Complexes of Rhenium and Osmium Polyhydrides with Metallic Lewis Acids: *X*-Ray Crystal Structure of $[\mathrm{Ag\{ReH_7(PPhPr^i{}_2)_2\}_2][PF_6]}$ *

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Bis(di-isopropylphenylphosphine)heptahydridorhenium(VII) (1) reacts with $\mathrm{AgPF_6}$, AgI, CuI, and $\mathrm{HgCl_2}$ to give the heterometallic complexes $[\mathrm{Ag\{ReH_7(PPhPr^i{}_2)_2\}_2][PF_6]}$ (2) and $[\mathrm{Ag\{ReH_7(PPhPr^i{}_2)_2\}][PF_6]}$ (3); $[\mathrm{AgI\{ReH_7(PPhPr^i{}_2)_2\}}]$ (4); $[\mathrm{CuI\{ReH_7(PPhPr^i{}_2)_2\}}]$ (5); and $[\mathrm{HgCl_2\{ReH_7(PPhPr^i{}_2)_2\}}]$ (6) respectively, without loss of hydrogen. Similarly, $[\mathrm{OsH_6(PPhPr^i{}_2)_2}]$ reacts with $\mathrm{HgCl_2}$ to give $[\mathrm{HgCl_2\{OsH_6(PPhPr^i{}_2)_2\}}]$. Complex formation is accompanied by only subtle changes in the hydride ^{1}H n.m.r. shifts (<1 p.p.m.). However, substantial changes occur in the ν(Re–H) i.r. absorption bands. Crystals of (2) are triclinic, space group $P\bar{1}$ ($Z = 2$), with lattice parameters $a = 13.188(6)$, $b = 16.014(6)$, $c = 14.827(6)$ Å, $\alpha = 112.47(3)$, $\beta = 101.03(3)$, and $\gamma = 90.65(3)°$. The structure was solved and refined to $R = 0.048$ ($R' = 0.047$) for 4 452 reflections having $2\theta \leqslant 50°$ (Mo-K_α *X*-radiation) collected at 200 K. The complex cation comprises a silver atom and two $\mathrm{Re(PPhPr^i{}_2)_2}$ fragments arranged linearly (Re–Ag–Re 172°, mean Re–Ag 2.873 Å). No evidence of the hydride ligands was found from the diffraction study.

Recently, attention has been drawn to the polyhydrido-complexes of transition metals by a number of papers dealing with their synthesis,[1–4] structure[3–6] and with various aspects of their chemistry, notably reactions with unsaturated[7] and saturated organic molecules.[8] One facet of their behaviour which has not been fully explored relates to their basicity. Perhaps the most interesting reported examples are those of the d^2 complexes $[\mathrm{WH_4(PMePh_2)_4}]$[9] and $[\mathrm{ReH_5(PMe_2Ph)_3}]$,[10a] and of the d^4 complex $[\mathrm{OsH_4(PMe_2Ph)_3}]$,[10] each of which reacts with acid to form the corresponding protonated species. In the cases of Re and Os the cationic complexes are unstable with respect to loss of hydrogen.

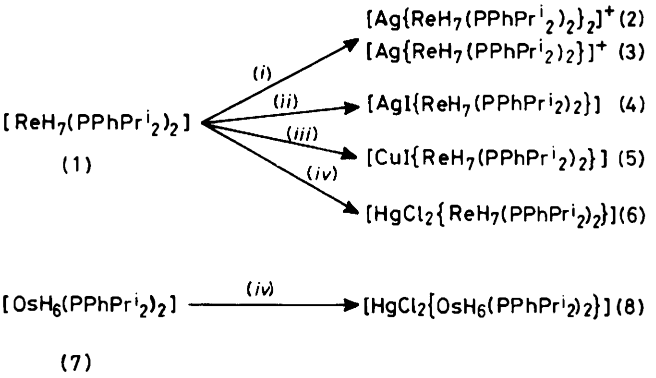
There exists a considerable body of work describing the Lewis basicity of bis(cyclopentadienyl)transition metal hydrides which is the subject of a recent review.[11] Of the few examples of the interaction of metallic Lewis acids with transition metal polyhydrides we may cite the work of Bell *et al.*[12] who reported that $[\mathrm{OsH_4(PEtPh_2)_3}]$ reacted with mercury(II) chloride in excess to afford a product containing no ν(Os–H) bands in the i.r. spectrum. Elemental analysis of the product suggested as many as nine moles of mercury per mole of osmium. More recently Rhodes *et al.*[13] have prepared the mixed-metal polyhydride complexes $[\mathrm{Cu\{ReH_5(PR_3)_3\}_2][PF_6]}$ ($\mathrm{PR_3 = PMePh_2}$ or $\mathrm{PMe_2Ph}$) and $[\mathrm{Re_4Cu_2H_{16}(PR_3)_8][PF_6]_2}$ by the reaction of $[\mathrm{Cu(NCMe)_4][PF_6]}$ with $[\mathrm{ReH_5(PR_3)_3}]$ and $[\mathrm{Re_2H_8(PR_3)_4}]$, respectively.

In this paper we describe the reactions of the d^0 complex $[\mathrm{ReH_7(PPhPr^i{}_2)_2}]$ and the d^2 complex $[\mathrm{OsH_6(PPhPr^i{}_2)_2}]$ with a range of metallic Lewis acids.

Results and Discussion

Reactions of Bis(di-isopropylphenylphosphine)heptahydrido-rhenium(VII).—On adding a solution of silver hexafluorophosphate in dichloromethane to a toluene solution of $[\mathrm{ReH_7(PPhPr^i{}_2)_2}]$ (1)[5] a dense colourless liquid separated without evolution of hydrogen (Scheme). Scratching or seeding converted the liquid to a colourless crystalline mass for which partial elemental analysis suggested the formula $[\mathrm{Ag\{ReH_7(PPhPr^i{}_2)_2\}_2][PF_6]}$ (2). A profound change in the hydride environment on formation of the salt was indicated by i.r. spectroscopy: the moderately sharp ν(ReH) peaks in the spectrum of $[\mathrm{ReH_7(PPhPr^i{}_2)_2}]$ (1) (1 985w, 1 937m, and 1 900s cm^{-1}) became a very broad (2 000—1 670 cm^{-1}) almost featureless, absorption band in the spectrum of (2) (Table 1). Surprisingly, this effect was not reflected in the ^{1}H n.m.r. spectrum (90 MHz) of (2) which displayed a high-field signal at δ −6.20 p.p.m. (28 °C), hardly different from that of the parent hydride (1). However, whereas the latter signal was a sharp triplet, the signal for (2) was broad and featureless although at −50 °C it became partially resolved into four peaks. This pattern, in particular the peak separations, remained constant when the spectrum was measured at 200 MHz (−80 °C) and hence the pattern was interpreted as a doublet of triplets [J(PH) 17, mean $J(^{107}\mathrm{Ag}/^{109}\mathrm{AgH})$ 23 Hz (the individual couplings were not resolved)]. Phosphorus-31 n.m.r. appeared more sensitive to the changed rhenium environment on adduct formation. Thus the singlet observed for (1) at δ 55.3 p.p.m. is shifted to δ 49.7 p.p.m. on formation of (2), although interestingly the latter shows no evidence of coupling to ^{107}Ag/^{109}Ag even at −80 °C. Reaction of (2) with 1,10-phenanthroline regenerated (1) in good yield.

