)	Cl(13)-W(1)-Cl(11)	89.7(2)
Cl(13)-W(1)-Cl(12)	100.2(2)	Cl(14)-W(1)-Cl(11)	100.4(2)
Cl(14)-W(1)-Cl(12)	89.3(2)	Cl(14)-W(1)-Cl(13)	146.1(1)
P(1)-W(1)-Cl(11)	78.0(2)	P(1)-W(1)-Cl(12)	75.2(2)
P(1)-W(1)-Cl(13)	69.9(2)	P(1)-W(1)-Cl(14)	143.7(1)
P(2)-W(1)-Cl(12)	75.2(2)	P(2)-W(1)-Cl(12)	78.0(3)
P92)-W(1)-Cl(13)	143.9(1)	P(2)-W(1)-Cl(14)	69.8(2)
P(2)-W(1)-P(1)	75.0(2)	P(3)-W(1)-Cl(11)	70.3(2)
P(3)-W(1)-Cl(12)	143.4(1)	P(3)-W(1)-Cl(13)	78.3(2)
P(3)-W(1)-Cl(14)	75.0(2)	P(3)-W(1)-P(1)	134.7(1)

Table 1.1 (continued)

P(3)-W(1)-P(2)	124.2(2)	P(4)-W(1)-Cl(11)	143.6(1)
P(4)-W(1)-Cl(12)	70.0(2)	P(4)-W(1)-Cl(13)	74.0(2)
P(4)-W(1)-Cl(14)	79.1(2)	P(4)-W(1)-P(1)	123.3(2)
P(4)-W(1)-P(2)	135.1(1)	P(4)-W(1)-P(3)	74.6(2)
C(11)-P(1)-W(1)	116.1(7)	C(12)-P(1)-W(1)	115.9(8)
C(12)-P(1)-C(11)	105.1(10)	C(13)-P(1)-W(1)	109.4(7)
C(13)-P(1)-C(11)	105.7(10)	C(13)-P(1)-C(12)	103.5(10)
C(22)-P(2)-W(1)	116.0(7)	C(23)-P(2)-W(1)	111.7(7)
C(23)-P(2)-C(22)	105.8(10)	C(32)-P(2)-W(1)	117.1(8)
C(32)-P(2)-C(22)	102.2(10)	C(32)-P(2)-C(23)	102.5(10)
C(21)-P(3)-W(1)	115.7(7)	C(31)-P(3)-W(1)	116.3(7)
C(31)-P(3)-C(21)	103.5(10)	C(33)-P(3)-W(1)	109.8(7)
C(33)-P(3)-C(21)	106.5(10)	C(33)-P(3)-C(31)	103.9(11)
C(41)-P(4)-W(1)	116.9(8)	C(42)-P(4)-W(1)	115.4(8)
C(42)-P(4)-C(41)	104.7(10)	C(43)-P(4)-W(1)	111.0(7)
C(43)-P(4)-C(41)	101.2(11)	C(43)-P(4)-C(42)	106.2(12)
C(23)-C(13)-P(1)	110.8(13)	C(13)-C(23)-P(2)	109.1(14)
C(43)-C(33)-P(3)	109.1(13)	C(33)-C(43)-P(4)	109.3(14)
Cl(5)-Sb(1)-Cl(4)	89.8(3)	Cl(6)-Sb(1)-Cl(4)	89.5(3)
Cl(6)-Sb(1)-Cl(5)	90.0(4)	Cl(2)-Sb(2)-Cl(1)	90.2(3)
Cl(3)-Sb(2)-Cl(1)	90.1(3)	Cl(3)-Sb(2)-Cl(2)	89.9(3)
Cl(4)-Sb(1)-Cl(4B)	180.0(2)	Cl(5)-Sb(1)-Cl(4B)	90.2(3)
Cl(5)-Sb(1)-Cl(5B)	180.0(3)	Cl(6)-Sb(1)-Cl(5B)	90.0(3)
Cl(4)-Sb(2)-Cl(6B)	90.5(3)	Cl(6)-Sb(1)-Cl(6B)	180.0(2)
Cl(1)-Sb(2)-Cl(1B)	180.0(2)	Cl(2)-Sb(2)-Cl(1B)	89.8(3)
Cl(2)-Sb(2)-Cl(2B)	180.0(3)	Cl(3)-Sb(2)-Cl(1B)	90.0(3)
Cl(3)-Sb(2)-Cl(3B)	180.0(2)	Cl(2)-Sb(2)-Cl(3B)	90.1(3)

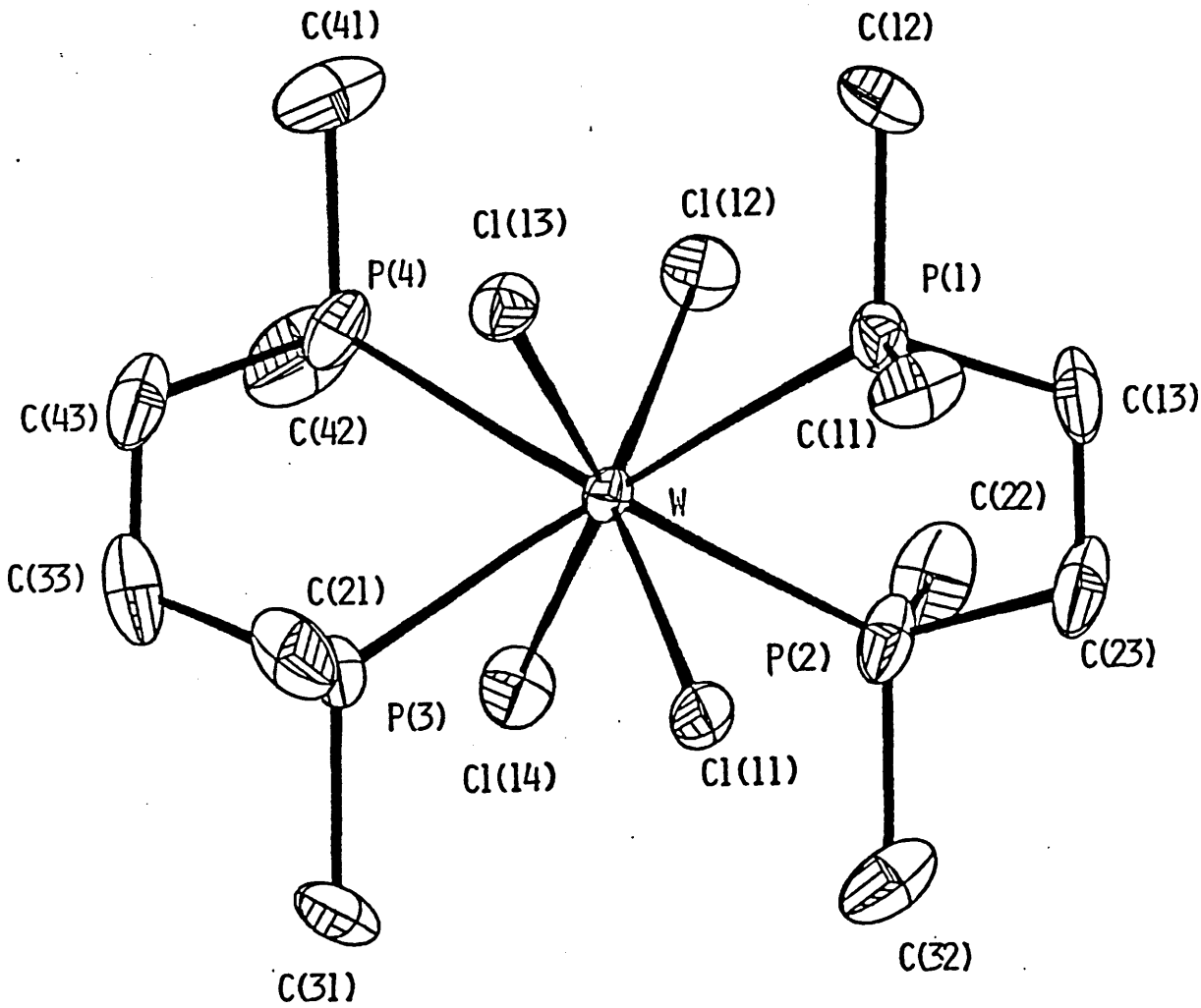


Figure 1.2 : The crystal structure of the $[WCl_4(DMPE)_2]^+$ cation.

Bis[1,2-bis(dimethylphosphino)ethane](tetrahydridoaluminato)hydrido-tungsten(II) dimer.

For both tungsten and molybdenum, the interaction of excess $LiAlH_4$ with *trans*-$MCl_2(DMPE)_2$ in Et_2O gives the M(II) hydridoaluminohydrido complex , $[(DMPE)_2HM(\mu\text{-}H)_2Al(H)(\mu\text{-}H)]_2$, as yellow air and moisture sensitive crystals. The chromium analogue is obtained by the same method as well[6]. The IR spectrum shows strong bands at 1681 and 1650 cm^{-1} attributable to terminal Al-H and bridging W-H-Al stretches. The ^1H NMR spectra are not very useful since the bands are broad as a result of the ^{27}Al quadrupole, phosphorus couplings and the paramagnetism; also the molecules are doubtless rigid as in similar species[6]. The bands though poorly resolved are in similar positions to those in the PMe_3 compounds[6] with terminal Al-H and $Al(\mu\text{-}H)_2Al$ bands at *ca.* 4.10 ppm, the CH_2 and CH_3 resonances of DMPE around 1.58 ppm and the $Al(\mu\text{-}H)_2M$ bands around -5.50 ppm. For the tungsten compound there is a band at -8.30 ppm which would be due to the terminal W-H. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 20.84 ppm with ^{183}W satellites ($^1J_{W\text{-}P}$ = 108.55 Hz.). Due to twinning, X-ray quality crystals of the tungsten compound could not be obtained but suitable crystals of the molybdenum compound were found.

The structure of the molybdenum complex as $[(DMPE)_2HMo(\mu\text{-}H)_2Al(H)(\mu\text{-}H)]_2$has been confirmed by X-ray crystallography. A diagram of the dimeric molecule is shown in Figure 1.3; selected bond lengths and angles are given in Table 1.2. Although the $Al(\mu\text{-}H)_2Al$ hydrogens were the only ones that were reliably located , the structure is similar in most respects to those for other hydridoaluminohydrido complexes[27]. The relative position of the molybdenum atom to the plane of the $Al(\mu\text{-}H)_2Al$ bridge strongly suggests that if, as is likely, the Mo···Al links are also *via* $Mo(\mu\text{-}H)_2Al$ bridges, then a terminal hydrogen is also present on the Al atom. That this is the case is shown by the ^{27}Al NMR spectrum which falls in the region for 5-coordinate aluminium[6,27,28]. The four phosphorus atoms coordinate in an approximately planar manner and the single hydrogen on molybdenum is presumed to occupy the apparent vacant site "*trans*" to the coordination of the two bridging hydrogens. The

molybdenum is thus 7-coordinate as in the similar molybdenum(II) and tungsten(II) PMe_3 complexes[6]. In view of the approximate planarity of the MoP_4 unit with *trans* Mo-P-Mo angles of 149° and 169°, a distorted mono-capped octahedral structure is a possibility. The absence of confirmed positions for the hydrogens make it difficult to have much confidence in this assignment, however.

Bis[1,2-bis(dimethylphosphino)ethane]tetrahydridotungsten(IV).

Interaction of $[WH(AlH_4)(DMPE)_2]_2$ with MeOH in hexane gives a yellow solution from which $WH_4(DMPE)_2$ is isolated as pale yellow crystals in *ca.* 70% yield. The molybdenum tetrahydride, which was obtained by sodium amalgam reduction of *trans*-$MoCl_2(DMPE)_2$ under hydrogen[8], can also be obtained by methanolysis of the hydridoaluminohydrido complex. The IR spectrum of $WH_4(DMPE)_2$ is very similar to the chromium and molybdenum analogues[7,8], having W-H bands at 1745 and1720cm^{-1} The room temperature ^1H NMR spectrum shows a symmetric pattern with two sharp outer lines and three bands in the central region (Figure 1.4). This phenomenon has been observed before[9,29,30] and is characteristic of complexes of the type MH_4L_4 (M = Mo, W; L = a phosphine ligand). It indicates that these complexes are stereochemically rigid on the NMR timescale at or near room temperature. As the temperature is raised this pattern transforms to a binomial quintet centred at *ca.* -5.46 ppm ($^2J_{P-H}$ = 29.22 Hz. at 333K) (Figures 1.5 and 1.6). This change is due to an intramolecular exchange process in which all the protons have equal coupling to all of the ^{31}P nuclei. Although this is observed for all reported tungsten complexes[9,29,30], some of the molybdenum complexes do not seem to have a limiting low temperature spectrum which is not a binomial quintet[9]. For chromium and moybdenum, $MH_4(DMPE)_2$ complexes are non-rigid at room temperature having resonances at -6.91 ppm ($^2J_{P-H}$ = 56.1 Hz.)[7] and - 5.51. ppm ($^2J_{P-H}$ = 31.5 Hz.)[8] respectively. From the ^1H NMR spectrum of $WH_4(DMPE)_2$ at 343K the $^1J_{W-H}$ coupling constant is found to be 18.16 Hz. (Figure 1.6) .

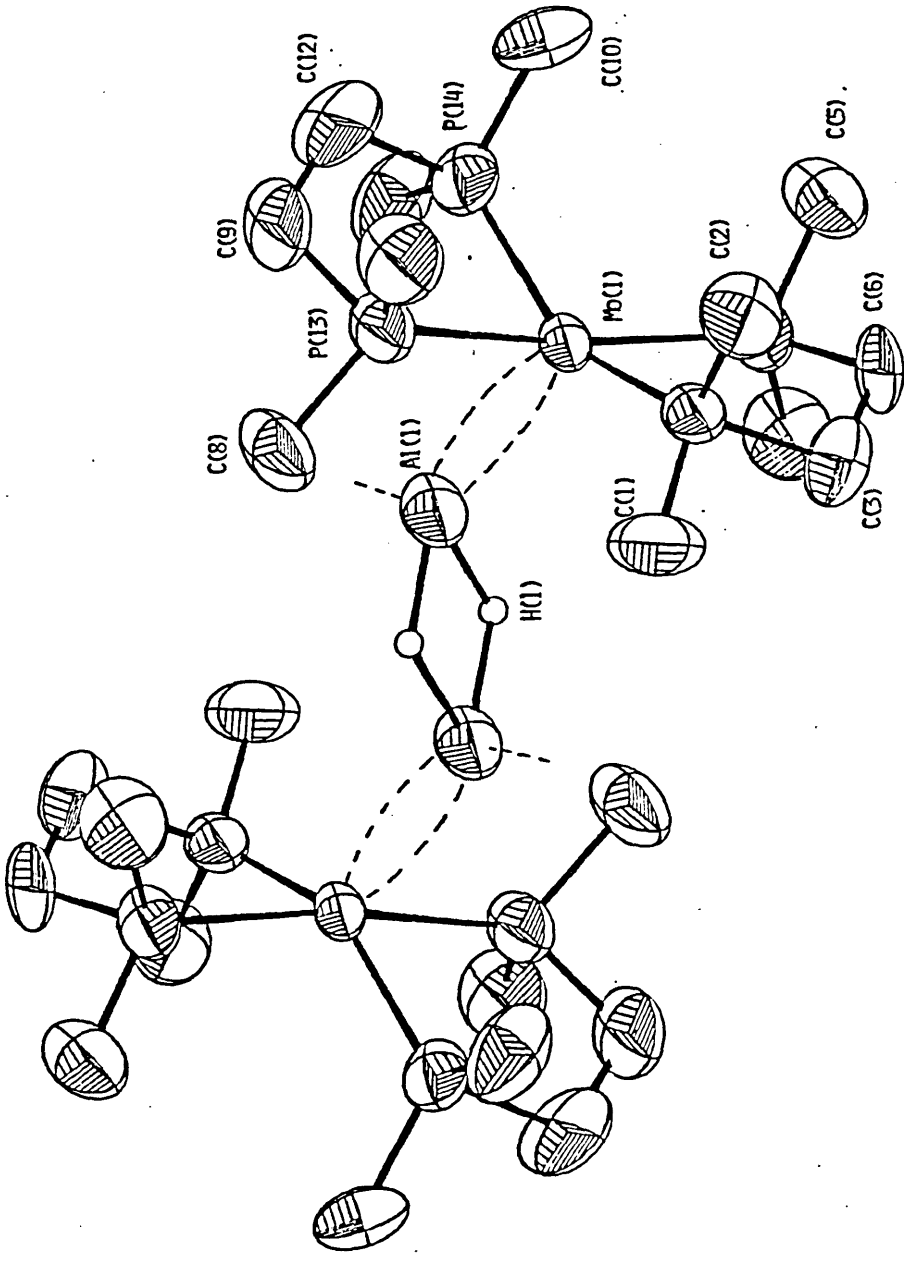


Figure 1.3 : The crystal structure of one of the two independent molecules of $[MoH(AlH_4)(DMPE)_2]_2$. Bonds to presumed H atoms shown by dashed lines .

