Transition Metal–Hydrogen–Alkali Metal Bonds: Synthesis and Crystal Structures of [K(18-crown-6)][$W(PMe_3)_3H_5$], [Na(15-crown-5)][$W(PMe_3)_3H_5$] and [{$W(PMe_3)_3H_5Li$}$_4$] and Related Studies*

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The new compounds K[$W(PMe_3)_3H_5$], [K(18-crown-6)][$W(PMe_3)_3H_5$] (18-crown-6 = 1,4,7,10,-13,16-hexaoxacyclooctadecane), Na[$W(PMe_3)_3H_5$], [Na(15-crown-5)][$W(PMe_3)_3H_5$], (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane), [{$W(PMe_3)_3H_5Li$}$_4$], K[$W(\eta\text{-}C_5H_5)(PMe_3)H_4$], [K(18-crown-6)][$W(\eta\text{-}C_5H_5)(PMe_3)H_4$], [K(18-crown-6)][$W(\eta\text{-}C_5H_4Et)(PMe_3)H_4$], K[*cis*-$Re(PMe_3)_4H_2$], [K(18-crown-6)][*cis*-$Re(PMe_3)_4H_2$], [$W(PMe_3)_3H_5(SnBu^n_3)$], [$W(\eta\text{-}C_5H_5)(PMe_3)H_4(SnBu^n_3)$], [$Re(PMe_3)_4H_2(SnBu^n_3)$], [$H(\eta\text{-}C_5H_5)_2ZrW(PMe_3)_3H_5$], [$Cl(\eta\text{-}C_5H_5)_2ZrW(PMe_3)_3H_5$], [{$(Ph_3P)Au$}$_3W(PMe_3)_3H_4$]$Cl\cdot xCH_2Cl_2$ and [K(18-crown-6)][$Mo(\eta\text{-}C_5H_5)_2H$] are reported. The X-ray crystal structures of [K(18-crown-6)][$W(PMe_3)_3H_5$], [Na(15-crown-5)][$W(PMe_3)_3H_5$], [{$W(PMe_3)_3H_5Li$}$_4$], [K(18-crown-6)][*cis*-$Re(PMe_3)_4H_2$], [{$(Ph_3P)Au$}$_3W(PMe_3)_3H_4$]$Cl\cdot 0.15CH_2Cl_2$ and [K(18-crown-6)]-[$Mo(\eta\text{-}C_5H_5)_2H$] have been determined. The crystal structures of [K(18-crown-6)][$W(PMe_3)_3H_5$] and [Na(15-crown-5)][$W(PMe_3)_3H_5$] have also been determined by neutron diffraction. Evidence for the presence of a degree of covalent bonding in the systems M–H–M′, where M = W and M′ = Li, Na or K and M = Re, M′ = K, is discussed.

Covalent transition-metal(M)–alkali-metal(M′) moieties, represented here by M–M′ or M–H–M′ have been characterised previously for lithium-containing compounds such as [{$M(\eta\text{-}C_5H_5)_2H(\mu\text{-}Li)$}$_4$],[1–5] and in other molybdenum,[6] tantalum,[7] niobium,[8,9] rhenium,[10] iridium,[11] platinum[12] and nickel–olefin derivatives.[13] Related M–Mg and M–Al and M–H–Al bonds have been found in compounds such as [$Mo(\eta\text{-}C_5H_5)_2H$-{$MgPr^i(\mu\text{-}Br)_2Mg(OEt_2)$}$_2$],[14–17] [$Mo(\eta\text{-}C_5H_5)_2H${$MgBr(thf)$}] (thf = tetrahydrofuran)[18,19] and [{$(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)$}$_2$].[20] Many of these compounds were prepared by treatment of transition-metal hydride compounds which have a sufficiently acidic metal hydrogen, with either an organolithium derivative, or, for magnesium, with Grignard reagents, or for aluminium, with trialkylaluminium compounds. We have called this synthetic strategy the alkane–elimination reaction (1).

$$M\text{–}H + RM' \longrightarrow M\text{–}M' + RH \qquad (1)$$

Here we report a further study of the synthesis and chemistry of M–H–M′ systems starting from polyhydride compounds such as [$W(PMe_3)_3H_6$] **1**[21] and [$Re(PMe_3)_4H_3$]. Preliminary reports of part of this work have been published.[22,23] The compounds [{$W(PMe_3)_3H_5Li$}$_4$][20,24] and [{$KOs(PMe_2Ph)_3H_3$}$_2$],[25] which has Os–H–K bonds, were described independently during the course of this study.

Results and Discussion

Treatment of [$W(PMe_3)_3H_6$] **1** in tetrahydrofuran at 60 °C with an excess of potassium hydride gave the microcrystalline pyrophoric pale yellow K[$W(PMe_3)_3H_5$] **2** in near-quantitative yields. Monitoring the reaction by ^1H NMR spectroscopy showed complete conversion of [$W(PMe_3)_3H_6$] **1** into **2** in 3 d. The analytical and spectroscopic data which characterise **2**, and all the other new compounds, are given in Table 1 or in the Experimental section. These data will not be discussed further unless the interpretation is not straightforward.