The discovery of (2), ostensibly a 'complex' between a nine-



Scheme. (*i*) $\mathrm{AgPF_6}$; (*ii*) AgI; (*iii*) CuI; (*iv*) $\mathrm{HgCl_2}$

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* μ-Argentio-bis[bis(di-isopropylphenylphosphine)heptahydrido-rhenium(VII)] hexafluorophosphate.

Supplementary data available (No. SUP 23978, 35 pp.): H-atom co-ordinates, thermal parameters, full bond lengths and angles, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Table 1. Selected ^{1}H and ^{31}P n.m.r. data and i.r. metal–hydride stretching bands

Compound	^{1}H				^{31}P [a]		
	Solvent [b]	θ/°C	δ(H)/p.p.m.	J(PH)/Hz	θ/°C	δ(P)/p.p.m.	$\nu_{max.}$(M–H) [c]/cm^{-1}
(1) $[ReH_7(PPhPr^i_2)_2]$	C_6D_6	28	−6.23	19	28	56.6	1 985w, 1 937m, 1 900s
	CD_2Cl_2				28	55.3	
(2) $[Ag\{ReH_7(PPhPr^i_2)_2\}_2][PF_6]$	CD_2Cl_2	28	−6.20		28	49.7	2 000br, 1 965br, 1 900br, 1 815br
		−50	−6.36 [d]	17	−80	47.5	
(3) $[Ag\{ReH_7(PPhPr^i_2)_2\}][PF_6]$	CD_2Cl_2	20	−6.40 [e]	16	28	40.0	2 000br w, 1 715br m
		−80	−5.48 −7.16		−80	39.9	
(4) $[AgI\{ReH_7(PPhPr^i_2)_2\}]$	C_7D_8	28	−6.27	19	−60	54.4	2 010w, 1 930 (sh), 1 895m
		−60	−6.16	18			
(5) $[CuI\{ReH_7(PPhPr^i_2)_2\}]$	C_6D_6	28	−6.15	18	28	51.4	2 030w, 1 990m, 1 970 (sh), 1 700br w
(6) $[HgCl_2\{ReH_7(PPhPr^i_2)_2\}]$	CD_2Cl_2	−80	−6.17 [f]	20	−80	50.1 [g]	2 060w, 1 960w, 1 908m
(7) $[OsH_6(PPhPr^i_2)_2]$	C_6D_6	28	−9.21 [h]	9	28	53.3 [i]	1 975m, 1 910s
	C_7D_8	−80	−9.22	8			
(8) $[HgCl_2\{OsH_6(PPhPr^i_2)_2\}]$	C_7D_8	−10	−8.57 [j]	8	−90	45.1 [k]	2 150w, 2 075s, 2 045 (sh), 1 895m

[a] ^{1}H decoupled. [b] C_7D_8 = perdeuteriotoluene. [c] Nujol mull. [d] J(AgH) = 23 Hz. [e] J(AgH) = 16 Hz. [f] J(HgH) = 94 Hz. [g] J(HgP) = 215 Hz. [h] J(OsH) = 46 Hz. [i] J(OsP) = 139 Hz. [j] J(HgH) = 45 Hz. [k] J(HgP) = 139 Hz.

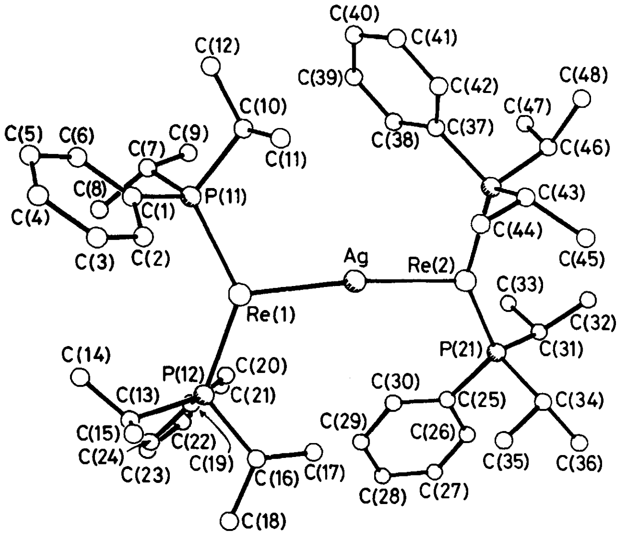

Figure 1. The cation $[Ag\{ReH_7(PPhPr^i_2)_2\}_2]^+$ of (2) showing the labelling of atoms other than hydrogen atoms

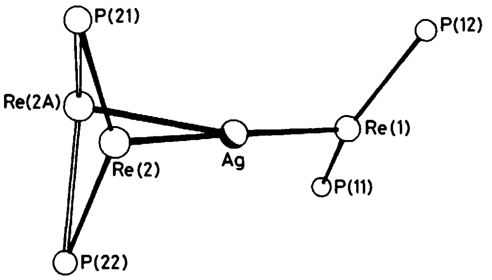

Figure 2. The heavy-atom core of $[Ag\{ReH_7(PPhPr^i_2)_2\}_2]^+$ showing the relative positions of the disordered sites Re(2) and Re(2A)

co-ordinate d^0 transition metal compound and a metallic Lewis acid raised a number of questions concerning the nature of the bonding in the adduct. For example, does the bond depend primarily on the direct interaction between the metal atoms, as in $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2]^+$,[14] or does the binding involve a substantial interaction with the hydride envelope as is apparently the case for $[Cu\{ReH_5(PMePh_2)_3\}_2]^+$[13]? In order to answer such questions a single-crystal X-ray diffraction study of (2) was undertaken.