Table 1.2 : Bond lengths (Å) and angles (°) for $[MoH(AlH_4)(DMPE)_2]_2$.

Bond lengths.

P(11)-Mo(1)	2.414(6)	P(12)-Mo(1)	2.417(7)
P(13)-Mo(1)	2.398(8)	P(14)-Mo(1)	2.410(6)
C(1)-P(11)	1.844(24)	C(2)-P(11)	1.799(18)
C(3)-P(11)	1.837(27)	C(4)-P(12)	1.797(25)
C(5)-P(12)	1.840(21)	C(6)-P(12)	1.920(17)
C(7)-P(13)	1.824(23)	C(8)-P(13)	1.847(23)
C(9)-P(13)	1.822(22)	C(10)-P(14)	1.813(22)
C(11)-P(14)	1.815(20)	C(12)-P(14)	1.859(29)
C(6)-C(3)	1.420(29)	C(12)-C(9)	1.469(31)
P(21)-Mo(2)	2.417(7)	P(22)-Mo(2)	2.409(7)
P(23)-Mo(2)	2.390(7)	P(24)-Mo(2)	2.419(6)
C(1B)-P(21)	1.814(17)	C(2B)-P(21)	1.814(27)
C(3B)-P(21)	1.821(22)	C(4B)-P(22)	1.796(22)
C(5B)-P(22)	1.831(28)	C(6B)-P(22)	1.836(24)
C(10B)-P(23)	1.838(23)	C(11B)-P(23)	1.832(19)
C(12B)-P(23)	1.882(20)	C(7B)-P(24)	1.841(20)
C(8B)-P(24)	1.831(24)	C(9B)-P(24)	1.841(24)
C(6B)-C(3B)	1.524(23)	C(12B)-C(9B)	1.534(26)
Al(1)-Mo(1)	2.578(9)	Al(2)-Mo(2)	2.565(9)
Al(1)-Al(1a)	2.661(15)	Al(2)-Al(2b)	2.644(14)
H(1)-Al(1)	1.64(23)	H(2)-Al(2)	1.77(28)
H(1)-Al(1a)	1.66(26)	H(2)-Al(2a)	1.73(26)

Table 1.2 (continued)

Bond angles.

P(11)-Mo(1)-Al(1)	113.1(3)	P(12)-Mo(1)-Al(1)	109.1(3)
P(12)-Mo(1)-P(11)	79.3(2)	P(13)-Mo(1)-Al(1)	82.1(3)
P(13)-Mo(1)-P(11)	95.0(3)	P(13)-Mo(1)-P(12)	168.7(2)
P(14)-Mo(1)-Al(1)	97.3(3)	P(14)-Mo(1)-P(11)	148.3(2)
P(14)-Mo(1)-P(12)	99.6(3)	P(14)-Mo(1)-P(13)	80.1(3)
C(1)-P(11)-Mo(1)	121.9(7)	C(2)-P(11)-Mo(1)	121.6(8)
C(2)-P(11)-C(1)	99.0(10)	C(3)-P(11)-Mo(1)	109.3(6)
C(3)-P(11)-C(1)	102.4(11)	C(3)-P(11)-C(2)	98.9(12)
C(4)-P(12)-Mo(1)	117.7(9)	C(5)-P(12)-Mo(1)	123.8(9)
C(5)-P(12)-C(4)	98.9(11)	C(6)-P(12)-Mo(1)	108.5(8)
C(6)-P(12)-C(4)	106.2(12)	C(6)-P(12)-C(5)	99.3(10)
C(7)-P(13)-Mo(1)	117.9(9)	C(8)-P(13)-Mo(1)	125.9(10)
C(8)-P(13)-C(7)	99.3(11)	C(9)-P(13)-Mo(1)	111.0(8)
C(9)-P(13)-C(7)	99.1(12)	C(9)-P(13)-C(8)	99.1(11)
C(10)-P(14)-Mo(1)	124.1(8)	C(11)-P(14)-Mo(1)	120.3(10)
C(11)-P(14)-C(10)	97.5(11)	C(12)-P(14)-Mo(1)	110.1(7)
C(12)-P(14)-C(10)	98.0(13)	C(12)-P(14)-C(11)	102.8(11)
C(6)-C(3)-P(11)	108.0(18)	C(3)-C(6)-P(12)	108.5(14)
C(12)-C(9)-P(13)	112.3(17)	C(9)-C(12)-P(14)	110.3(19)
P(21)-Mo(2)-Al(2)	114.5(3)	P(22)-Mo(2)-Al(2)	110.3(3)
P(22)-Mo(2)-P(21)	79.8(2)	P(23)-Mo(2)-Al(2)	79.6(3)
P(23)-Mo(2)-P(21)	95.1(3)	P(23)-Mo(2)-P(22)	170.0(2)
P(24)-Mo(2)-Al(2)	96.9(3)	P(24)-Mo(2)-P(21)	147.0(2)
P(24)-Mo(2)-P(22)	99.2(2)	P(24)-Mo(2)-P(23)	80.3(2)
C(1B)-P(21)-Mo(2)	120.3(8)	C(2B)-P(21)-Mo(2)	119.0(8)
C(2B)-P(21)-C(1B)	102.3(10)	C(3B)-P(21)-Mo(2)	111.7(7)

Table 1.2 (continued)

C(3B)-P(21)-C(1B)	100.5(9)	C(3B)-P(21)-C(2B)	99.8(11)
C(4B)-P(22)-Mo(2)	124.4(11)	C(5B)-P(22)-Mo(2)	118.2(10)
C95B)-P(22)-C(4B)	100.5(15)	C(6B)-P(22)-Mo(2)	111.1(7)
C(6B)-P(22)-C(4B)	99.7(12)	C(6B)-P(22)-C(5B)	98.7(12)
C(10B)-P(23)-Mo(2)	118.0(8)	C(11B)-P(23)-Mo(2)	126.8(9)
C(11B)-P(23)-C(10B)	97.8(11)	C(12B)-P(23)-Mo(2)	111.1(7)
C(12B)-P(23)-C(10B)	99.4(11)	C(12B)-P(23)-C(11B)	99.1(10)
C(7B)-P(24)-Mo(2)	121.3(7)	C(8B)-P(24)-Mo(2)	117.7(8)
C(8B)-P(24)-C(7B)	100.1(10)	C(9B)-P(24)-Mo(2)	110.6(6)
C(9B)-P(24)-C(7B)	101.3(11)	C(9B)-P(24)-C(8B)	103.2(11)
C(6B)-C(3B)-P(21)	110.4(14)	C(3B)-C(6B)-P(22)	111.1(15)
C(12B)-C(9B)-P(24)	111.1(16)	C(9B)-C(12B)-P(23)	107.1(15)
H(1)-Al(1)-H(1a)	72.5(12)	Al(1)-H(1)-Al(1b)	107.6(13)
H(2)-Al(2)-H(2a)	81.7(15)	Al(2)-H(2)-Al(2b)	98.3(14)

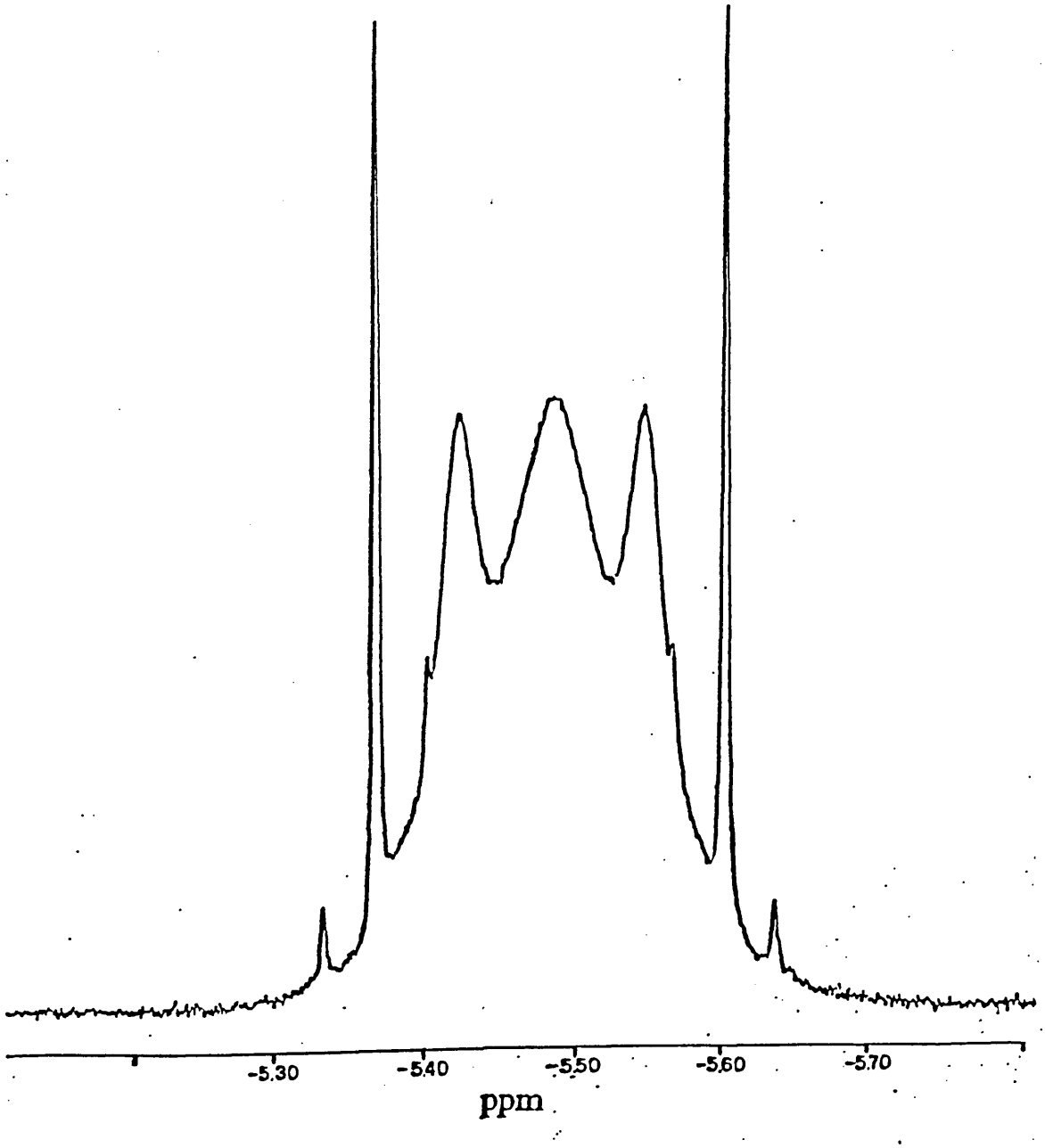


Figure 1.4 : ^1H NMR spectrum of $WH_4(DMPE)_2$ at 296K .

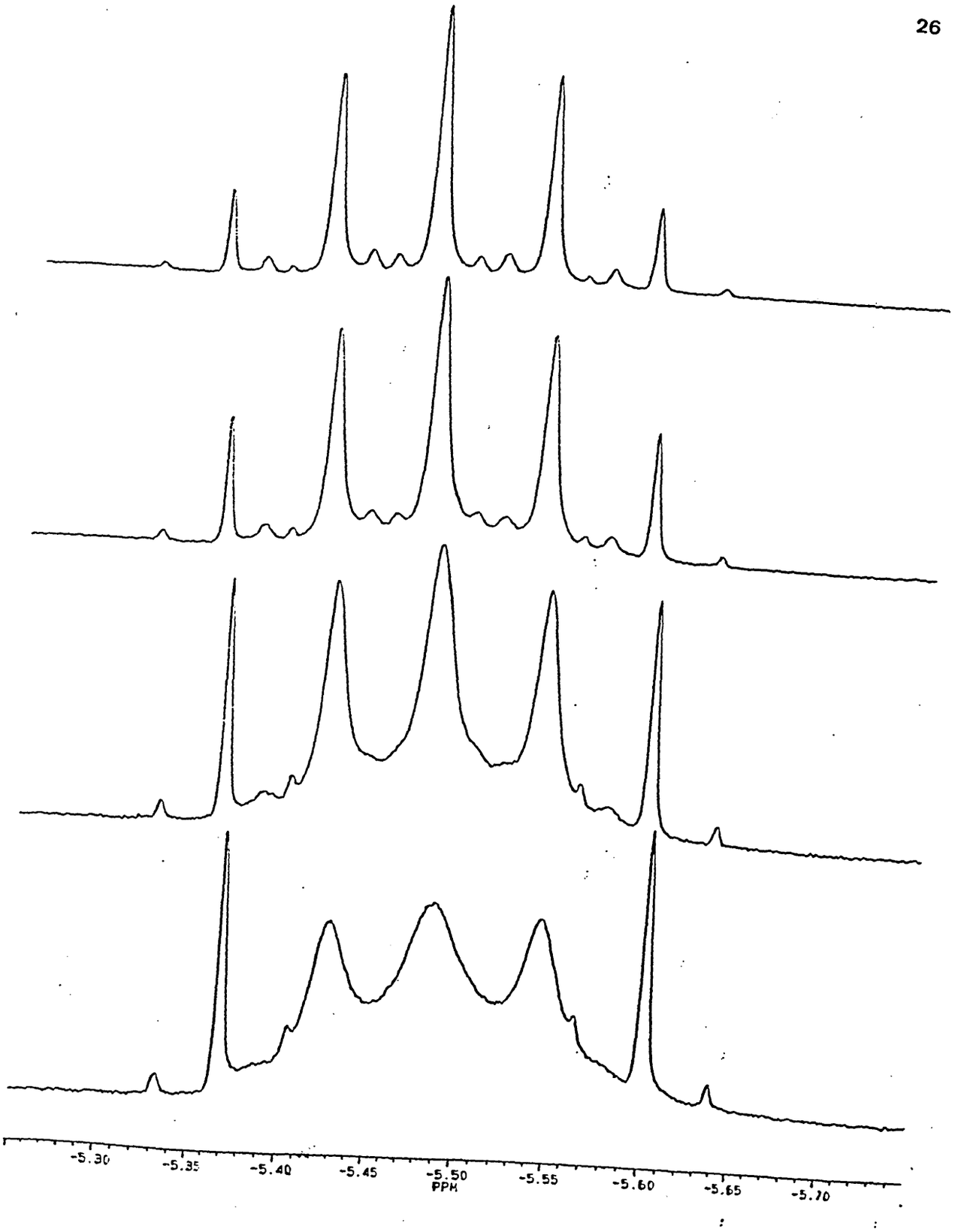


Figure 1.5 : ^1H NMR spectra of $WH_4(DMPE)_2$ at 303, 313, 323 and 333K (from bottom to top).