The crystal lattice is comprised of discrete $[Ag\{ReH_7(PPhPr^i_2)_2\}_2]^+$ (Figures 1 and 2) and $[PF_6]^-$ ions. Although the positions of the four phosphorus atoms, the silver, and one of the rhenium atoms [Re(1)] are well defined, the second rhenium atom is disordered between two sites, Re(2) (60%) and Re(2A) (40%). Nevertheless it is apparent that the metal atoms are joined in an almost linear chain [172° and 166° for Re(2) and Re(2A) respectively] with a mean Re–Ag separation of 2.873 Å (Table 2). As the sum of the empirical covalent radii is approximately 2.8 Å, substantial metal-metal interaction must be inferred.

The mean P–Re–P angle (Table 3) of 134° (range 125—143°) is smaller than the values of 141—147° found in $[ReH_7(PPhPr^i_2)_2]$,[5] 138.9° in $[ReH_7(PPh_3)_2]$,[5] and 146.8° in $[ReH_7(PMe_2Ph)_2]$.[15] This compression of the P–Re–P angle possibly arises simply from the increased steric interaction within the co-ordination sphere of the rhenium as a result of changing the co-ordination number from nine to ten. However, this argument presumes a structure for the product which is closely similar to that of the starting material.

We have recently established[16] the structures of $[ReH_7(PPhPr^i_2)_2]$ and $[ReD_7(PPhPr^i_2)_2]$ in two different crystalline modifications. Both independent molecules have structures best described as derived from a monocapped square antiprism with the phosphine ligands occupying opposite vertices of the capped square face (C_{2v}). The geometry about Re(1) in the present structure is consistent with the silver atom capping the other square face of the original monocapped square antiprism. Thus the observed P–Re(1)–Ag angles of 113.2(1) and 108.5(1)° may be compared with a value of 115.2° calculated on a bond repulsion model (repulsion exponent $n = 6$) of a bicapped square antiprism [Figure 3(a)] with 10 identical ligands.[17]

Inspection of the corresponding angles about Re(2) and Re(2A) suggest very different co-ordination geometries. Calculations suggest[17] that for the case of 10 equivalent ligands, the tetracapped trigonal prism (C_{3v}) and the sphenocorona (C_{2v}) [Figure 3(b) and (c)] should be of comparable energy to the bicapped square antiprism. In the case of Re(2) the observed bond angles [P(21)–Re(2)–P(22), 142.9; Ag–Re(2)–P(21), 122.8; Ag–Re(2)–P(22), 93.8°] may be rationalized by placing Ag, P(21), and P(22) in the sites E, J, and A

Table 2. Bond lengths (Å) and other internuclear distances for $[Ag\{ReH_7(PPhPr^i_2)_2\}_2][PF_6]$ (2)

Re(1)–Ag	2.838(2)	Re(1)–P(11)	2.435(4)	C(7)–C(8)	1.52(2)	C(7)–C(9)	1.51(2)
Re(1)–P(12)	2.446(3)	Re(2A)–Re(2)	1.054(2)	C(10)–C(11)	1.54(2)	C(10)–C(12)	1.51(2)
Re(2A)–Ag	3.001(2)	Re(2A)–P(21)	2.521(5)	C(13)–C(14)	1.50(2)	C(13)–C(15)	1.52(2)
Re(2A)–P(22)	2.660(4)	Re(2)–Ag	2.779(2)	C(16)–C(17)	1.55(2)	C(16)–C(18)	1.53(2)
Re(2)–P(21)	2.457(4)	Re(2)–P(22)	2.390(4)	C(31)–C(32)	1.52(3)	C(31)–C(33)	1.52(2)
P(11)–C(1)	1.86(1)	P(11)–C(7)	1.86(1)	C(34)–C(35)	1.56(3)	C(34)–C(36)	1.53(4)
P(11)–C(10)	1.87(1)	P(12)–C(13)	1.86(1)	C(43)–C(44)	1.54(2)	C(43)–C(45)	1.59(3)
P(12)–C(16)	1.87(1)	P(12)–C(19)	1.87(1)	C(46)–C(47)	1.51(2)	C(46)–C(48)	1.53(2)
P(21)–C(25)	1.87(1)	P(21)–C(31)	1.83(1)	P–F(1)	1.58(1)	P–F(2)	1.58(1)
P(21)–C(34)	1.91(2)	P(22)–C(37)	1.86(1)	P–F(3)	1.60(1)	P–F(4)	1.58(1)
P(22)–C(43)	1.87(1)	P(22)–C(46)	1.86(1)	P–F(5)	1.62(1)	P–F(6)	1.61(1)

Table 3. Selected angles (°) in $[Ag\{ReH_7(PPhPr^i_2)_2\}_2][PF_6]$ (2)

Re(1)–Ag–Re(2)	172.4(1)	P(11)–Re(1)–P(12)	134.7(1)	C(16)–P(12)–Re(1)	114.8(4)	C(25)–P(21)–Re(2)	121.4(4)
Re(1)–Ag–Re(2A)	165.7(1)	P(11)–Re(1)–Ag	113.2(1)	C(13)–P(12)–Re(1)	114.5(4)	C(31)–P(21)–Re(2)	119.9(6)
Re(2)–Ag–Re(2A)	20.5(1)	P(12)–Re(1)–Ag	108.5(1)	C(19)–P(12)–Re(1)	103.7(4)	C(34)–P(21)–Re(2)	102.3(6)
P(21)–Re(2A)–P(22)	125.0(2)	P(21)–Re(2)–P(22)	142.9(1)	C(7)–P(11)–Re(1)	113.9(4)	C(43)–P(22)–Re(2)	106.5(6)
P(21)–Re(2A)–Ag	112.5(1)	P(21)–Re(2)–Ag	122.8(1)	C(10)–P(11)–Re(1)	116.6(5)	C(37)–P(22)–Re(2)	122.5(4)
P(22)–Re(2A)–Ag	83.7(1)	P(22)–Re(2)–Ag	93.8(1)	C(1)–P(11)–Re(1)	114.1(3)	C(46)–P(22)–Re(2)	117.1(4)
C(1)–P(11)–C(7)	104.9(6)	C(25)–P(21)–C(31)	103.5(5)	C(25)–P(21)–Re(2A)	112.1(5)	C(37)–P(22)–Re(2A)	109.7(3)
C(1)–P(11)–C(10)	102.6(4)	C(25)–P(21)–C(34)	103.3(8)	C(31)–P(21)–Re(2A)	105.3(6)	C(43)–P(22)–Re(2A)	129.8(6)
C(7)–P(11)–C(10)	103.2(6)	C(31)–P(21)–C(34)	103.9(8)	C(34)–P(21)–Re(2A)	126.4(6)	C(46)–P(22)–Re(2A)	105.7(4)
C(13)–P(12)–C(16)	103.8(6)	C(37)–P(22)–C(43)	102.7(6)				
C(13)–P(12)–C(19)	103.7(4)	C(37)–P(22)–C(46)	102.1(6)				
C(19)–P(12)–C(16)	101.9(4)	C(43)–P(22)–C(46)	103.6(7)				

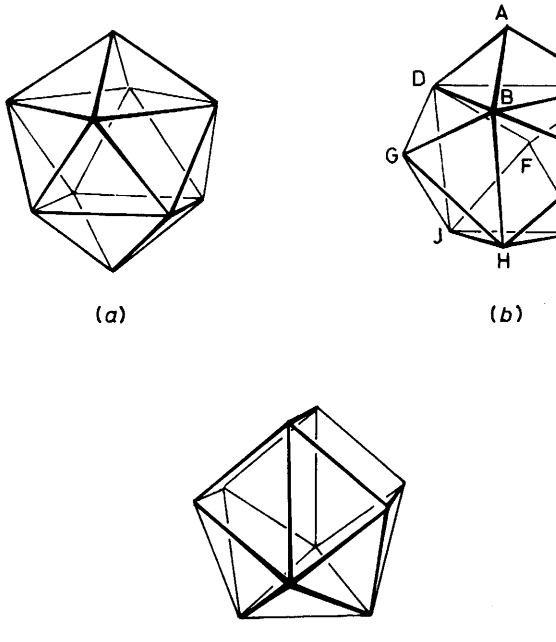

Figure 3. Idealized co-ordination geometries for 10 ligands: (*a*) bicapped square antiprism (D_{4d}); (*b*) tetracapped trigonal prism (C_{3v}) with co-ordination sites labelled according to ref. 17; (*c*) sphenocorona (C_{2v})

respectively (Figure 3) of the idealized tetracapped trigonal prism. The angles quoted above and in Table 3 may then be seen to compare favourably with their respective idealized angles of 138.5, 128.6, and 92.9°. Furthermore this model also rationalizes the unequal Re(2)–P bond distances (Table 2) as the steric repulsion on a ligand in position J [P(21)] is calculated to be somewhat greater than on a ligand at A [P(22)].

However, the geometry about Re(2A) cannot be explained as satisfactorily and it would, in any case, be imprudent to draw too many conclusions from a disordered structure in which the majority of the ligands, namely the hydrides, have not been located.

The ability of Ag^+ to act either as a Lewis acid or as a one-electron oxidant towards organo-transition metal complexes has been noted previously.[14,18] In the case of $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$, the adduct $[Ag\{Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)\}_2]^+$ is formed in spite of the redox potentials for the couples Ag^+–Ag and $[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$–$[Rh(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ favouring oxidation; the neutral rhodium compound is readily oxidised by $[Fe(\eta\text{-}C_5H_5)_2]^+$, a weaker oxidant than Ag^+.[14] For $[ReH_7L_2]$ (L = PPh_3, in CH_2Cl_2), one-electron oxidation is more difficult in that the cyclic voltammogram showed no evidence for electron transfer before 1.2 V. Thus, the absence of an electron-transfer process is less surprising.

The redox potential also reflects the electron richness of a transition metal complex and thus, perhaps, of its basicity towards Lewis acids. If this is the case, the surprising stability of (2) may well depend on reinforcement of the Ag–Re interactions by hydride bridges.

The reaction of $[MoH_4(PMe_2Ph)_4]$ with $AgBF_4$, in acetonitrile,[19] is rather different from that of $[ReH_7L_2]$. In this case, the product, $[MoH_2(PMe_2Ph)_4(NCMe)_2]^{2+}$, is thought to be formed *via* the loss of two electrons and the subsequent reductive elimination of dihydrogen.

Mixing solutions of $AgPF_6$ and (1) in equimolar proportions affords the pale yellow compound (3), deduced to be the 1 : 1 adduct $[Ag\{ReH_7(PPhPr^i_2)_2\}][PF_6]$ from elemental analysis. The i.r. spectrum of (3) differed significantly from those of (1) and (2) displaying a broad and weak absorption at *ca.* 2 000 cm^{-1} and a broad peak at 1 715 cm^{-1} of medium intensity. The low frequency of the latter suggests a stronger Ag–H interaction than is implied for (2) or in the other compounds discussed herein except perhaps for the CuI adduct (5) (see below). Proton n.m.r. spectroscopy (28 °C) showed a hydride signal at δ −6.40 p.p.m. as an ill-resolved 'doublet of triplets' [$J(^{107}Ag/^{109}AgH)$ 16 and J(PH) 16 Hz]. Observation of a silver coupling at room temperature suggests that (3) is less labile than (2). At low temperatures the hydride signal broadens into two featureless peaks [δ −5.48 (3 H) and −7.16 p.p.m. (4 H)]. The corresponding ^{31}P n.m.r. spectrum consists of a singlet, slightly broadened relative to the 28 °C spectrum.

Attempts to prepare mixed adducts of silver by reacting a 1 : 1 mixture of Ag^+ and (1) with the ligands cyclo-octa-1,5-diene and trimethylphosphine were unsuccessful. In both cases only $[Ag\{ReH_7(PPhPr^i_2)_2\}]X$ ($X = PF_6^-$ or BF_4^-) was isolated. However, it was noted that on addition of iodide ions to a chloroform solution of (2) a yellow colour was generated and no precipitate of AgI was formed. Very subtle changes in the hydride chemical shift and coupling constant to ^{31}P were also noted. Using a more direct approach, it was found that on stirring a suspension of AgI in dichloromethane with an equimolar quantity of (1) all of the solid dissolved to give a bright yellow solution from which the product was isolated as a yellow oil, (4). This is postulated to be $[AgI\{ReH_7(PPhPr^i_2)_2\}]$. In both the i.r. and n.m.r. spectra adduct (4) was barely distinguishable from $[ReH_7(PPhPr^i_2)_2]$. However a low-frequency i.r. spectrum showed a strong band at 165 cm^{-1} attributable to ν(Ag–I). This value is considerably lower than that observed for AgI (206 cm^{-1}), presumably a consequence of a weakening of the AgI bond on adduct formation.