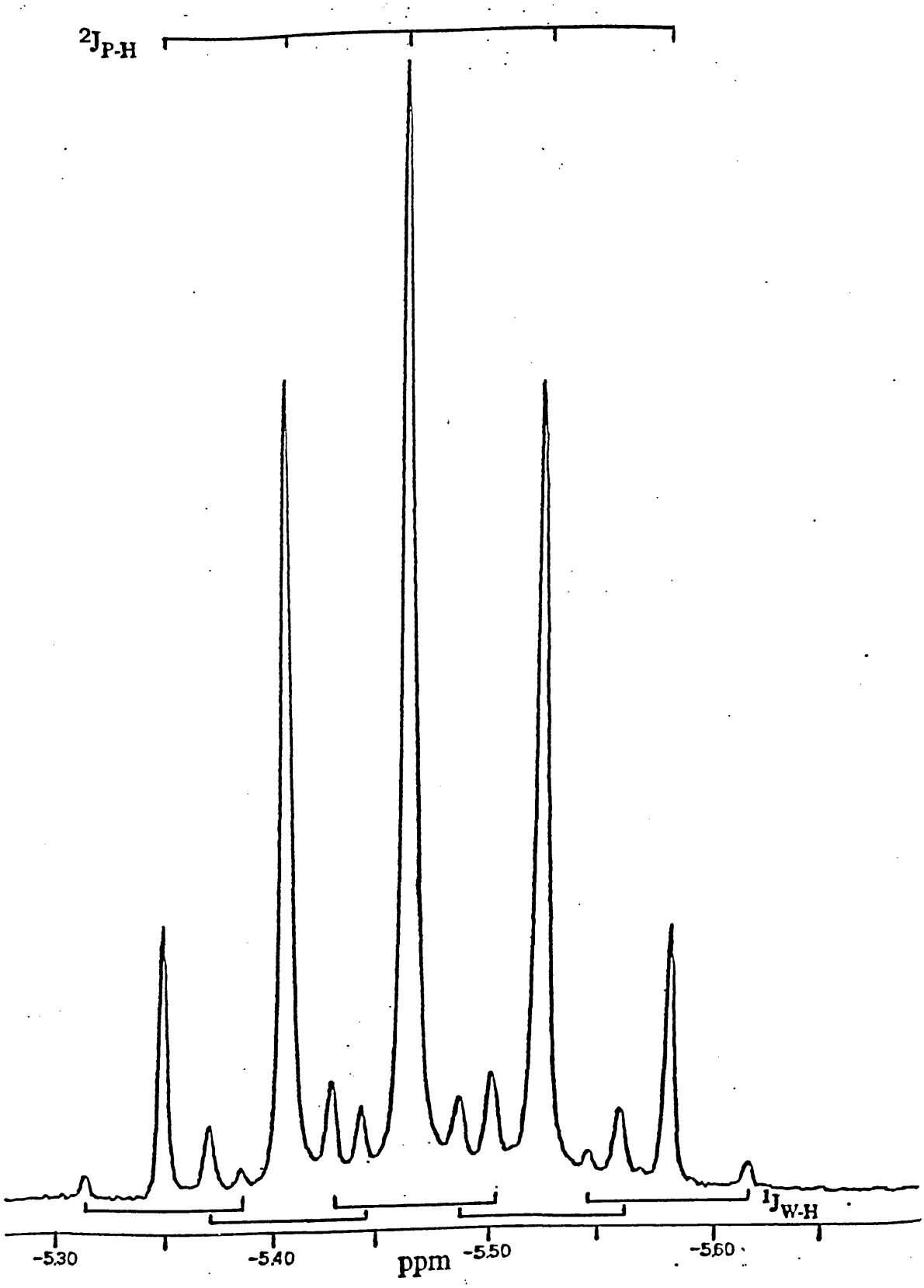


Figure 1.6 : ^1H NMR spectrum of $WH_4(DMPE)_2$ at 343K .

Table 1.3 : Physical and analytical[a] data for tungsten DMPE complexes.

Compound	Colour	M.Pt. / °C	Analytical Data % C	H	N	Other
$WCl_2(DMPE)_2$	Dark red	310-312	25.1	5.8	-	22.1(P)
			(26.0)	(5.8)	-	(22.3)
$[WCl(\eta^2\text{-MeCN})(DMPE)_2]BPh_4$	Pale green	190-192	51.1	6.2	1.4	-
			(51.9)	(6.3)	(1.6)	-
$[WCl_4(DMPE)_2]SbCl_6$	Dark green	230-232	15.3	3.4	-	12.5(P)
			(15.0)	(3.4)	-	(12.9)
$[WH(AlH_4)(DMPE)_2]_2$	Bright yellow	213-215 decomp.	28.0	7.2	-	23.8(P)
			(28.0)	(7.0)	-	(24.0)

Table 1.3 (continued)

Compound	Colour	M.Pt. / °C	Analytical Data % C	H	N	Other
$WH_4(DMPE)_2$	Pale yellow	150-152	29.5	7.4	-	25.4(P)
			(29.4)	(7.4)	-	(25.4)

[a] Calculated values in parentheses.

Table 1.4 : ^{1}H NMR data for tungsten DMPE compounds [a].

Compound	δ / ppm	Assignment	
$WCl_2(DMPE)_2$	19.55 (s)	4H	$PC\underline{H}_2$
	-3.99 (s)	12H	$P\underline{Me}_2$
$[WCl(\eta^2\text{-}MeCN)(DMPE)_2]BPh_4$	7.31-6.96 (m)	20H	$B\underline{Ph}_4$
(CD_3CN)	3.42 (s)	3H	$C\underline{H}_3CN$
	1.57-1.35 (m)	32H	DMPE
$[WH(AlH_4)(DMPE)_2]_2$	4.10 (m)	4H	terminal Al-$\underline{H}$ & Al-$\underline{H}$-Al
	1.58 (m)	32H	DMPE
	-5.50 (m)	4H	W-$\underline{H}$-Al
	-8.30 (m)	2H	terminal W-$\underline{H}$

Table 1.4 (continued)

Compound	δ / ppm	Assignment	
$WH_4(DMPE)_2$	1.56-1.43 (m)	32H	DMPE
	-5.46 (m)	4H	W-H

[a] All spectra in C_6D_6 unless otherwise stated.

EXPERIMENTAL

Microanalyses were by Pascher, Remagen and Imperial College Microanalytical Laboratories. Melting points were determined in sealed capillaries and are uncorrected. Spectrometers : IR, Perkin-Elmer 1720 Fourier Transform, spectra in Nujol mulls , (values in cm^{-1}). NMR, Bruker WM-250 and Jeol FX90Q. δ values in ppm in C_6D_6 unless otherwise stated, and referenced to $SiMe_4$ (^1H) , external 85% H_3PO_4 (^{31}P) and external $[Al(H_2O)_6]^{3+}$ (^{27}Al). EPR, Varian E-12 (X-band in CH_2Cl_2 at 293K). Conductivity: Data Scientific PTI-18 Conductivity Meter (*ca.* 0.01 M solutions). Magnetic moments were measured at 30°C on the Jeol FX90Q by the Evans' method in toluene[31].

X-ray crystallography : Crystals were sealed under argon in thin-walled glass capillaries. All crystallographic measurements were made at 293K using a CAD4 diffractometer and graphite monochromated Mo-K_α radiation ($\lambda = 0.71069$Å).

All manipulations were carried out under purified argon, dinitrogen or under vacuum. Solvents were distilled under argon from sodium-benzophenone (hexane, Et_2O and THF), sodium (toluene and MeOH) or calcium hydride (CH_2Cl_2 and MeCN). WCl_4[32] and DMPE[33] were prepared according to the literature. $WCl_4(THF)_2$ was prepared by adding excess THF to $WCl_4(SEt_2)_2$[34] and stirring for a few minutes when the THF complex precipitates as an orange powder which was collected washed with THF (3 x 30 cm^3) and dried . Sodium naphthalenide was prepared by adding a slight excess of finely cut sodium to a solution of naphthalene in THF . The solution was stirred for 12 hours , filtered and titrated against 0.01M hydrochloric acid.

***Trans*-bis[1,2-bis(dimethylphosphino)ethane]dichlorotungsten(II).**

To a suspension of $WCl_4(THF)_2$ (6.00 g; 13.00 mmol) in THF (100 cm^3) at 0°C was added DMPE (4.50 cm^3; 27.00 mmol) and sodium naphthalenide (92 cm^3 of 0.28M solution in THF; 26 mmol). The solution was stirred at room temperature for *ca.* 18 hours, filtered and evaporated to dryness. The naphthalene was removed by sublimation *in vacuo* and the remaining residue was extracted with warm hexane (4 x 50 cm^3). The combined extracts were concentrated (*ca.* 100 cm^3), filtered and cooled (-78°C) to give 2.10 g of dark red crystals of *trans*-$WCl_2(DMPE)_2$. Further crops of crystals may be obtained from the supernatant. Combined yield 2.51 g (35%).

IR : 1418s, 1291m, 1277s, 1227w, 1112m, 1073m, 989m, 927vs, 921vs, 888s, 859s, 832s, 784s, 730s, 698s, 630s, 452m, 324s .

NMR : $^{31}P\{^1H\}(CDCl_3)$: 16.93 (s) ; $^1J_{W\text{-}P}$ = 157.29 Hz .

Magnetic moment : μ_{eff} = 2.20 BM .

***Trans*-(η^2-acetonitrile)(chloro)[1,2-bis(dimethylphosphino)ethane]tungsten(II) - tetraphenylborate.**

To *trans*-$WCl_2(DMPE)_2$ (0.31 g; 0.56 mmol) in MeCN (50 cm^3) was added an excess of $NaBPh_4$ (0.40 g; 1.17 mmol). The solution was refluxed for *ca.* 24 hours, cooled and filtered. After evaporation the residue was extracted with CH_2Cl_2 (30 cm^3) and the extract evaporated to dryness. The residue was crystallised from MeCN to give a pale green crystalline solid. Yield 0.35 g (71%).

IR : 3050s, 3032s, 1945w, 1881w, 1814w, 1580m, 1428s, 1416s, 1299m, 1288m, 1267w, 1182w, 1149w, 1033w, 944s, 930s, 891m, 865w, 851w, 793w, 745s, 710s, 703s, 697m, 649m, 625w, 615m, 604s, 485w, 452w .

Conductivity (MeCN) : Λ_M = 86 ohm^{-1} cm^2 mol^{-1}.

NMR : $^{31}P\text{-}\{^1H\}(CD_3CN)$: 14.92 (s) ; $^1J_{W\text{-}P}$ = 118.52 Hz .

Trans-bis[1,2-bis(dimethylphosphino)ethane]tetrachlorotungsten(V) - hexachloroantimonate(V).

To *trans*-$WCl_2(DMPE)_2$ (0.30 g, 0.54 mmol) in MeCN (50 cm^3) was added $SbCl_5$ (1.20 cm^3 of 1M solution in CH_2Cl_2 ; 1.20 mmol). The initial red solution was refluxed for *ca.* 12 hours, after which the colour was green. The solution was filtered, concentrated (*ca.* 15 cm^3) and cooled (-20°C) to give dark green crystals. Further crops of crystals may be obtained from the supernatant. Combined yield 0.33 g (73%) .

IR : 1413s, 1295m, 1284s, 1247w, 1132w, 1086w, 1001w, 938vs, 901s, 853w, 794w, 749m, 717s, 659m, 643w, 453m .

Conductivity (MeCN) : $\Lambda_M = 90\ ohm^{-1}.cm^2.mol^{-1}$.

Bis[1,2-bis(dimethylphosphino)ethane](tetrahydridoaluminato)-hydridotungsten(II) dimer.

To *trans*-$WCl_2(DMPE)_2$ (0.22 g; 0.40 mmol) in Et_2O (50 cm^3) at -78°C was added a suspension of $LiAlH_4$ (0.12 g; 3.20 mmol) in Et_2O (30 cm^3). Upon warming to room temperature the solution turned orange and gas was evolved. After stirring for *ca.*12 hours the solution was filtered, concentrated (*ca.* 50 cm^3) and cooled (-20°C) to give yellow crystals. Further crops of crystals may be obtained from the supernatant. Combined yield 0.29 g (72%) .

IR : 1681s, 1650s, 1420s, 1336s, 1291m, 1275s, 1228w, 1118w, 1077w, 936vs, 922vs, 886s, 836s, 787m, 696s, 636s, 575m, 535m, 461m.

NMR : $^{31}P\{^1H\}$: 20.84 (s) ; $^1J_{W\text{-}P} = 108.55$ Hz.

$^{27}Al\{^1H\}$: 99 (br s) ('t', $w_{1/2} = 4500$ Hz.) .

The molybdenum analogue was obtained similarly from *trans*-$MoCl_2(DMPE)_2$[2]. X-ray quality crystals were grown from Et_2O .

Bis[1,2-bis(dimethylphosphino)ethane]tetrahydridotungsten(IV).

To a solution of $[WH(AlH_4)(DMPE)_2]_2$ (0.42 g; 0.41 mmol) in hexane (30 cm^3) was

added MeOH dropwise until gas evolution ceased. The solution was filtered, evaporated to dryness and extracted with hexane. The filtered extract was concentrated (*ca.* 10 cm^3) and cooled (-20°C) to give pale yellow crystals. Further crops of crystals may be obtained from the supernatant. Combined yield 0.14 g (70%) .

IR : 1745m, 1720s, 1415m, 1283m, 1270s, 1230w, 1115w, 1080w, 923vs, 885s, 835s, 787s, 700s, 639s, 549w, 456m .

NMR : $^{31}P\{^1H\}$: 22.92 (s) ; $^1J_{W\text{-}P}$ = 81.97 Hz .