In a reaction similar to that described for AgI, copper(I) iodide and $[ReH_7(PPhPr^i_2)_2]$ gave a solid formulated as $[CuI\{ReH_7(PPhPr^i_2)_2\}]$ (5) on the basis of elemental analysis and molecular weight determination (vapour pressure osmometry). A significant difference between (4) and (5) was observed in the i.r. spectra. The latter compound has a broad, weak band at *ca.* 1 700 cm^{-1} suggestive of a greater degree of interaction between copper and the hydride ligands.

Mercury(II) chloride is well known[20] for its ability to interact with electron-rich transition metal complexes. Under rigorously anhydrous conditions it was found to react with (1) to form a white compound (6) formulated as $[HgCl_2\{ReH_7(PPhPr^i_2)_2\}]$ from elemental analysis and integration of the ^1H n.m.r. spectrum. An important feature of the n.m.r. spectra of this compound was the observation of coupling between ^{199}Hg and both the ^1H and ^{31}P nuclei attached to rhenium even at room temperature. Compound (6) has no absorption in the i.r. spectrum between 1 900 and 1 650 cm^{-1}.

Synthesis and Reactions of Bis(di-isopropylphenylphosphine)hexahydridoosmium.—Douglas and Shaw[10b] isolated the hexahydride complex $[OsH_6(PMe_2Ph)_2]$ as a yellow oil. It was thought that reactions of d^2 compounds of this type with metallic Lewis acids would provide an interesting comparison with the rhenium chemistry described above. For consistency and also because di-isopropylphenylphosphine has proved a useful ligand in stabilizing polyhydride complexes and in promoting crystallinity, we chose to synthesize $[OsH_6(PPhPr^i_2)_2]$ by an extension of reported procedures.

Following the method of Chatt *et al.*[21] for the preparation of $[OsX_4(PR_3)_2]$ and $[OsX_3(PR_3)_3]$ (X = Cl or Br; $PR_3 = PPr^n_3$, PPr^n_2Ph *etc.*), osmium tetraoxide and an excess of di-isopropylphenylphosphine were reacted in refluxing ethanol for 3 h. The light brown precipitate was isolated but did not analyse satisfactorily for either $[OsCl_4(PPhPr^i_2)_2]$ or $[OsCl_3(PPhPr^i_2)_3]$. Purification by recrystallization was difficult because of the compound's very low solubility in solvents such as dichloromethane. The i.r. spectrum of the crude solid was dominated by a very strong, sharp band at 848 cm^{-1}, suggesting the presence of a *trans* O=Os=O group.[22] A similar case is that of the reaction of OsO_4 with triphenylphosphine in HCl–EtOH which has been discussed by Salmon and Walton.[23] On the basis of this analogy and the evidence presented here it is reasonable to formulate the light brown material as $[OsO_2Cl_2(PPhPr^i_2)_2]$, possibly contaminated with some $[OsCl_4(PPhPr^i_2)_2]$.

Reduction of the light brown solid with lithium aluminium hydride in tetrahydrofuran afforded, after chromatography, colourless crystals of $[OsH_6(PPhPr^i_2)_2]$ (7) in 40—50% yield. A ^1H n.m.r. signal at δ −9.21 p.p.m. [triplet with ^{187}Os satellites J(PH) 9; J(OsH) 46 Hz] was assigned to the six hydride ligands made equivalent by an intramolecular rearrangement process. The chemical shift may be compared with a value of δ −8.60 p.p.m. reported for $[OsH_6(PMe_2Ph)_2]$. On cooling to −80 °C the hydride signal broadened slightly but showed no sign of separating into different components.

Equimolar quantities of $HgCl_2$ and (7) reacted together in toluene without hydrogen evolution to form a colourless crystalline compound (8), formulated as $[HgCl_2\{OsH_6(PPhPr^i_2)_2]\}$ on the basis of elemental analysis, and the integrated ^1H n.m.r. spectrum. The latter (−10 °C) displayed a high-field triplet (δ —8.57 p.p.m.) with ^{199}Hg satellites [J(HgH) 45 Hz]. Coupling to ^{199}Hg was also observed in the ^{31}P n.m.r. spectrum. Mixing $HgCl_2$ and (7) in a 1 : 2 ratio yielded only (8).

The basicity of the central transition metal polyhydride complexes has been noted previously. For example the seven- and eight-co-ordinate complexes $[OsH_4(PMe_2Ph)_3]$ and $[ReH_5(PMe_2Ph)_3]$ have been shown[10,11] by conductometric titration to react with one equivalent of hydrogen chloride in methanol, although the protonated species proved unstable and decomposed with the elimination of H_2. In other cases such as $[WH_4(PR_3)_4]$ [$PR_3 = PMePh_2$,[9] PMe_2Ph, $PBuPh_2$, $P(OPr^i)_3$ *etc.*[24]] stable monoprotonated species have been isolated. It is also well established[11,25,26] that traces of acid catalyse H/D exchange between polyhydride complexes and solvents such as EtOD, presumably *via* a protonated intermediate. On the other hand the complexes are inert in basic media. None of the neutral, nine-co-ordinate polyhydride complexes is reported to form a protonated adduct, an observation in accord with intuitive expectations, as these complexes have d^0 configurations and presumably utilize all nd, $(n + 1)s$, and $(n + 1)p$ orbitals in binding the nine ligands already present in the co-ordination sphere. Nevertheless both $[ReD_7(PPh_3)_2]$[26] and $[WH_6(PPhPr^i_2)_3]$[25] have been shown to undergo rapid acid-catalysed H/D exchange and there seems to be no compelling reason, other than those mentioned above, to suppose that the mechanism operating for nine-co-ordinate complexes differs from that of the seven- and eight-co-ordinate species. It is therefore reasonable to speculate that H/D exchange for the nine-co-ordinate species involves an intermediate or transition state in which the metal is ten-co-ordinate. This is supported by the results reported here, namely that $[ReH_7(PPhPr^i_2)_2]$ does exhibit Lewis-base properties and is capable of expanding its co-ordination sphere.