CHAPTER 2

THE SYNTHESIS AND CHARACTERISATION OF $[Ag_2(DMPE)_4][BPh_4]_2$

Introduction.

There are a number of monomeric, dimeric and tetrameric phosphine complexes of silver(I)[35,36]. With monophosphines, the general formula for the complexes is AgP_nX, where X = halide or pseudohalide, and P = a tertiary phosphine. For triaryl and mixed alkyl / aryl tertiary phosphines n could be 1to 4, whereas for trialkyl phosphines n is usually 1. The 1 : 1 complexes are tetrameric with either cubane or chair structures, depending on the steric requirements of X and the phosphine[37-44] (Figure 2.1).

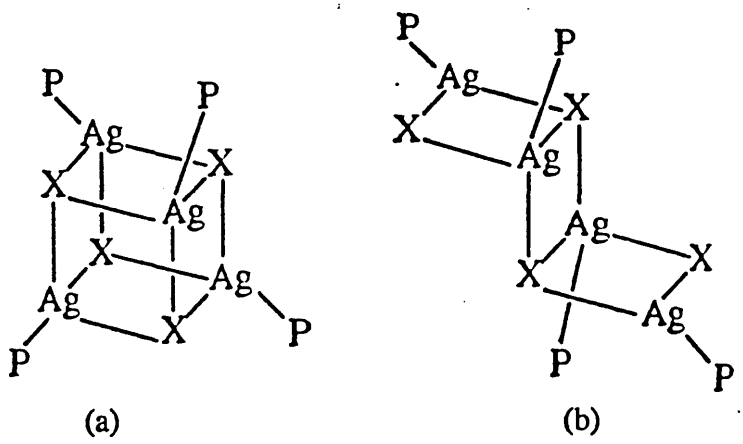


Figure 2.1 : Cubane (a) and chair (b) structures for R_3PAgX complexes.

There are also some 1 : 1 complexes with bulky phosphine ligands [e.g. PBu^t_3, PCy_3 and $P(o\text{-}MeC_6H_4)_3$] and X = ClO_4, which have linear two-coordinate monomeric structures[45].The 1 : 2 complexes are generally dimeric with bridging X. For bulky phosphines [e.g. PBu^t_3[46] and $P(mes)_3$[47]] the complexes contain the linear cation $[R_3P\text{-}Ag\text{-}PR_3]^+$. Complexes where n = 3 are not very common. The only example which has been characterised by X-ray crystallography is $AgCl(PPh_3)_3$[48]. It is monomeric with a distorted tetrahedral arrangement around the silver ion. 1 : 4 complexes are also rare. No structures have been determined, but some have been detected by ^{31}P NMR in solution and are believed to be tetrahedral with the halide ion not coordinated. The elimination of a phosphine group to give the corresponding 1: 3 complex is thought to be quite facile[49].

Diphosphine complexes of silver tend to be dimers or tetramers with bridging phosphines, having a general formula of $AgXP_2$ (X = halide; P_2 = diphosphine)[50-53]. With 2,11-bis(diphenylphosphinomethyl)benzo[*c*]phenanthrene, monomeric complexes are known[54].

This chapter describes the synthesis and characterisation of a new type of silver(I) diphosphine complex, containing no halide or pseudohalide ions.

Results and discussion.

The interaction of AgO_3SCF_3 with two equivalents of DMPE and of sodium tetraphenylborate in MeCN allows isolation of the colourless, air stable complex $[Ag_2(DMPE)_4][BPh_4]_2$. It is soluble in MeCN, and sparingly soluble in CH_2Cl_2 and THF. X-ray quality crystals were obtained by slow evaporation of a MeCN solution of the complex in air. The crystal structure contains a dimeric cation, and $[BPh_4]^-$ anions. A diagram of the cation which lies on a centre of symmetry, is shown in Figure 2.2. Selected bond lengths and angles are given in Table 2.1 .

In the dication, each silver ion is coordinated by two phosphorus atoms from a chelating DMPE ligand and then by one phosphorus from each of two bridging DMPE ligands. The AgP_4 geometry is distorted tetrahedral, the largest distortion arising from the restricted bite of the chelating DMPE [P-Ag-P = 83.5(2)°]. The Ag-P distances vary considerably, over a range of almost 0.1°, with those in the chelate ring the larger. Distances in other four-coordinate silver phosphine complexes vary from 2.42 - 2.50Å. The ^1H and ^{31}P NMR spectra are consistent for the structure. Attempts to oxidise the cation to a silver(II) species, chemically or electrochemically were unsuccessful.

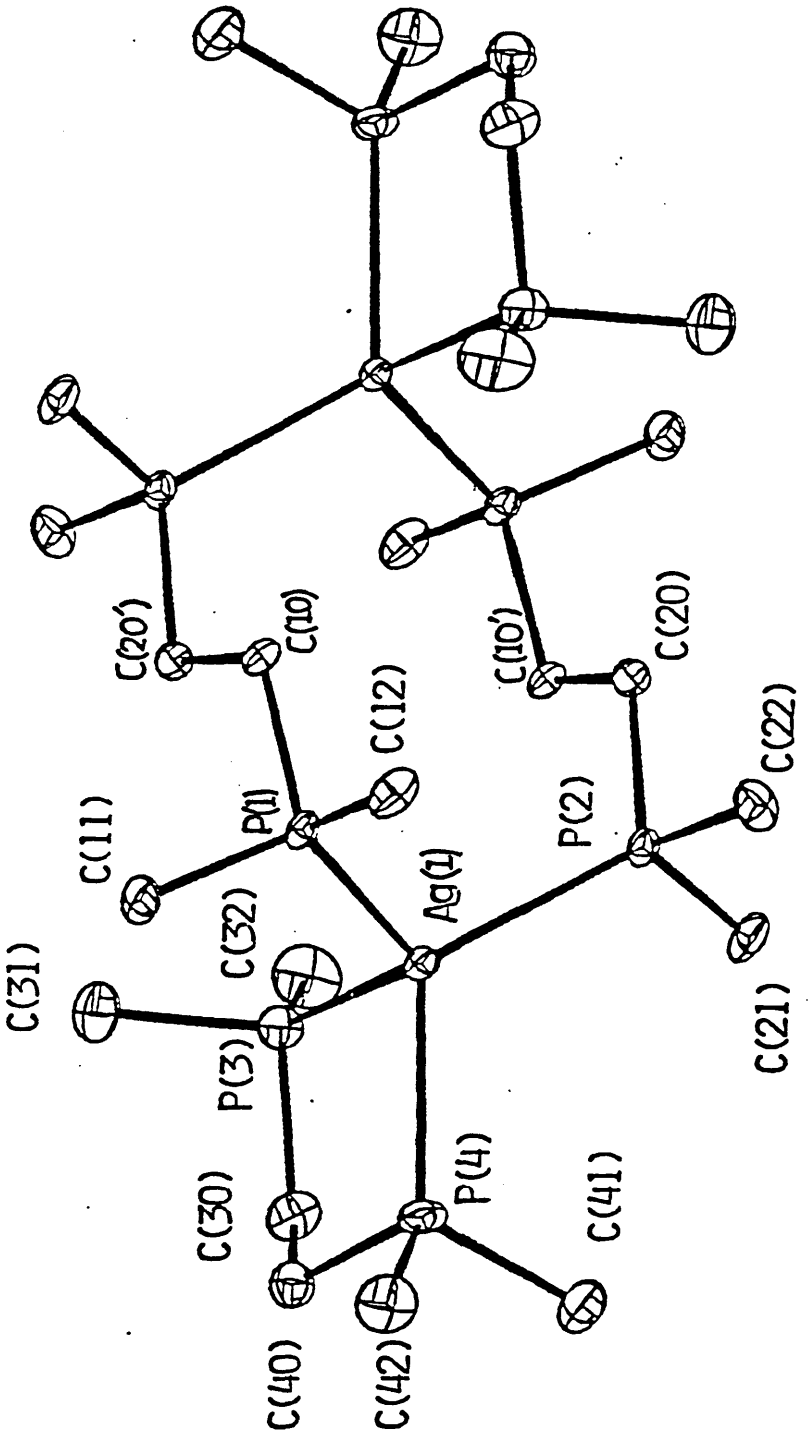


Figure 2.2 : The crystal structure of the $[(DMPE)Ag(\mu\text{-}DMPE)]_2^{2+}$ cation.

Table 2.1 : Selected bond lengths and angles for $[(DMPE)Ag(\mu\text{-}DMPE)]_2^{2+}$.

Bond lengths (Å).

P(1)-Ag(1)	2.471(4)	P(2)-Ag(1)	2.465(4)
P(3)-Ag(1)	2.557(6)	P(4)-Ag(1)	2.491(4)
C(10)-P(1)	1.840(11)	C(11)-P(1)	1.842(12)
C(12)-P(1)	1.829(14)	C(20)-P(2)	1.827(10)
C(21)-P(2)	1.856(12)	C(22)-P(2)	1.850(13)
C(30)-P(3)	1.837(13)	C(31)-P(3)	1.860(19)
C(32)-P(3)	1.856(19)	C(40)-P(4)	1.864(13)
C(41)-P(4)	1.906(17)	C(42)-P(4)	1.791(18)
C(10)-C(20')	1.551(16)	C(40)-C(30)	1.446(19)

Bond angles (°).

P(2)-Ag(1)-P(1)	109.6(2)	P(3)-Ag(1)-P(1)	114.1(2)
P(3)-Ag(1)-P(2)	114.4(2)	P(4)-Ag(1)-P(1)	115.6(2)
P(4)-Ag(1)-P(2)	117.6(2)	P(4)-Ag(1)-P(3)	83.5(2)
C(10)-P(1)-Ag(1)	113.8(4)	C(11)-P(1)-Ag(1)	117.7(4)
C(11)-P(1)-C(10)	103.6(5)	C(12)-P(1)-Ag(1)	116.1(5)
C(12)-P(1)-C(10)	101.2(5)	C(12)-P(1)-C(11)	102.2(6)
C(20)-P(2)-Ag(1)	115.3(4)	C(21)-P(2)-Ag(1)	115.3(4)
C(21)-P(2)-C(20)	102.7(6)	C(22)-P(2)-Ag(1)	117.8(5)
C(22)-P(2)-C(20)	99.2(5)	C(22)-P(2)-C(21)	104.1(7)
C(30)-P(3)-Ag(1)	102.9(5)	C(31)-P(3)-Ag(1)	118.0(6)
C(31)-P(3)-C(30)	99.8(7)	C(32)-P(3)-Ag(1)	128.0(5)
C(32)-P(3)-C(30)	101.9(7)	C(32)-P(3)-C(31)	101.6(9)
C(40)-P(4)-Ag(1)	103.9(5)	C(41)-P(4)-Ag(1)	115.3(5)
C(41)-P(4)-C(40)	100.5(7)	C(42)-P(4)-Ag(1)	126.4(6)
C(42)-P(4)-C(40)	105.0(7)	C(42)-P(4)-C(41)	102.4(8)
P(2)-C(20)-C(10')	111.7(9)	P(1)-C(10)-C(20')	111.4(9)
C(40)-C(30)-P(3)	115.4(10)	C(30)-C(40)-P(4)	114.4(8)

EXPERIMENTAL

Microanalysis was by Imperial College Microanalytical Laboratories. Details of spectrometers and experimental procedures are given in the experimental section of Chapter 1.

Tetrakis[bis(1,2-dimethylphosphino)ethane] disilver(I)bis(tetraphenylborate).

To AgO_3SCF_3 (0.20 g; 0.78 mmol) in MeCN (30 cm^3) was added DMPE (0.30 cm^3; 1.80 mmol) and $NaBPh_4$ (0.59 g; 1.70 mmol). The solution was stirred for *ca.* 18 hours, when the solvent was removed, the white residue washed with Et_2O (2 x 15 cm^3) and extracted into CH_2Cl_2 (3 x 30 cm^3). Reduction in volume and cooling (-20°C) gave 0.45 g of a white powder. Further crops of the compound may be obtained from the supernatant. Combined yield 0.87 g (77%). Melting point 205-207°C.

Analytical data : Found C, 59.6; H, 7.3 . $C_{72}H_{104}Ag_2B_2P_8$ requires C,59.9; H,7.2%.

Conductivity (MeCN) : Λ_M = 175 ohm^{-1} cm^2 mol^{-1} .

NMR : ^1H (CD_3CN) : 7.23-6.90 (m, 10H, $B\underline{Ph}_4$); 1.66 (s, 16H, -$C\underline{H}_2$-);

1.15 (s, 48H, $C\underline{H}_3$) .

$^{31}P\{^1H\}$ (CD_3CN) : -19.54 (s) and -26.32 (s) in a 1 : 1 ratio .

IR : 3052m, 3036m, 1934w, 1878w, 1814w, 1579m, 1424s, 1419s, 1299w, 1288w, 1270w, 1174w, 1148w, 1133w, 1092m, 1063w, 1032m, 940s, 908m, 889m, 878m, 845w, 748s, 730s, 703s, 671w, 645w, 624m, 613s, 500w, 474w, 464w .

CHAPTER 3

THE SYNTHESIS AND CHARACTERISATION

OF

RHENIUM IMIDO COMPLEXES

CHAPTER 3

Introduction

Arylimido and alkylimido complexes have been known for a long time and have continued to attract attention. For rhenium(V) the first reported example was Re(NPh) - $Cl_3(PEt_2Ph)_2$ made by Chatt and Rowe in 1962, by direct aminolysis of the rhenium oxo complex, $ReOCl_3(PEt_2Ph)_2$, with phenylamine (Scheme 3.1)[55].

$$ReOCl_3(PEt_2Ph)_2 + PhNH_2 \longrightarrow Re(NPh)Cl_3(PEt_2Ph)_2 + H_2O$$

Scheme 3.1

Although this route did not proceed analogously with alkylamines, it was, however, used to prepare an extensive series of arylimido rhenium(V) complexes of general formula $Re(N\text{-}p\text{-}XC_6H_4)Cl_3L_2$[56] where X = I, Br, Cl, F, Me, OMe, COMe, CN, NH_2, NMe_2, and p-$C_6H_4NH_2$; L = PPh_3, PEt_3, PEt_2Ph and L_2 = depe, dppe . The first alkylimido rhenium(V) complexes were reported by Shandles and Murmann in 1965[57]. These were salts of the $[Re(NMe)(MeNH_2)_4Cl]^{2+}$ cation isolated as the chloride, iodide, perchlorate and tetraphenylborate. The corresponding hydroxy complexes, $[Re(NMe)(MeNH_2)_4OH]X_2$ where X = I or ClO_4 , were also prepared by hydrolysis of the chloro ligand. Alkylimido rhenium(V) complexes have also been isolated from the reaction of $ReOCl_3(PPh_3)_2$ with 1,2-dialkylhydrazinehydrochlorides (Scheme 3.2)[58].

$$ReOCl_3(PPh_3)_2 + RNH\text{-}NHR\cdot 2HCl \longrightarrow Re(NR)Cl_3(PPh_3)_2 + RNH_3Cl + HCl + PPh_3O$$

R = Me, Et, Pr^n, Cy

Scheme 3.2

Complexes prepared in this way included those derivatives obtained from the substitution of the PPh_3 groups by other ligands such as PEt_2Ph, $PEtPh_2$, dppe and $AsMe_2Ph$. The first reported X-ray crystal structure of a rhenium(V) imido complex was that of $Re(NMe)Cl_3(PEtPh_2)_2$[59], prepared by the above method.

Later on, an improved synthesis of some of the already known rhenium(V) arylimido complexes was reported. It was found that by reaction of $ReOCl_3(PPh_3)_2$ with RNSO (R = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) in boiling benzene the corresponding arylimido complexes are obtained (Scheme 3.3)[60].

$$ReOCl_3(PPh_3)_2 + RNSO \longrightarrow Re(NR)Cl_3(PPh_3)_2 + SO_2$$

Scheme 3.3

The reactions of the above arylimido complexes have been extensively studied since then, and have generated a number of new rhenium(V) imido species. Some reactions involve the replacement of one or both of the PPh_3 groups[61]. Others are substitution reactions of the chloro ligands where the Re=NR moiety is again conserved. A series of methyl derivatives (prepared from $Re(NPh)Cl_3(PMe_3)_2$ and dimethylmagnesium) was one of the first sets of organoimido rhenium(V) complexes to appear in the literature[62].

A number of species containing both imido and hydrido ligands have been isolated from the interaction of $Re(NPh)Cl_3(PPh_3)_2$ with sodium isopropanolate, zinc oxide or triethylamine in alcoholic solutions[63].

Rhenium(V) imido complexes containing sterically hindered thiolate ligands have also been reported, isolated from reaction of the related starting material, $Re(NR)Cl_3(PPh_3)_2$ (R = Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$) with Htipt and triethylamine (Htipt = 2,4,6-tri - isopropylbenzenethiol)[64].

Latest additions to the series of rhenium(V) imido species include some novel cyclopentadienyl complexes[65,66], an unstable rhenium(V) anion[67], $[Re(NBu^t)_2(xylyl)_2]^-$, $Re(NPh)Cl_3(NH_2CMe_3)_2$[68], $Re(NBu^t)_2(NO)(xylyl)_2$[67] and

$Re(NBu^t)(mes)(\sigma,\eta^5\text{-}C_{27}H_{32})$[67] (Figure 3.1).

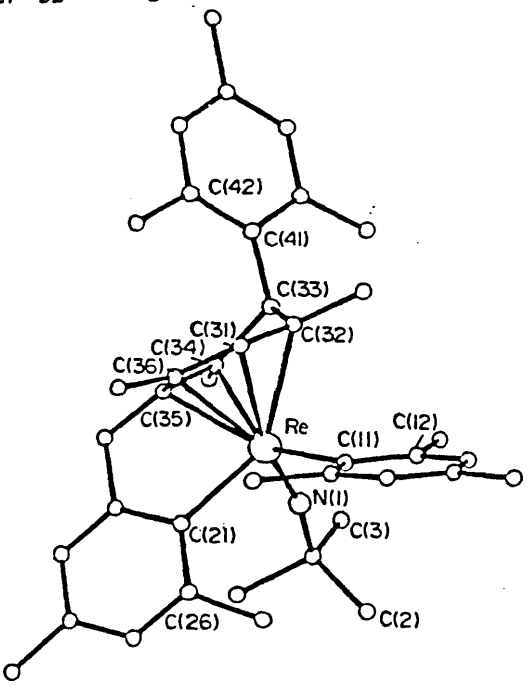


Figure 3.1 : The crystal structure of $Re(NBu^t)(mes)(\sigma,\eta^5\text{-}C_{27}H_{32})$.

Rhenium(VI) imido complexes are not as common as the rhenium(V) analogues. $Re(N\text{-}p\text{-}MeC_6H_4)Cl_4(OPPh_3)$ was thought to be one of the products from the oxygenation of $[Re(N\text{-}p\text{-}MeC_6H_4)Cl_3(PPh_3)]_n$ in CCl_4 or benzene[69]. $Re(NR)Cl_4$ - $(POCl_3)$, where R = CCl_3 or C_2Cl_5 , and the corresponding salts $Ph_4As[Re(NR)Cl_5]$ have also been reported[70,71]. $ReOCl_4$ was found to react with PhNCO to give $[Re(NPh)Cl_4]_n$, which in THF or MeCN gives the adducts $Re(NPh)Cl_4(THF)$ and $Re(NPh)Cl_4(MeCN)$ respectively. Interaction with Me_4NCl gave $[Me_4N][Re(NPh)$ - $Cl_5]$[68]. Recently two organometallic rhenium(VI) imido complexes, $Re(NBu^t)_2R_2$ (R = mes[72], xylyl[67]), have been prepared and characterised by X-ray crystallography. An interesting rhenium(VI) imido complex is $[Re(NBu^t)_2(\mu\text{-}NBu^t)]_2$[72] which has been prepared by reduction of the rhenium(VII) complex, $Re(NBu^t)_3(OSiMe_3)$. Another dimeric rhenium(VI) imido complex is $Re_2(NBu^t)_3Br(O)(mes)(CH_2Me_2C_6H_2O)$[13] (Figure 3.2).

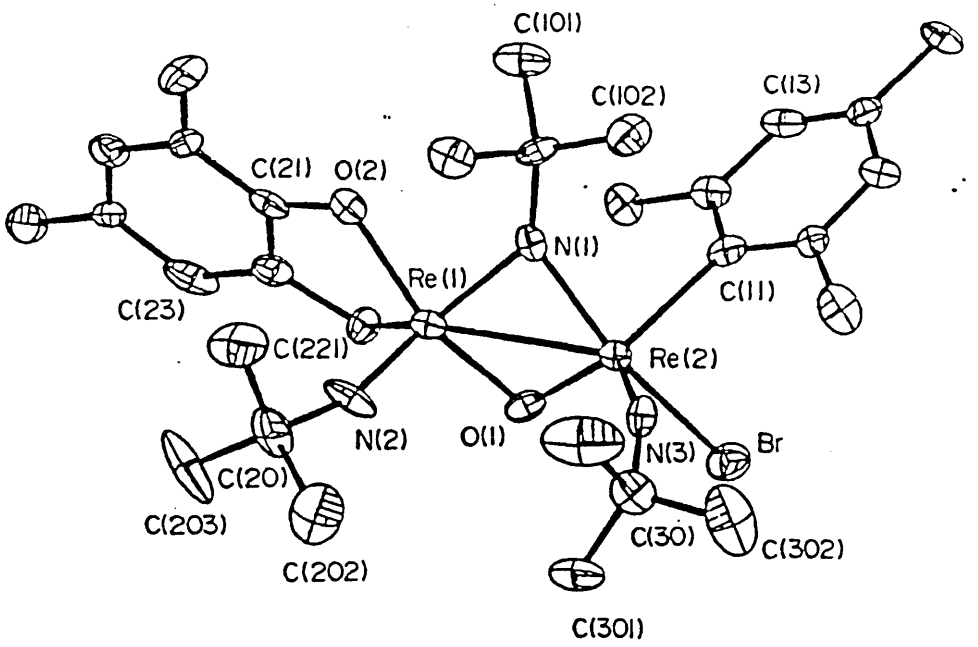


Figure 3.2 : The crystal structure of $Re_2(NBu^t)_3Br(O)(mes)(CH_2Me_2C_6H_2O)$.

The first examples of rhenium(VII) imido complexes were reported by Nugent *et al.*[73,74]. The reaction of $ReO_3(OSiMe_3)$ with $Bu^tNHSiMe_3$ was found to give $Re(NBu^t)_3(OSiMe_3)$[74]. However, when a deficiency of the amine is used the dimeric complex, $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}OReO_3)$[73,74] is formed (Figure 3.3).

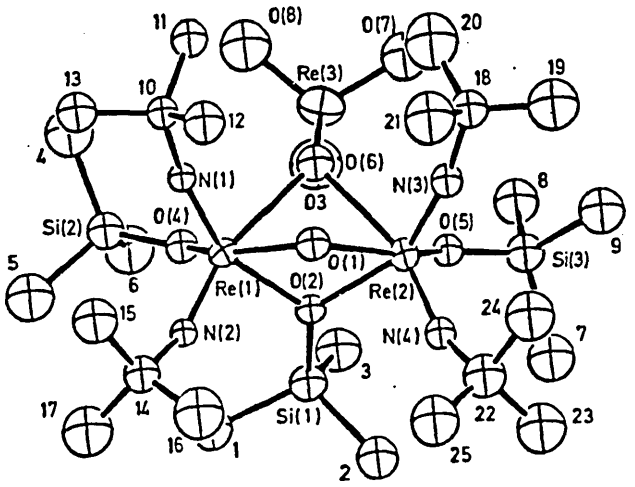


Figure 3.3 : The structure of $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}OReO_3)$.

$Re(NBu^t)_2Cl_3$[75] and $Re(NBu^t)_3Cl$[72] are also well known rhenium(VII) imido

complexes and are both prepared from $Re(NBu^t)_3(OSiMe_3)$. All of the above have been characterised by X-ray crystallography, and have been widely used as starting materials for the preparation of other rhenium(VII) imido complexes. A series of aryl complexes, including some with oxo groups, has been prepared by Wilkinson *et al.*[67,72,76]. Schrock and co-workers have generated some rhenium(VII) bis-imido alkyl, alkylidene and alkylidyne complexes as well as some mixed alkyl / halide examples, such as $ReCl_2(NR)_2(CH_2Bu^t)$ where R = 2,6-diisopropylphenyl[75,77-79]. $Re(NBu^t)_3(OSiMe_3)$ was used by Hermann *et al.* in nucleophilic substitution reactions with organo-lithium or Grignard reagents to prepare new methyl, ethyl, allyl and phenylalkynyl derivatives[66]. Also, mono- and dinuclear methylrhenium(VII) imido complexes were isolated by sequential deoxygenation of ReO_3Me *via* decarboxylation upon treatment with 2,6-diisopropylphenyl isocyanate[66]. Halonitrene complexes of rhenium(VII) are also known[80]. With RNCO (R = 2,6-diisopropylphenyl isocyanate), $ReO_3(OSiMe_3)$ reacts to give a mixture of products believed to be $Re_2O_x(NR)_{7-x}$[74]. With $LiN(SiMe_3)_2$ the product is $(Me_3SiO)_2Re[N(SiMe_3)_2](NSiMe_3)_2$[81]. One of the latest reported examples of a rhenium(VII) imido complex is the *tert*-butylimido analogue of the perrhenate(VII) ion isolated as the lithium salt, $Li(TMED)Re(NBu^t)_4$[82].

In this chapter a range of novel rhenium imido species are introduced. $Re(NBu^t)_3Cl$ and $Re(NBu^t)_3(OSiMe_3)$ have been used in nucleophilic substitution reactions with lithium reagents, and a sodium salt, giving a number of rhenium(VII) complexes. Interaction of the chloride with dicobalt octacarbonyl gives a compound of stoichiometry $ReCo_3(NBu^t)_2(CO)_{10}$. Interaction of $AgCF_3CO_2$ with $Re(NBu^t)_3(OSiMe_3)$ and $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}OReO_3)$ (Figure 3.4) gives dimeric complexes with bridging CF_3CO_2 groups. $Re(NBu^t)_3Cl$ reacts with $SbCl_5$ in refluxing MeCN affording the bis-*tert*-butylimido salt, $[Re(NBu^t)_2Cl_2(MeCN)_2]SbCl_6$.

Results and discussion.

Dialkyl and arylphosphido complexes.

$Re(NBu^t)_3(OSiMe_3)$ reacts cleanly with $LiPR_2$ (R = Ph, $SiMe_3$) and LiPH(mes) in Et_2O at -78°C to give the corresponding phosphido complexes; $Re(NBu^t)_3PPh_2$, $Re(NBu^t)_3P(SiMe_3)_2$ and $Re(NBu^t)_3PH(mes)$. The diphenylphosphido complex is obtained as an oil from hexane, but can be crystallised from MeCN to give the product as a yellow crystalline solid in *ca.* 40% yield. $Re(NBu^t)_3P(SiMe_3)_2$ and $Re(NBu^t)_3$-PH(mes) are, however, obtained as yellow-orange solids from hexane in yields of *ca.* 60 and 45% respectively. All three have low melting points, are soluble in all common organic solvents, and are moderately air and moisture sensitive. The molecular ion is observed in the mass spectrum of all three complexes.There is a marked difference between the reactivities of $Re(NBu^t)_3X$, X = Cl or $OSiMe_3$, with the lithium reagents. Reaction of the chloride with $LiPPh_2$ gives $(Ph_2P)_2$ as the only identifiable product; characterised by its $^{31}P\{^1H\}$ NMR spectrum ($^{31}P\{^1H\}$ = -15.12 ppm in C_6D_6) and melting point (120°C)[83]. Similar species have been reported in reactions of Cp_2MCl_2 (M = Hf, Zr) with $LiPR_2$ (R = Et, Cy, Ph) at ambient temperature[84]. The ^1H NMR spectrum of the diphenylphosphido complex shows two multiplets (centred at 7.86 and 7.14 ppm) for the aromatic protons and a singlet for the NBu^t protons (at 1.26 ppm). The two multiplets do not show any temperature dependency from -90 to+100°C. This pattern is probably due to a complicated spin system, rather than fluxionality (as a result of phosphorus-*p* to metal-*d* π-bonding). The presence of three good π-donating ligands on the metal makes lone pair donation from phosphourus into the Re-P bond quite difficult. The ^{31}P NMR spectrum shows a quintet centred at -8.78 ppm, due to the coupling of the four *ortho*-H nuclei on the phenyl rings with the ^{31}P nucleus ($^4J_{P\text{-}H}$ = 7Hz.). Decoupling the proton resonances gives a sharp singlet at -8.78 ppm. For $Re(NBu^t)_3P(SiMe_3)_2$ the $SiMe_3$ protons are split into a doublet by the phosphorus nucleus ($^3J_{P\text{-}H}$ = 4.5 Hz.). The $^{31}P\{^1H\}$ NMR spectrum has a singlet at -212.33 ppm. The ^1H NMR spectrum of $Re(NBu^t)_3PH(mes)$ shows a doublet centred at 5.37 ppm for the phosphido proton ($^1J_{P\text{-}H}$ = 195 Hz.). The same coupling constant is observed in

the ^{31}P NMR spectrum of the complex, where the doublet is centred at -153.1 ppm. Terminal dialkyl- or diarylphosphido complexes are relatively rare; for rhenium there is the homoleptic anion $[Re(PCy_2)_4]^-$ [84-87].

Preliminary structural data on X-ray quality crystals of $Re(NBu^t)_3PPh_2$ confirm the monomeric nature of this complex. It crystallises in the $P\bar{1}$ space group. There are two crystallographically independent molecules in the asymmetric unit cell. The crystal structure of one of the two independent molecules is shown in Figure 3.4. A complete description of the crystal structure, including a table of bond lengths and angles will appear in a forthcoming publication.