It is interesting to question the role of the hydride ligands in binding the metal Lewis acids. In the absence of direct evidence from *X*-ray diffraction it is necessary to consider the spectroscopic data. Ginsberg[27] has commented on the insensitivity of the proton n.m.r. chemical shift to quite substantial changes in the co-ordination sphere of the metal (for example exchanging PR_3 for H^-). The n.m.r. data presented in Table 1 support the conclusion that the magnetic environment of the hydride ligands is barely altered on adduct formation. It is reasonable to suppose that any large interaction with the Lewis-acid metal atom, as for example if the hydrides were to bridge the metal–metal bond, would result in a correspondingly large change in the n.m.r. parameters, although the effect would be lessened by the dynamic averaging which occurs in fluxional systems. There exists therefore no unequivocal n.m.r. evidence for a strong Lewis-acid metal-hydride interaction.

On the other hand the metal-hydride stretching vibrations appear to be particularly sensitive to changes in the co-ordination sphere, although in a manner which is not well understood. Apparently similar compounds may display very different spectra in the ν(M–H) region. Thus, whereas $[WH_6(PPhPr^i{}_2)_3]$ has absorption maxima at 1 924w, 1 892w, 1 864m, 1 848s and 1 813s cm^{-1},[25] the corresponding peaks in $[WH_6(PMe_2Ph)_3]$ are reported at 1 834w, 1 792w, 1 755w, and 1 731s cm^{-1}.[28] Similar variation has been noted[26] with rhenium hydrides and may reflect fundamental changes in the co-ordination geometry. With regard to the data of Table 1 it appears that there may be a correlation between the mean vibrational frequency and the degree of co-ordination about the Lewis-acid centre. Thus complex (3) with only the rhenium hydride bound to silver has a substantial peak at 1 715 cm^{-1} whereas (6) with two chloride ligands has several peaks above 1 900 cm^{-1} [there is a similar though much less pronounced trend in ^2J(PH)]. It is probable that the low value of ν(ReH) in (3) is indicative of a degree of Ag–H interaction as is also suggested by the observation of silver–proton coupling (but not silver–phosphorus coupling). However important hydride bridging may be in determining the stability of the Re–Ag bond in (3) it cannot (from i.r. evidence) be invoked in the case of (6) nor of the complexes (4) and (8) which must therefore depend on direct metal–metal interaction for their stability.

Experimental

All experiments were carried out under dry oxygen-free nitrogen using Schlenk-tube techniques. Solvents were dried and distilled under nitrogen immediately prior to use. Nuclear magnetic resonance spectra were recorded on JEOL FX90Q and FX 200 spectrometers: ^{1}H spectra at 90 and 199.5 MHz, ^{31}P spectra at 36.2 MHz. Chemical shifts are quoted relative to $SiMe_4$ (^{1}H) and 85% H_3PO_4 (external) (^{31}P). Infrared spectra were recorded on Perkin-Elmer 297 and 457 spectrophotometers. Melting points were measured in sealed, evacuated tubes. The compound $[ReOCl_3(PPh_3)_2]$ was prepared according to the published method.[29]

Synthesis of $[ReOCl_3(PPhPr^i{}_2)_2]$.—To a suspension of $[ReOCl_3(PPh_3)_2]$ (1.8 g, 2.16 mmol) in toluene (40 cm^3) was added $PPhPr^i{}_2$ (1.2 cm^3) and the mixture stirred for 16 h. Most of the solvent was evaporated at reduced pressure leaving a slurry which was washed with diethyl ether (3 × 7 cm^3). The washings were discarded and the residue was dried *in vacuo*, affording $[ReOCl_3(PPhPr^i{}_2)_2]$ as yellow *microcrystals* (1.3 g, 1.93 mmol, 89%). The compound was recrystallized from dichloromethane (Found: C, 41.55; H, 6.0. $C_{24}H_{38}Cl_3OP_2Re$ requires C, 41.35; H, 5.5%); $\nu_{max.}$(ReO) 977 cm^{-1} (Nujol).

Synthesis of $[ReH_7(PPhPr^i{}_2)_2]$ (1).—To a suspension of $[ReOCl_3(PPhPr^i{}_2)_2]$ (1.4 g, 2.0 mmol) in tetrahydrofuran (thf) (40 cm^3) at −30 °C was added $LiAlH_4$ (0.27 g, 7.1 mmol) in small portions. The reaction mixture was stirred at this temperature for 2 h and then excess $LiAlH_4$ was destroyed with wet thf (*ca.* 5% H_2O). Evaporation of the solvent *in vacuo* at 20 °C left a grey residue which was extracted at −50 °C with dichloromethane and the extract filtered through sintered glass. The filtrate was evaporated *in vacuo* and the resulting brown oil was dissolved in hexane and applied to an alumina chromatography column under nitrogen. Elution with hexane afforded a crude product which was further purified by repeated recrystallization from hexane. Ultimately, large colourless *crystals* of $[ReH_7(PPhPr^i{}_2)_2]$ were isolated (0.48 g, 0.82 mmol, 41%), m.p. 91 °C (Found: C, 49.65; H, 8.25. $C_{24}H_{45}P_2Re$ requires C, 49.55; H, 7.8%).

Preparation of $[OsO_2Cl_2(PPhPr^i{}_2)_2]$.—Di-isopropylphenylphosphine (19 cm^3, 15 g, 78 mmol) was added to a solution of osmium tetraoxide (4 g, 15.7 mmol) and concentrated hydrochloric acid (8 cm^3) in ethanol (150 cm^3). The mixture was heated under reflux for 3 h, cooled, and the solid product removed by filtration. After washing with ethanol (3 × 20 cm^3) and drying there remained a light brown microcrystalline solid, predominantly $[OsO_2Cl_2(PPhPr^i{}_2)_2]$ (9.31 g, 82%) (Found: C, 41.55; H, 6.05; Cl, 11.1. $C_{24}H_{38}Cl_2O_2OsP_2$ requires C, 42.3; H, 5.6; Cl, 10.4%).

Preparation of $[OsH_6(PPhPr^i{}_2)_2]$ (7).—A suspension of $[OsO_2Cl_2(PPhPr^i{}_2)_2]$ (9.31 g, 12.9 mmol) in thf (60 cm^3) was treated with small portions of $LiAlH_4$ (1.72 g, 45.15 mmol) and the mixture stirred for 2 h. Excess $LiAlH_4$ was destroyed with wet thf until effervescence ceased, and the solvent was evaporated under reduced pressure. The residue was extracted with hexane and the extract applied to a short alumina column under nitrogen. Evaporation of the hexane eluate afforded colourless *crystals* of $[OsH_6(PPhPr^i{}_2)_2]$ (3.06 g, 41%). The compound was recrystallized from toluene, m.p. 92 °C [Found: C, 49.6; H, 7.8%; M^+ 586. $C_{24}H_{44}OsP_2$ requires C, 49.2; H, 7.75%; $M(^{192}Os)$ 586]; peak area ratio (^{1}H n.m.r.), $C\mathit{H}Me_2 : Os\mathit{H} = 4 : 6.1$.

Synthesis of $[Ag\{ReH_7(PPhPr^i{}_2)_2\}_2][PF_6]$ (2).—A solution of silver(I) hexafluorophosphate (0.062 g, 0.245 mmol) in dichloromethane (2 cm^3) was added dropwise to a toluene solution of $[ReH_7(PPhPr^i{}_2)_2]$ (0.285 g, 0.49 mmol in 3 cm^3). The dense liquid phase, which separated initially, solidified on standing. After 24 h the supernatant liquid was decanted off and the solid washed with toluene and diethyl ether to afford on drying white *crystals* of $[Ag\{ReH_7(PPhPr^i{}_2)_2\}_2][PF_6]$ (0.183 g, 53%) (Found: C, 40.6; H, 6.55. $C_{48}H_{90}AgF_6P_5Re_2$ requires C, 40.7; H, 6.4%).

Synthesis of $[Ag\{ReH_7(PPhPr^i{}_2)_2\}][PF_6]$ (3).—From a reaction similar to that described above but with equimolar proportions of $AgPF_6$ and $[ReH_7(PPhPr^i{}_2)_2]$ in dichloromethane–diethyl ether were isolated pale yellow crystals of $[Ag\{ReH_7(PPhPr^i{}_2)_2\}][PF_6]\cdot 0.5Et_2O$ (53%) (Found: C, 35.7; H, 5.75. $C_{26}H_{50}AgF_6O_{0.5}P_3Re$ requires C, 35.8; H, 5.75%).

Reaction of $[ReH_7(PPhPr^i{}_2)_2]$ *with* AgI.—Silver iodide (0.0174 g, 0.07 mmol) was suspended in dichloromethane (2 cm^3) and $[ReH_7(PPhPr^i{}_2)_2]$ (0.043 g, 0.07 mmol) was added. The mixture was stirred for 2 h. The resulting yellow solution was evaporated under reduced pressure affording a yellow oil. Attempts to crystallize the oil from diethyl ether were unsuccessful.

Synthesis of $[CuI\{ReH_7(PPhPr^i{}_2)_2\}]$ (5).—Copper(I) iodide (0.019 g, 0.1 mmol) was suspended in dichloromethane (2 cm^3) and $[ReH_7(PPhPr^i{}_2)_2]$ (0.059 g, 0.1 mmol) added. On stirring the mixture for 20 min all the solid dissolved giving a pale yellow solution. The volume of solvent was reduced *in vacuo* and the precipitated solid was isolated and washed with diethyl ether (3 × 2 cm^3) to afford pale yellow crystals of $[CuI\{ReH_7(PPhPr^i{}_2)_2\}]$ [Found: C, 37.0; H, 5.75%; *M* (C_6H_6), 778. $C_{24}H_{45}CuIP_2Re$ requires C, 37.3; H, 5.85%; *M*, 772].

Table 4. Atomic positional parameters (fractional co-ordinates) for $[Ag\{ReH_7(PPhPr^i{}_2)_2\}_2][PF_6]$ (2)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Re(1)	999(1)	9 548(1)	2 895(1)	C(19)	−1 751	9 246	1 644
Re(2A)	1 217(1)	5 696(1)	1 909(1)	C(26)	−2 382(8)	4 547(5)	1 519(8)
Re(2)	1 312(1)	5 995(1)	2 691(1)	C(27)	−3 385	4 734	1 193
Ag(1)	1 211(1)	7 723(1)	2 677(1)	C(28)	−3 546	5 550	1 076
P(11)	2 457(2)	10 229(2)	2 542(2)	C(29)	−2 704	6 178	1 284
P(12)	−822(2)	9 832(2)	2 864(2)	C(30)	−1 702	5 991	1 610
P(21)	−239(3)	4 952(2)	2 302(4)	C(25)	−1 541	5 176	1 728
P(22)	3 162(3)	6 077(2)	2 956(3)	C(31)	−199(12)	3 733(10)	1 631(11)
C(2)	2 623(6)	11 816(5)	4 283(6)	C(32)	750(14)	3 415(11)	2 125(13)
C(3)	2 878	12 737	4 876	C(33)	−259(16)	3 475(13)	522(12)
C(4)	3 269	13 309	4 487	C(34)	−393(16)	5 066(12)	3 595(13)
C(5)	3 406	12 960	3 505	C(35)	−804(21)	6 006(16)	4 100(18)
C(6)	3 151	12 039	2 912	C(36)	−1 137(19)	4 367(15)	3 662(17)
C(1)	2 760	11 467	3 301	C(38)	3 553(7)	6 734(6)	1 533(6)
C(7)	2 273(9)	10 113(9)	1 224(9)	C(39)	4 128	7 205	1 150
C(8)	1 334(10)	10 553(10)	907(10)	C(40)	5 068	7 700	1 724
C(9)	2 267(13)	9 139(10)	522(10)	C(41)	5 433	7 722	2 682
C(10)	3 742(9)	9 773(9)	2 766(8)	C(42)	4 859	7 251	3 065
C(11)	4 135(11)	9 943(10)	3 878(9)	C(37)	3 919	6 757	2 491
C(12)	4 563(10)	10 103(10)	2 364(11)	C(43)	3 665(13)	6 613(10)	4 338(10)
C(13)	−1 070(9)	11 045(7)	3 225(8)	C(44)	3 417(16)	7 600(12)	4 839(14)
C(14)	−754(11)	11 433(8)	2 537(10)	C(45)	3 301(18)	6 005(15)	4 868(16)
C(15)	−602(10)	11 617(8)	4 318(9)	C(46)	3 763(10)	4 982(8)	2 571(9)
C(16)	−1 423(9)	9 471(7)	3 718(8)	C(47)	3 693(12)	4 550(9)	1 459(9)
C(17)	−1 501(10)	8 431(8)	3 417(10)	C(48)	4 892(11)	5 047(9)	3 112(10)
C(18)	−2 489(9)	9 807(8)	3 837(9)	P	−3 787(3)	12 321(2)	1 860(3)
C(20)	−1 578(5)	8 376(5)	1 024(5)	F(1)	−3 258(7)	11 950(6)	2 667(7)
C(21)	−2 312	7 883	156	F(2)	−4 091(8)	11 322(5)	1 059(7)
C(22)	−3 219	8 259	−91	F(3)	−4 327(6)	12 716(6)	1 068(6)
C(23)	−3 392	9 129	530	F(4)	−4 856(6)	12 306(6)	2 193(6)
C(24)	−2 658	9 622	1 397	F(5)	−3 472(7)	13 350(5)	2 679(6)
				F(6)	−2 710(6)	12 362(5)	1 511(7)