Attempts to deprotonate $Re(NBu^t)_3PH(mes)$ in the hope of obtaining a phosphinidene[89] species, $[(Bu^tN)_3Re{=}P(mes)]^-$, by use of Bu^nLi in hexane, MeLi in Et_2O or by refluxing in toluene with Et_3N were unsuccessful. Although deprotonation occurs, other reactions follow and the only rhenium containing species isolated was the rhenium(VI) dimer, $[Re(NBu^t)_2(\mu\text{-}NBu^t)]_2$, whose structure has been determined[72] . From the Bu^nLi reaction in hexane the only other product that could be isolated was a colourless, crystalline solid that has been found to be the cyclophosphane $[P(2,4,6\text{-}Me_3C_6H_2)]_3$. Cyclophosphanes, $(PR)_n$, n = 3-6, are known compounds[88-92]. The trimers, with bulky R groups[91] , have two of the R groups on one side of the P_3 plane. The $^{31}P\{^1H\}$ NMR spectrum of $[P(mes)]_3$ has two singlets at -111.20 and -118.35 ppm in a 2:1 ratio that are in close agreement with values reported for similar compounds[89]. The mechanism of this reaction leading to the formation of the rhenium(VI) dimer and the cyclophosphane is not clear. The oily lithium containing residue has eluded characterisation.

Dialkyl- and diarylamido complexes.

The interaction of $Re(NBu^t)_3Cl$ with $LiNMe_2$ in Et_2O at -78°C gives an orange-brown solution from which the dimethylamido complex, $Re(NBu^t)_3NMe_2$, is isolated as a yellow high boiling oil, in *ca.* 35% yield. However, a similar reaction with $LiNPh_2$ does not proceed in the same manner. At -78°C a deep red solution is obtained, which

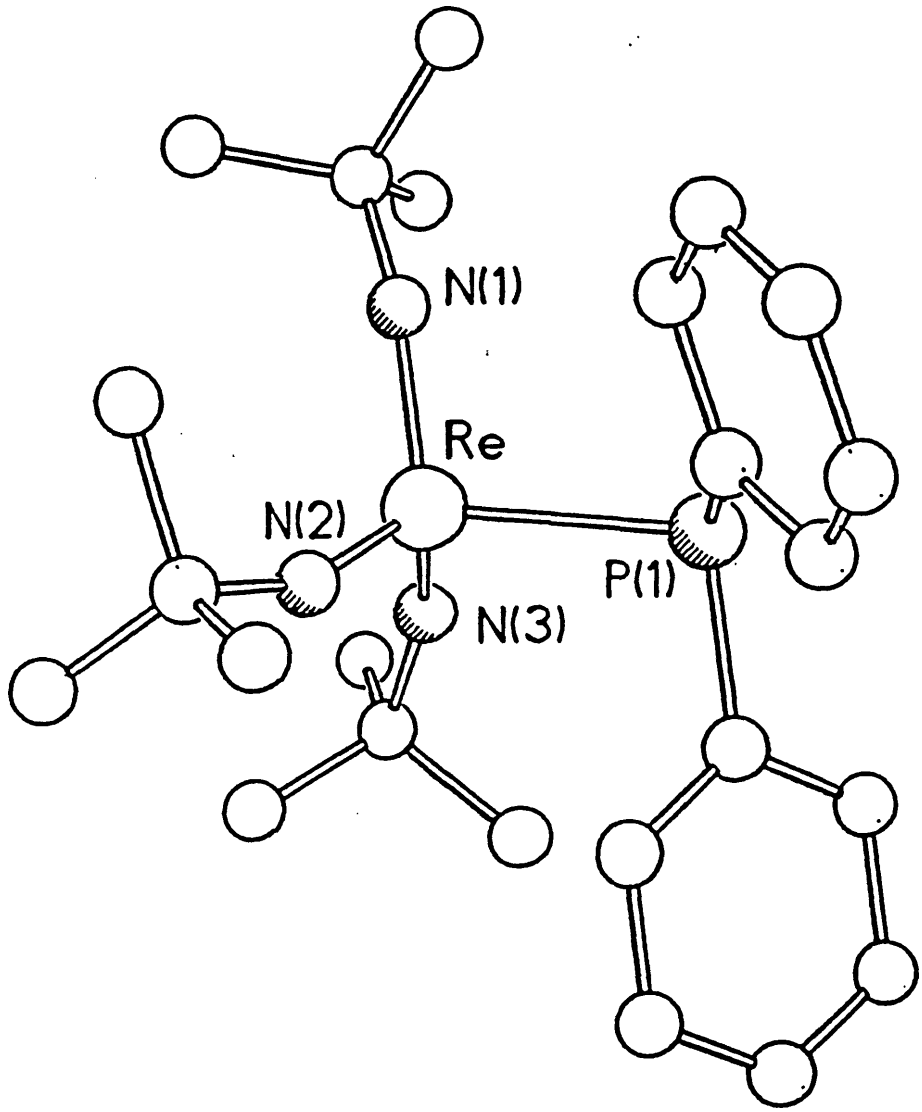


Figure 3.4 : The crystal structure of one of the two independent molecules of $Re(NBu^t)_3PPh_2$.

does not change colour upon warming up to room temperature. No well defined products could be isolated from this solution. If $Re(NBu^t)_3(OSiMe_3)$ is used instead, then the diphenylamido complex, $Re(NBu^t)_3NPh_2$, is isolated as a bright yellow, low melting, crystalline solid in *ca.* 53% yield. Both amido complexes are moderately air and moisture sensitive. The mass spectra for both complexes show the corresponding molecular ions. The ^1H NMR spectrum of the dimethylamido complex shows two singlets at 1.37 and 3.35 ppm, in a 4.5 : 1 ratio, for the NBu^t and NMe_2 protons respectively. As before, with $Re(NBu^t)_3PPh_2$, the analogous diphenylamido complex has two multiplets (centred at 7.00 and 7.23 ppm) for the aromatic protons, which do not show any temperature dependency over the same temperature range. The NBu^t protons appear as a singlet at 1.29 ppm.

The phosphiniminato complex.

Interaction of $Re(NBu^t)_3Cl$ with $LiN{=}PPh_3$ in refluxing toluene gives the phosphin - iminato complex, $Re(NBu^t)_3(N{=}PPh_3)$, as a yellow solid in *ca.* 33% yield. It is moderately air and moisture sensitive and is sparingly soluble in hexane, but has good solubility in Et_2O, THF, toluene etc. . In the ^1H NMR spectrum two multiplets are seen for the aromatic protons (centred at 7.02 and 7.44 ppm) and a singlet for the NBu^t protons (at 1.44 ppm). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 15.28 ppm. The IR spectra for all reported phosphiniminato complexes show a strong band in the 1050-1200 cm^{-1} region, assigned as the asymmetric stretching vibration of the MNP unit[93,94]. For $Re(NBu^t)_3(N{=}PPh_3)$ this vibration occurs at 1094 cm^{-1}. Phosphiniminato complexes have been known since 1973[95]. Since that time a number of synthetic routes to these compounds have been devised[93,94]. One of the most generally useful methods is from metal halides and trimethylsilyl substituted imino - phosphoranes (eg. $Me_3SiN{=}PPh_3$), which have a high tendency of forming the leaving group Me_3SiX (X = halide, especially Cl or F). Although this method is very clean, it is, however, very slow for $Re(NBu^t)_3Cl$. Interaction of $Re(NBu^t)_3Cl$ with excess $Me_3SiN{=}PPh_3$ in refluxing toluene for *ca.* 36 hours gave a mixture of starting

material and product. On the other hand, The method which proved to be successful for $Re(NBu^t)_3Cl$ (ie. use of $LiNPPh_3$) has not led to generally useful results in the past.[94,96].

Interaction of $Re(NBu^t)_3Cl$ with $SbCl_5$ in refluxing MeCN.

This reaction produces the bis-*tert*-butylimido salt, $[Re(NBu^t)_2Cl_2(MeCN)_2]SbCl_6$, in about 72% yield. The removal of an imido group by chlorination has also been observed in the reaction of $Cr(NBu^t)_2Cl_2$ with Cl_2[97], which gives $Cr(NBu^t)Cl_3$. In niether case has the fate of the imido group been ascertained. As expected the rhenium salt is obtained essentially quantitatively by the interaction of $Re(NBu^t)_2Cl_3$ with $SbCl_5$ in refluxing MeCN (Scheme 3.4).

$$Re(NBu^t)_2Cl_3 + 2MeCN + SbCl_5 \longrightarrow [Re(NBu^t)_2Cl_2(MeCN)_2]SbCl_6$$

Scheme 3.4

The salt crystallises from MeCN as large deep red-orange crystals that are soluble in MeCN, THF, CH_2Cl_2 and $CHCl_3$. The conductivity in MeCN corresponds to a 1:1 electrolyte (Λ_M = 111 ohm^{-1} cm^2 mol^{-1}). The IR spectrum has two stretches for the CN group at 2292 and 2319 cm^{-1}, above the value for free MeCN (2255 cm^{-1}). The high values indicate absence of Re-N π-bonding which normally lowers the CN stretching frequency[98]. In the ^1H NMR spectrum there are two singlets, at 2.22 and 1.64 ppm, in a 1 : 3 ratio, corresponding to the MeCN and NBu^t protons respectively.

X-ray quality crystals were obtained by recrystallisation of the salt from CH_2Cl_2. Preliminary structural data show the acetonitriles in a *cis* , and the chlorides in a *trans* configuration, as shown in Figure 3.5 .A complete description of the crystal structure, including a table of bond lengths and angles will appear in a forthcoming publication.

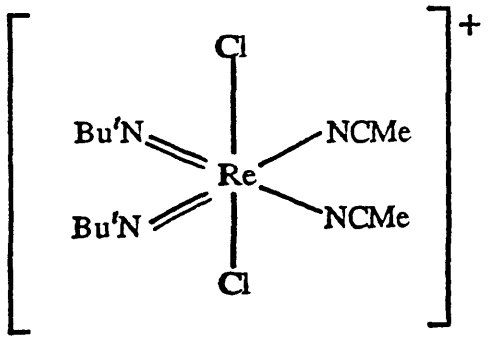


Figure 3.5 : The structure of $[Re(NBu^t)_2Cl_2(MeCN)_2]^+$ cation.

Interaction of $Re(NBu^t)_3Cl$ with $Co_2(CO)_8$.

The interaction of $Re(NBu^t)_3Cl$ and $Co_2(CO)_8$ in hexane leads to the isolation of dark red-violet crystals of a compound of stoichiometry $ReCo_3(NBu^t)_2(CO)_{10}$. The compound is moderately air and moisture sensitive and is soluble in common organic solvents. Spectroscopic data are not instructive but the ^1H NMR spectrum has a singlet at 0.88 ppm for the NBu^t group, while the IR spectrum has a complicated carbonyl region. The structure of the molecule which has mirror symmetry was determined by X-ray crystallography and is shown in Figure 3.6. Bond lengths and angles are given in Table 3.1 .

The geometry is best described in terms of a butterfly structure with the wing fold along the vector Re···Co(1) which lies on the crystallographic mirror plane. In each $ReCo_2$ wing triangle the Re-Co distances are very similar [2.581(5), 2.602(5) Å] and a Co-Co distance of 2.435(6) Å seems to indicate equivalent strength. The capping imido function bonds slightly asymmetrically, with Co-N distances of 1.98(1) [Co(1)] and 1.89(1) Å [Co(2)] and Re-N 2.02(1) Å. On the other hand, the CO bridging across the Co(1)···Co(2) edge is almost symmetrical, with Co-C distances of 1.94(2) 1.96(2) Å. The Co(2)···Co(2a) distance between wingtips is 3.571(7) Å. If the imido functions act as 4 electron donors, the total electron count is 62 and the structure is then immediately classified as an arachno derivative of an octahedral parent.

There are several precedents for μ_3-NR groups in cluster chemistry, for example for

tungsten[99], where π overlaps in the NPh bridge are discussed and for ruthenium[100]. Gold compounds[101] have NPh bridging separate $AuPR_3$ groups. As far as we are aware no μ_3 bridged species of rhenium have previously been reported.

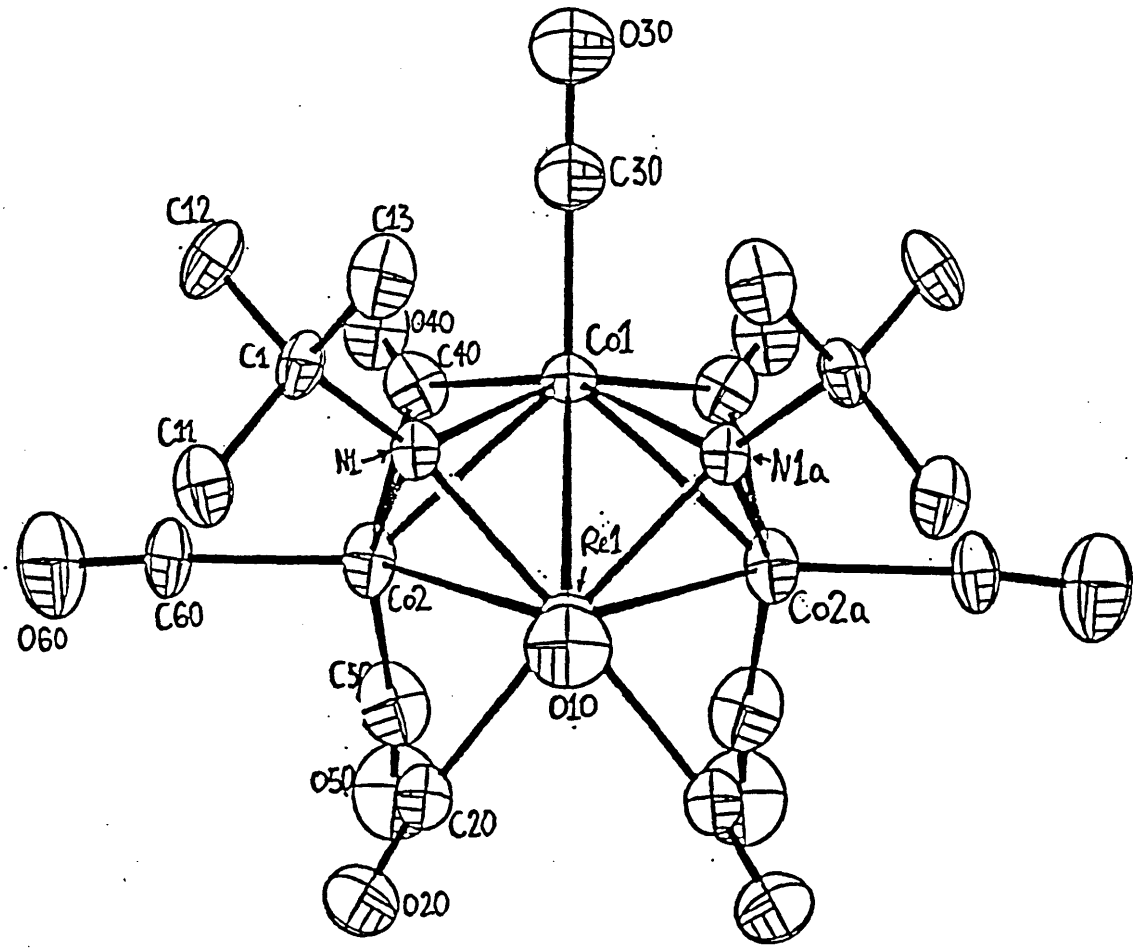


Figure 3.6 : The crystal structure of $ReCo_3(\mu_3\text{-}NBu^t)_2(\mu\text{-}CO)_2(CO)_8$.

Table 3.1 : Bond lengths (Å) and angles (°) for $ReCo_3(\mu_3\text{-}NBu^t)_2(\mu\text{-}CO)_2(CO)_8$.

Bond lengths.

C(10)-Re(1)	1.918(24)	C(20)-Re(1)	2.026(17)
N(1)-Re(1)	2.017(13)	C(30)-Co(1)	1.758(23)
C(40)-Co(1)	1.957(18)	N(1)-Co(1)	1.982(13)
N(1)-Co(2)	1.888(13)	C(40)-Co(2)	1.941(16)
C(50)-Co(2)	1.803(21)	C(60)-Co(2)	1.809(18)
O(10)-C(10)	1.132(27)	O(20)-C(20)	1.088(20)
O(30)-C(30)	1.137(28)	C(1)-N(1)	1.548(19)
C(11)-C(1)	1.537(24)	C(12)-C(1)	1.498(22)
C(13)-C(1)	1.501(24)	O(40)-C(40)	1.168(18)
O(50)-C(50)	1.125(21)	C(60)-O(60)	1.093(22)
Co(1)-Co(2a)	3.571(7)	Co(1)-Re(1)	2.602(5)
Co(2)-Re(1)	2.581(5)		

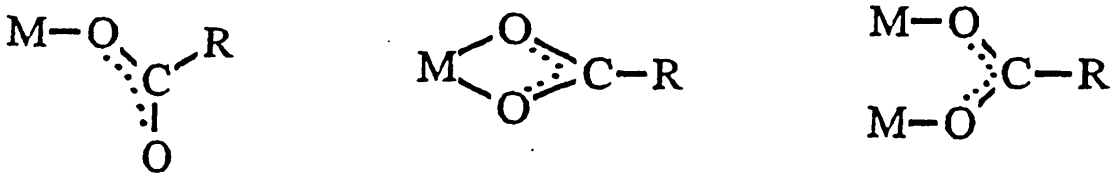
Bond angles

C(20)-Re(1)-C(10)	92.7(7)	C(20)-Re(1)-C(20a)	78.5(5)
N(1)-Re(1)-Co(1)	48.8(3)	N(1)-Re(1)-Co(2)	46.5(3)
N(1)-Re(1)-C(10)	99.0(6)	N(1)-Re(1)-C(20)	96.8(6)
N(1)-Re(1)-C(20a)	167.6(4)	N(1)-Re(1)-N(1a)	85.5(7)
Co(2)-Co(1)-Co(2a)	94.3(2)	C(40)-Co(1)-C(30)	94.4(9)
N(1)-Co(1)-C(30)	107.5(8)	N(1)-Co(1)-C(40)	157.9(5)
N(1)-Co(1)-N(1a)	87.4(6)	C(40)-Co(1)-C(40a)	88.3(10)
C(50)-Co(2)-N(1)	157.2(7)	C(60)-Co(2)-N(1)	106.1(8)
C(60)-Co(2)-C(50)	94.0(10)	C(40)-Co(2)-N(1)	90.7(6)
C(50)-Co(2)-C(40)	96.1(8)	C(60)-Co(2)-C(40)	101.0(8)
O(10)-C(10)-Re(1)	177.7(18)	O(20)-C(20)-Re(1)	171.2(15)
Co(1)-N(1)-Re(1)	81.2(5)	Co(2)-N(1)-Re(1)	82.7(5)

Table 3.1 (continued)

C(1)-N(1)-Re(1)	138.0(8)	Co(2)-C(40)-Co(1)	77.7(6)
O(30)-C(30)-Co(1)	173.6(24)	O(40)-C(40)-Co(1)	143.4(13)
Co(2)-N(1)-Co(1)	77.9(5)	C(1)-N(1)-Co(1)	131.2(8)
C(1)-N(1)-Co(2)	124.7(10)	O(40)-C(40)-Co(2)	139.0(13)
O(50)-C(50)-Co(2)	174.8(19)	O(60)-C(60)-Co(2)	170.3(19)
C(11)-C(1)-N(1)	105.1(13)	C(12)-C(1)-N(1)	109.0(13)
C(12)-C(1)-C(11)	112.8(15)	C(13)-C(1)-N(1)	109.0(13)
C(13)-C(1)-C(11)	110.8(15)	C(13)-C(1)-C(12)	110.0(15)
C(50)-Co(2)-Co(1)	117.0(7)		

Interaction of $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}OReO_3)$ with $AgCF_3CO_2$ in THF leads to substitution of the bridging perrhenate group by $CF_3CO_2^-$, and the isolation of $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}O_2CCF_3)$ as a yellow-orange solid in *ca.* 44% yield. It is moderately air and moisture sensitive, and soluble in all common organic solvents. There are three resonances in the ^1H NMR spectrum of the complex (at 1.42, 0.25 and 0.13 ppm) in a 4 : 1 : 2 ratio, corresponding to the NBu^t, bridging $OSiMe_3$ and terminal $OSiMe_3$ protons. The ^{19}F NMR spectrum shows a singlet at 57.52 ppm. The IR spectrum has two strong bands at 1680 and 1454 cm^{-1}, assigned as the asymmetric and symmetric vibrations of the OCO unit respectively. Extensive studies have been made on the IR spectra of many carboxylate complexes, having known X-ray crystal structures[102,103]. Carboxylate groups can coordinate to metals in a number of ways, most commonly as (i) a unidentate ligand, (ii) a chelating ligand or (iii) a bridging ligand.(Figure 3.7).



(i) (ii) (iii)

Figure 3.7 : Common bonding types for carboxylate groups.

Comparison of the separation between asymmetric and symmetric stretching frequencies (Δ) with those found in the corresponding sodium or potassium salts (referred to as the free carboxylate ion) provides a good measure of the ligation type[102]. Generally complexes with bridging carboxylate groups have Δ values similar to those in the corresponding free carboxylate ion. For the above rhenium complex $\Delta = 228\ cm^{-1}$, which is comparable to the recorded value for $NaCF_3CO_2$ ($\Delta = 223\ cm^{-1}$)[102]. Preliminary structural data on X-ray quality crystals of the complex confirm the dimeric structure of the complex and the presence of bridging trifluoroacetate group. The compound crystallises in the monoclinic $P2_1/m$ space group. The crystal structure of

the complex is shown in Figure 3.8. A complete description of the structure, including a table of bond lengths and angles will appear in a forthcoming publication.

A rhenium(V) dimeric complex , $[Re(NBu^t)_2]_2(\mu\text{-}OSiMe_3)(\mu\text{-}O_2CCF_3)$, is isolated as a yellow solid, from the interaction of $Re(NBu^t)_3(OSiMe_3)$ with excess $AgCF_3CO_2$ in THF. From the IR spectrum Δ is found to be 224 cm^{-1} (asymmetric and symmetric stretching vibrations at 1674 and 1450 cm^{-1} respectively). As before, this is very close to the Δ value for $NaCF_3CO_2$, implying the presence of a bridging trifluoroacetate group. The ^1H NMR spectrum shows 2 singlets at 1.44 and 0.13 ppm (in a 4 : 1 ratio) for the NBu^t and $OSiMe_3$ protons. The ^{19}F NMR spectrum shows a singlet at 60.18 ppm.

Interaction of $Re(NBu^t)_3Cl$ with sodium pyrazolate.

The interaction of $Re(NBu^t)_3Cl$ with one equivalent of the sodium salt of pyrazole in THF at -78°C gives $Re(NBu^t)_3(C_3H_3N_2)$ as can be established from mass and NMR spectroscopy. The mass spectrum indicates that the complex is monomeric in the gas phase, while the ^1H NMR spectrum shows a singlet for the imido protons (at 1.53 ppm) and an ABC pattern for the pyrazolate protons (at 7.68, 7.59 and 5.95 ppm). The ratio of the imido protons to pyrazolate protons is found to be 9 : 1 by integration. A similar ^1H NMR pattern has been reported for (trimethylsilyl)pyrazole, $Me_3Si(C_2H_3N_2)$[104]. The chelating abilities of the pyrazolate anions are well known. Most commonly they form bridges with both N atoms bound to metals[105,106].

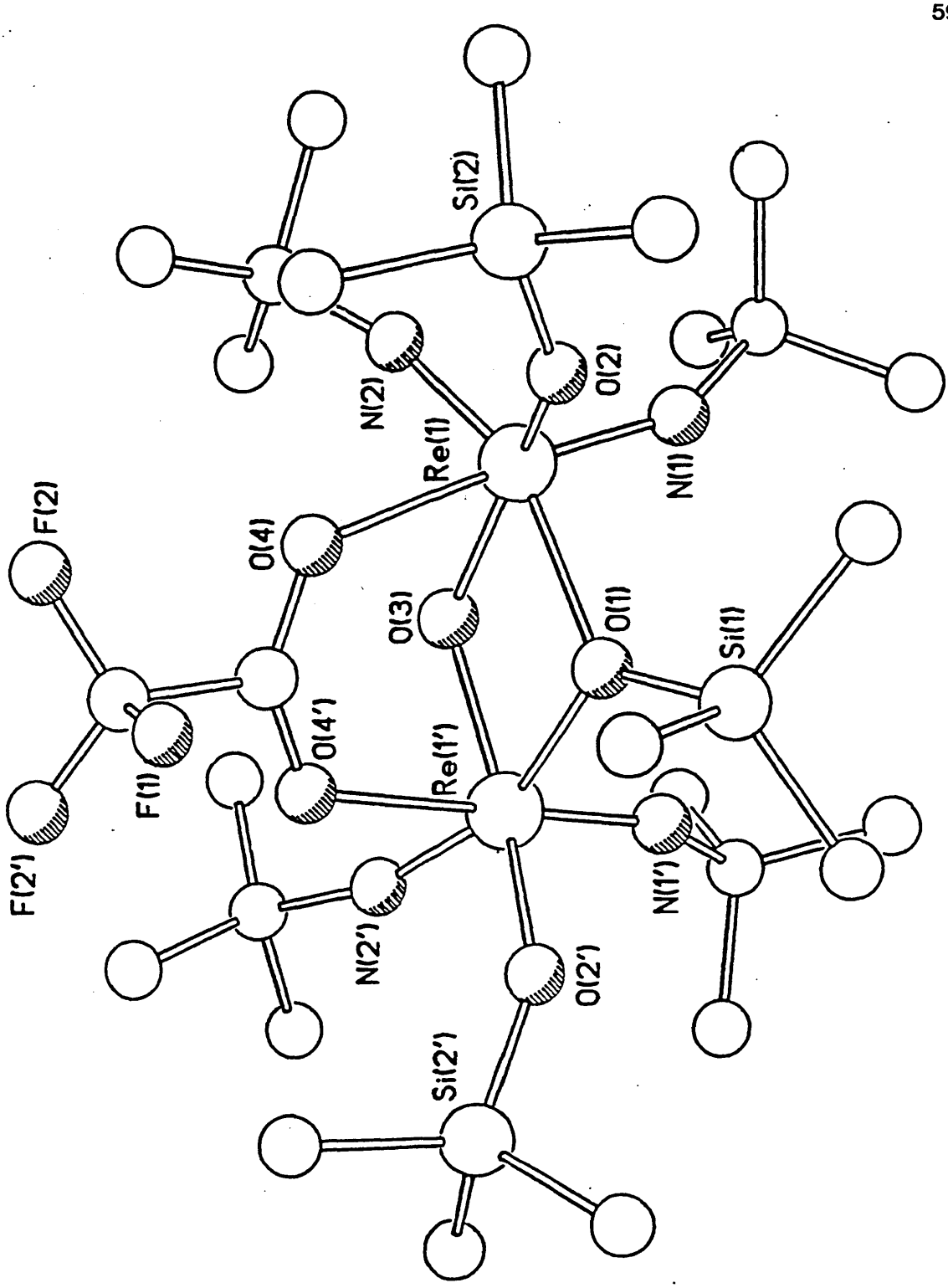


Figure 3.8 : The crystal structure of $[Re(NBu^t)_2(OSiMe_3)](\mu\text{-}O)(\mu\text{-}OSiMe_3)$-$(\mu\text{-}O_2CCF_3)$.

Table 3.2 : Physical and analytical[a] data for rhenium imido complexes.

Compound	M.Pt / °C	Analytical Data % C	H	N	Other
$Re(NBu^t)_3NMe_2$	oil	38.1	7.5	12.4	-
		(37.9)	(7.5)	(12.6)	-
$Re(NBu^t)_3NPh_2$	61-63	52.0	6.6	9.6	-
		(50.8)	(6.6)	(9.9)	-
$Re(NBu^t)_3PPh_2$	51-53	49.3	6.4	7.3	5.5(P)
		(49.3)	(6.4)	(7.2)	(5.3)
$Re(NBu^t)_3P(SiMe_3)_2$	64-66	37.8	7.9	7.1	5.5(P)
		(37.5)	(7.9)	(7.3)	(5.4)

Table 3.2 (continued)

Compound	M.Pt. / °C	Analytical Data % C	H	N	Other
$Re(NBu^t)_3PH(mes)$	85-87	45.2	7.1	7.2	-
		(45.8)	(7.1)	(7.6)	-
$Re(NBu^t)_3(NPPh_3)$	161-163	53.4	6.3	8.2	4.8(P)
		(53.3)	(6.3)	(8.3)	(4.6)
$[Re(NBu^t)_2Cl_2(MeCN)_2]SbCl_6$	146-148 decomp	17.9	3.0	7.0	34.3(Cl)
		(17.7)	(3.0)	(7.0)	(34.8)
$ReCo_3(NBu^t)_2(CO)_{10}$	178-180	28.1	2.6	3.7	18.7(O)
		(27.5)	(2.3)	(3.6)	(20.4)

Table 3.2 (continued)

Compound	M.Pt. / °C	Analytical Data % C	H	N	Other
$Re_2(NBu^t)_4(O)(OSiMe_3)_3(O_2CCF_3)$	113-115	28.2	5.0	5.3	6.0(F)
		(30.1)	(6.0)	(5.3)	(5.7)
$Re_2(NBu^t)_4(OSiMe_3)(O_2CCF_3)$	70-72	28.8	5.2	6.2	5.8(O)
		(29.4)	(5.3)	(6.5)	(5.6)
$Re(NBu^t)_3(C_3H_3N_2)$	150-152	35.8	5.5	17.0	-
		(38.6)	(6.5)	(15)	-

[a] Calculated values in parentheses.

Table 3.3 : ^{1}H NMR data for rhenium imido complexes [a].

Compound	δ / ppm	Assignment	
$Re(NBu^t)_3NMe_2$	3.35 (s)	6H	$N\underline{Me}_2$
	1.37 (s)	27H	$N\underline{Bu}^t$
$Re(NBu^t)_3NPh_2$	7.23, 7.00 (m)	10H	$N\underline{Ph}_2$
	1.29 (s)	27H	$N\underline{Bu}^t$
$Re(NBu^t)_3PPh_2$	7.86, 7.14 (m)	10H	$P\underline{Ph}_2$
	1.26 (s)	27H	$N\underline{Bu}^t$
$Re(NBu^t)_3P(SiMe_3)_2$	1.37 (s)	27H	$N\underline{Bu}^t$
	0.49 (d)	18H	$P(Si\underline{Me}_3)_2$ ($^{3}J_{P-H}$ = 4.5 Hz.)