Synthesis of $[HgCl_2\{ReH_7(PPhPr^i{}_2)_2\}]$ (6).—Mercury(II) chloride (0.027 g, 0.1 mmol) and $[ReH_7(PPhPr^i{}_2)_2]$ (0.058 g, 0.1 mmol) were reacted in dry toluene (1 cm^3). The solids dissolved and pentane (1 cm^3) was added. On cooling to −20 °C pure white crystals of $[HgCl_2\{ReH_7(PPhPr^i{}_2)_2\}]$ (6) were precipitated (0.040 g, 47%) (Found: C, 34.15; H, 5.8. $C_{24}H_{45}Cl_2HgP_2Re$ requires C, 33.8; H, 5.3%).

Synthesis of $[HgCl_2\{OsH_6(PPhPr^i{}_2)_2\}]$ (8).—Following the method used for (6) above, $HgCl_2$ (0.027 g) and (7) (0.10 g) afforded white *crystals* of $[HgCl_2\{OsH_6(PPhPr^i{}_2)_2\}]$ (8) as the toluene hemi-solvate (0.083 g, 87%) (Found: C, 36.1; H, 5.65. $C_{24}H_{44}Cl_2HgOsP_2\cdot 0.5\ C_6H_5Me$ requires C, 36.6; H, 5.35%).

Reaction of (2) *with* 1,10-*Phenanthroline*.—A sample of (2) (0.153 g, 0.108 mmol) dissolved in dichloromethane (1 cm^3) was treated with 1,10-phenanthroline (phen) (0.039 g, 0.216 mmol). After the mixture was stirred for 5 min, diethyl ether (6 cm^3) was added, and the fine precipitate separated by centrifuging. The supernatant liquid yielded (1) (0.104 g, 0.178 mmol), identified by i.r. and ^1H n.m.r. spectroscopy. The solid residue was $[Ag(phen)_2][PF_6]$ (0.060 g, 0.098 mmol) (Found: C, 47.25; H, 2.5; N, 8.15. $C_{24}H_{16}AgF_6N_4P$ requires C, 47.0; H, 2.65; N, 9.15%).

X-*Ray Crystal Structure of* $[Ag\{ReH_7(PPhPr^i{}_2)_2\}_2][PF_6]$ (2).—*Crystal data*. $[C_{48}H_{90}AgP_4Re_2][PF_6]$, M = 1 416.4, triclinic, space group $P\bar{1}$ (no. 2), a = 13.188(6), b = 16.014(6), c = 14.827(6) Å, α = 112.47(3), β = 101.03(3), γ = 90.65(3)°, U = 2 828(2) $Å^3$ at 200 K [U = 2 893(2) $Å^3$ at 298 K], Z = 2, D_c = 1.16 g cm^{-3}, μ(Mo-K_α) = 48.6 cm^{-1}, $F(000)$ = 1 388, λ(Mo-K_α) = 0.710 69 Å, Mo-K_α X-radiation (graphite monochromator).

Crystal structure determination. Crystals of (2) were grown from a dichloromethane–toluene solvent mixture by the slow evaporation of CH_2Cl_2 at 5 °C. A yellow crystal of irregular shape was cooled to 200 K and intensity data were recorded on a Nicolet P3m four-circle automated diffractometer in the range $2.9 \leqslant 2\theta \leqslant 50°$ as previously described.[30] From 5 493 measured intensities, 4 954 were unique and 4 452 satisfied the criterion $I \geqslant 1.5\sigma(I)$. These were used in the final stages of solution and refinement after correction for Lorentz, polarisation, and X-ray absorption effects. The latter were estimated by an empirical method since the rather irregular morphology of the sample (mean radius 0.2 mm) defied accurate indexing and measurement: 400 azimuthal scan data in the range $10 \leqslant 2\theta \leqslant 50°$ were used to this effect.

The heavy-atom positions were determined by Patterson methods and the nature of the disorder became apparent in the first difference density synthesis. Re(2) is positionally disordered between the two sites Re(2) and Re(2A), in the ratio 60 : 40, determined by refining the site occupation factors while both isotropic thermal parameters were fixed as equivalent. The phosphorus atoms attached to both Re(2) and Re(2A) show markedly anisotropic thermal parameters, but they could not be resolved into separate atomic sites corresponding to the Re atom shift. The silver atom also shows quite marked anisotropic thermal parameters and this is assumed to be a consequence of the disorder at one end of the chain. On average the carbon atoms of the phosphine ligands attached to Re(2) [Re(2A)] show higher thermal motion than do those attached to Re(1) and consequently not all of these were refined with anisotropic thermal parameters. There was no evidence for the hydride ligands in any of the electron-density maps, even those calculated with a $\sin\theta \leqslant 0.2$. All other hydrogen atoms associated with the phosphine ligands were included at calculated positions (C–H 0.96 Å), 'riding' on their attached carbon atoms, and in the case of the isopropyl groups the methyl units were regarded as rigid groups. Selected bond lengths and interbond angles are given in Tables 2 and 3 with the final atomic positional parameters given in Table 4.

The final-difference density synthesis showed no peaks >1 e Å^{-3} or <1.5 e Å^{-3}, the largest remaining being in the vicinity of the Re(2), Re(2A), and Ag atoms. Refinement by block-cascade least squares converged at $R = 0.048$ ($R' = 0.047$) using a weighting scheme of the type $w = [\sigma^2(F_o) + gF^2]^{-1}$, where $g = 0.0004$. The analysis of the data thereafter in terms of $\sin\theta/\lambda$ and $|F|^2$ was reasonable. All computations were carried out on a Data General S230 computer using the SHELXTL suite of programs.[31] Scattering factors were from ref. 32.

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