Table 3.3 (continued)

Compound	δ / ppm		Assignment
$Re(NBu^t)_3PH(mes)$	6.78 (s)	2H	$C_6\underline{H}_2$
	5.37 (d)	1H	P-<u>H</u> ($^1J_{P-H}$ = 195 Hz.)
	2.65 (s)	6H	*o*-C<u>H</u>$_3$
	2.16 (s)	3H	*p*-C<u>H</u>$_3$
	1.27 (s)	27H	N<u>Bu</u>^{t}
$Re(NBu^t)_3(NPPh_3)$	7.44, 7.02 (m)	15H	NP<u>Ph</u>$_3$
	1.44 (s)	27H	N<u>Bu</u>^{t}
$[Re(NBu^t)_2Cl_2(MeCN)_2]SbCl_6$	2.22 (s)	6H	<u>Me</u>CN
(CD_3CN)	1.64 (s)	18H	N<u>Bu</u>^{t}

Table 3.3 (continued)

Compound	δ / ppm	Assignment	
$ReCo_3(NBu^t)_3(CO)_{10}$	0.88 (s)	-	N<u>Bu</u>^{t}
$Re_2(NBu^t)_4(O)(OSiMe_3)_3(O_2CCF_3)$	1.42 (s)	36H	N<u>Bu</u>^{t}
($CDCl_3$)	0.25 (s)	9H	μ-OSi<u>Me</u>$_3$
	0.13 (s)	18H	OSi<u>Me</u>$_3$
$Re_2(NBu^t)_4(OSiMe_3)(O_2CCF_3)$	1.44 (s)	36H	N<u>Bu</u>^{t}
($CDCl_3$)	0.13 (s)	9H	OSi<u>Me</u>$_3$
$Re(NBu^t)_3(C_3H_3N_2)$	7.68 (m)	1H	C_3<u>H</u>$_3N_2$
($CDCl_3$)	7.59 (m)	1H	C_3<u>H</u>$_3N_2$
	5.95 (m)	1H	C_3<u>H</u>$_3N_2$
[a] All spectra in C_6D_6 unless otherwise stated.	1.53 (s)	27H	N<u>Bu</u>^{t}

EXPERIMENTAL

Mass spectrometer : Kratos MS 902 at 70 eV. Spectra show isotopic envelopes for the rhenium containing ions but only peaks corresponding to those with ^{187}Re are listed. NMR : δ values in ppm in C_6D_6 unless otherwise stated, and referenced to $SiMe_4$ (^1H), external 85% H_3PO_4 (^{31}P) and $CFCl_3$ (^{19}F). Other details on the spectrometers used and experimental procedures are given in the experimental section of Chapter 1. Commercial chemicals were from Aldrich. The compounds $Re(NBu^t)_3Cl$[72], $Re(NBu^t)_3(OSiMe_3)$[74] and $[Re(NBu^t)_2(OSiMe_3)]_2(\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}OReO_3)$[74] were prepared according to the literature. The lithium reagents [$LiNMe_2$, $LiNPh_2$, $LiPPh_2$ and LiPH(mes)] were prepared by the interaction of the corresponding amine or phosphine with one equivalent of Bu^nLi in hexane at -78°C. $LiN{=}PPh_3$ was prepared from $HN{=}PPh_3$[107] and one equivalent of Bu^nLi in toluene at -78°C. The sodium salt of pyrazole was made by adding a suspension of NaH in THF to a solution of pyrazole in THF at -78°C. The solution was stirred for 30 minutes at room temperature, filtered, pumped down to dryness, and the residue washed with hexane (3 x 30 cm^3). $LiP(SiMe_3)_2$ was prepared by the interaction of $P(SiMe_3)_3$ with Bu^nLi in THF at -78°C.

Tris(*t*-butylimido)(dimethylamido)rhenium(VII).

To a solution of $Re(NBu^t)_3Cl$ (0.45 g; 1.03 mmol) in Et_2O (20 cm^3) at-78°C was added a cold suspension of $LiNMe_2$ (0.07 g; 1.37 mmol) in Et_2O (30 cm^3). After warming and stirring at room temperature for *ca.* 5 hours, the solution was evaporated and the residue extracted with hexane (2 x 5 cm^3). Evaporation of the extract left a yellow oil which was distilled under high vacuum at *ca.* 150°C. Yield 0.16 g (35%). Mass spectrum : 444(M^+), 429(M^+-Me), 373(M^+-NBu^t).

IR : 2968vs, 2921s, 2895s, 2859s, 2815s, 2771s, 1471s, 1452s, 1421m, 1356s, 1263s, 1211vs (NBu^t), 1128s, 1053w, 1024w, 1005w, 960s, 913s, 840m, 804s, 765m, 599s, 567m, 486s .

Tris(*t*-butylimido)(diphenylamido)rhenium(VII).

As above but using $Re(NBu^t)_3(OSiMe_3)$ (0.42 g; 0.86 mmol) in Et_2O (20 cm^3) and $LiNPh_2$ (0.19 g; 1.08 mmol) in Et_2O (30 cm^3). Concentration of the hexane extract (*ca.*20 cm^3) and cooling (-78°C) gave yellow crystals. Yield 0.26 g (53%).

Mass spectrum : 568(M^+), 553(M^+-Me), 497(M^+-NBu^t).

IR : 3078w, 3051w, 1592m, 1491s, 1357s, 1259s, 1200vs (NBu^t), 1126s, 1068w, 1025w, 992w, 930m, 880m, 836w, 803w, 746s, 694s, 597w, 562w, 510m, 484w.

Tris(*t*-butylimido)[bis(trimethylsilyl)phosphido]rhenium(VII).

As above, from $Re(NBu^t)_3(OSiMe_3)$ (0.55 g; 1.13 mmol) in Et_2O (20 cm^3) and $Li[P(SiMe_3)_2]$ (0.26 g; 1.41 mmol) in Et_2O (30 cm^3). Concentration of the hexane extract (*ca.*20 cm^3) and cooling (-78°C) gave a yellow crystalline solid. Yield 0.28 g (43%) .

Mass spectrum : 577(M^+), 562(M^+-Me), 520(M^+-Bu^t), 504(M^+-$SiMe_3$), 406(M^+ - 3 x Bu^t), 333(M^+-3 x Bu^t, $SiMe_3$) .

IR : 1357s, 1265m, 1242s, 1211vs (NBu^t), 1129m, 1024w, 910w, 835s, 748w, 689w, 626m, 596w, 530w, 491w, 456w, 426m .

NMR : $^{31}P\{^1H\}$: -212.33 (s) .

Tris(*t*-butylimido)(diphenylphosphido)rhenium(VII).

As above, from $Re(NBu^t)_3(OSiMe_3)$ (0.51 g; 1.04 mmol) in Et_2O (20 cm^3) and $LiPPh_2$ (0.25 g; 1.30 mmol) in Et_2O (30 cm^3). The hexane extract was evaporated to dryness and the residue was crystallised from MeCN to give an orange-yellow crystalline solid. Yield 0.24 g (40%).

Mass spectrum : 585(M^+), 570(M^+-Me), 555(M^+-2 x Me), 514(M^+-NBu^t).

IR : 3069w, 3053w, 1950w, 1879w, 1806w, 1583w, 1435m, 1357s, 1267m, 1211vs(NBu^t), 1129m, 1088w, 1067w, 1027m,804m, 737s, 693s, 596w, 531w, 501m, 473w, 432w.

NMR : $^{31}P\{^1H\}$: - 8.78 (s).

^{31}P : - 8.78 (quintet $^4J_{P-H}$ = 7 Hz. ; coupling to four *o*-hydrogens on C_6H_5 rings).

Tris(*t*-butylimido)(mesitylphosphido)rhenium(VII).

As above, from $Re(NBu^t)_3(OSiMe_3)$ (0.63 g; 1.29 mmol) in Et_2O (20 cm^3) and LiPH(mes) (0.25 g; 1.58 mmol) in Et_2O (30 cm^3). Concentration of the hexane extract (*ca.* 10 cm^3) and cooling (-78°C) gave yellow crystals. Yield 0.42 g (60%).

Mass spectrum : 551(M^+), 536(M^+-Me), 478(M^+ - Me, Bu^t,H), 463(M^+-2xMe, Bu^t, H), 431(M^+-mes, H).

IR : 2328m(P-H), 1714w, 1602m, 1357s, 1290w, 1261m, 1211vs(NBu^t), 1123s, 1026m, 845m, 804s, 598m, 550w, 490w.

NMR : $^{31}P\{^1H\}$: -153.16 (s).

^{31}P : -153.16 (d, J_{P-H} = 195 Hz.).

Tris(*t*-butylimido)(triphenylphosphiniminato)rhenium(VII).

To a solution of $Re(NBu^t)_3Cl$ (0.38g; 0.87 mmol) in toluene (20 cm^3) was added a solution of $LiN{=}PPh_3$ (0.30g; 1.06 mmol) in toluene(20 cm^3) and the solution refluxed for *ca.* 12 hours. After evaporation the residue was extracted with hexane (2x30 cm^3) which was concentrated (*ca.*30 cm^3), filtered and cooled (-20 cm^3) to give an orange-brown powder. Recrystallisation from Et_2O gave a yellow crystalline solid. Yield 0.20g (33%).

Mass spectrum : 676(M^+), 661(M^+-Me), 646(M^+-2xMe), 605(M^+-Bu^t), 400(M^+-$NPPh_3$) .

IR : 3074w, 3055w, 1966w, 1897w, 1823w, 1586w, 1436s, 1353s, 1262w, 1206vs (NBu^t), 1133s, 1110s, 1094s, 1025m, 999m, 802m, 752m, 714s, 693s, 594m, 529s, 477m, 444m .

NMR : $^{31}P\{^1H\}$: 15.28 (s) .

Bis(*t*-butylimido)dichlorobis(acetonitrile)rhenium(VII)hexachloroantimonate(V).

To a solution of $Re(NBu^t)_3Cl$ (0.40g; 0.92 mmol) in MeCN (30 cm^3) was added $SbCl_5$ (1 cm^3 of 1M solution in CH_2Cl_2; 1.00 mmol) and the solution refluxed for *ca.* 12 hours. After evaporation to dryness, the residue was washed with Et_2O (2x30 cm^3) and extracted with MeCN (10 cm^3). Concentration (*ca.* 5 cm^3) and cooling (-20°C) gave bright orange-red crystals. Further crops of crystals may be obtained from the supernatant. Combined yield 0.54g (72%) .

IR : 2319s and 2292s (CN), 1414w, 1363s, 1246m, 1200s(NBu^t), 1159m, 1028m, 944s, 796m, 612m, 477m, 404w, 337vs(Sb-Cl).

The compound is obtained similarly from $Re(NBu^t)_2Cl_3$ in yield of *ca.* 95% or above.

$ReCo_3(\mu_3\text{-}NBu^t)_2(\mu\text{-}CO)_2(CO)_8$.

To a solution of $Re(NBu^t)_3Cl$ (0.35g; 0.80 mmol) in hexane (30 cm^3) at -78°C was added a solution of $Co_2(CO)_8$ (0.42g; 1.2 mmol) in hexane (10 cm^3). The solution was allowed to warm up to room temperature and was stirred for an additional 5 hours. Concentration (*ca.* 10 cm^3), filtration and cooling (-20°C) gave dark red-violet crystals. Yield 0.20g (33%).

Mass spectrum : 758(M^+-CO), 730(M^+-2xCO), 702(M^+-3xCO), 674(M^+-4xCO), 646(M^+-5xCO), 618(M^+-6xCO), 590(M^+-7xCO), 562(M^+-8xCO), 534(M^+-9xCO) 506(M^+-10xCO)

IR : 2077s, 2033s, 1994s, 1923s, 1893s, 1387m, 1362m, 1171m, 1014w, 673w, 641w, 622w, 601m, 563w, 531w, 510w, 493w, 459m, 405w.

Bis[bis(*t*-butylimido)(trimethylsiloxo)rhenium(VII)](μ-oxo)(μ-trimethylsiloxo)(μ-trifluoroacetato).

To a solution of $AgCF_3CO_2$ (0.11 g; 0.50 mmol) in THF (30 cm^3) at -78°C was added a solution of $[Re(NBu^t)_2(OSiMe_3)](\mu\text{-}O)(\mu\text{-}OSiMe_3)(\mu\text{-}OReO_3)$ (0.45 g; 0.38 mmol) in

THF (20 cm^3). The solution was allowed to warm up to room temperature and was stirred for *ca.* 18 hours. Evaporation to dryness followed by extraction of the residue with hexane (2 x 20 cm^3), concentration (*ca.* 10 cm^3) and cooling (-78°C) gave yellow crystals. Yield 0.18 g (44%).

IR : 1735m, 1682s, 1454m, 1360s, 1249s, 1203vs(NBu^t), 1145s, 1024w, 940s, 832s, 799m, 753m, 679m, 612m, 589m, 565m, 520m, 482m, 457w, 374w .

NMR : ^{19}F ($CDCl_3$) : 57.52 (s).

Bis[bis(*t*-butylimido)rhenium(V)](μ-trimethylsiloxo)(μ-trifluoroacetato).

To a solution of $AgCF_3CO_2$ (0.28 g; 1.27 mmol) in THF (30 cm^3) at -78°C was added a solution of $Re(NBu^t)_3(OSiMe_3)$ (0.50 g; 1.02 mmol) in THF (20 cm^3). After warming, and stirring at room temperature for *ca.* 18 hours, the solution was evaporated to dryness and the residue extracted with hexane (2 x 20 cm^3). Concentration (*ca.* 10 cm^3) and cooling (-78°C) gave a yellow solid. Yield 0.57 g (65%).

IR : 1674s, 1450m, 1359s, 1248s, 1208vs(NBu^t), 1136s, 1063w, 1024w, 909s, 840s, 805m, 750m, 637w, 601w, 560w, 520w, 488w .

NMR : ^{19}F : 60.18 (s) .

Tris(*t*-butylimido)pyrazolatorhenium(VII).

To a solution of $Re(NBu^t)_3Cl$ (0.56 g; 1.29 mmol) in THF (20 cm^3) at -78°C was added a cold solution of sodium pyrazolate (0.15 g: 1.67 mmol) in THF (30 cm^3). After warming and stirring at room temperature for *ca.* 18 hours, the solution was evaporated to dryness, and extracted with hexane (2 x 20 cm^3). Concentration (*ca.* 5 cm^3) and cooling (-78°C) gave an orange-red solid. Yield 0.19 g (32%).

Mass spectrum : 467(M^+), 464(M^+ - 3 xH), 452(M^+ - Me), 396(M^+ - NBu^t), 351(M^+ - NBu^t, 3 x Me).

IR : 1488m, 1361s, 1260s, 1231s, 1205s(NBu^t), 1185m, 1162m, 1147m, 1050s, 1032s, 948m, 920w, 836m, 797m, 743s, 678w, 624m, 597w, 557w, 482w .

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