When tetrahydrofuran solutions of [$W(PMe_3)_3H_6$] and 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) were stirred with an excess of KH a rapid reaction with effervescence occurred and, after heating at 60 °C for 12 h, excellent crystals of [K(18-crown-6)][$W(PMe_3)_3H_5$] **3** could be isolated. Compound **3** was also prepared by addition of a slight excess of 18-crown-6 to tetrahydrofuran solutions of **2**.

Treatment of compound **1** with sodium hydride gave pyrophoric cream coloured Na[$W(PMe_3)_3H_5$] **4** in high yield. Addition of NaH to a tetrahydrofuran solution of [$W(PMe_3)_3H_6$] and 15-crown-5 (1,4,7,10,13-pentaoxacyclopentadecane) gave yellow crystals of [Na(15-crown-5)][$W(PMe_3)_3H_5$] **5** in excellent yield. In one preparation a crystal weighing 0.5 g and measuring 1.5 × 0.8 × 0.7 cm was isolated by cooling a tetrahydrofuran solution to −30 °C overnight. Compound **5** could be also prepared by addition of 1 equivalent of 15-crown-5 to a tetrahydrofuran solution of **4**.

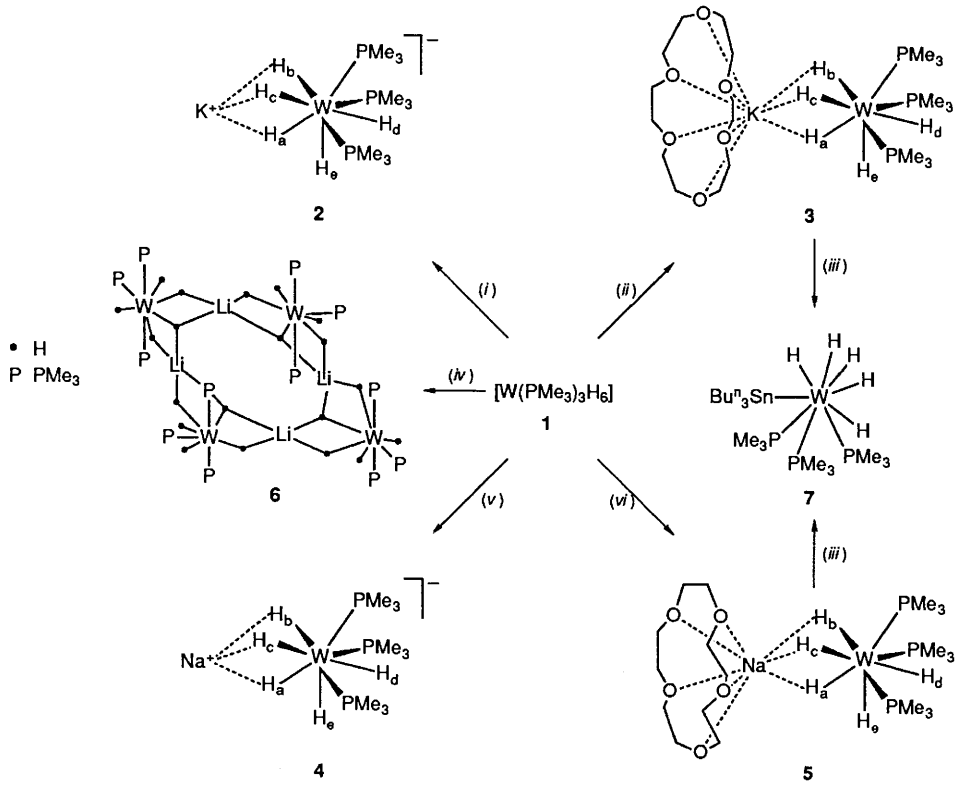
Treatment of compound **1** in pentane with an excess of *n*-butyllithium in hexane gave, after 2 d, yellow microcrystalline [{$W(PMe_3)_3H_5Li$}$_4$] **6**. The crystallinity of **6** was highly dependent upon the purity of the [$W(PMe_3)_3H_6$]; freshly sublimed [$W(PMe_3)_3H_6$] yielded crystals of suitable quality for single-crystal X-ray diffraction studies whilst less pure [$W(PMe_3)_3H_6$] typically yielded amorphous powders.

The compounds **1**–**6** are soluble in tetrahydrofuran, sparingly soluble in diethyl ether and insoluble in toluene and hexane. They are thermally stable but are extremely sensitive to air and to proton sources. Powders are pyrophoric but larger crystals

* 18-crown-6 = 1,4,7,10,13,16-Hexaoxacyclooctadecane and 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: mmHg ≈ 133 Pa.



Scheme 1 (*i*) KH in thf at 50 °C for 4 d, yield 95%; (*ii*) KH and 18-crown-6 in thf at room temperature (r.t.) for 2 d, 84%; (*iii*) $SnBu^n_3Cl$ in thf at r.t. for 10 min, 30%; (*iv*) $LiBu^n$ in hexane for 24 h, >95%; (*v*) NaH in thf at 60 °C for 4d, 95%; (*vi*) NaH and 15-crown-5 in thf at 60 °C for 3 d, 89%

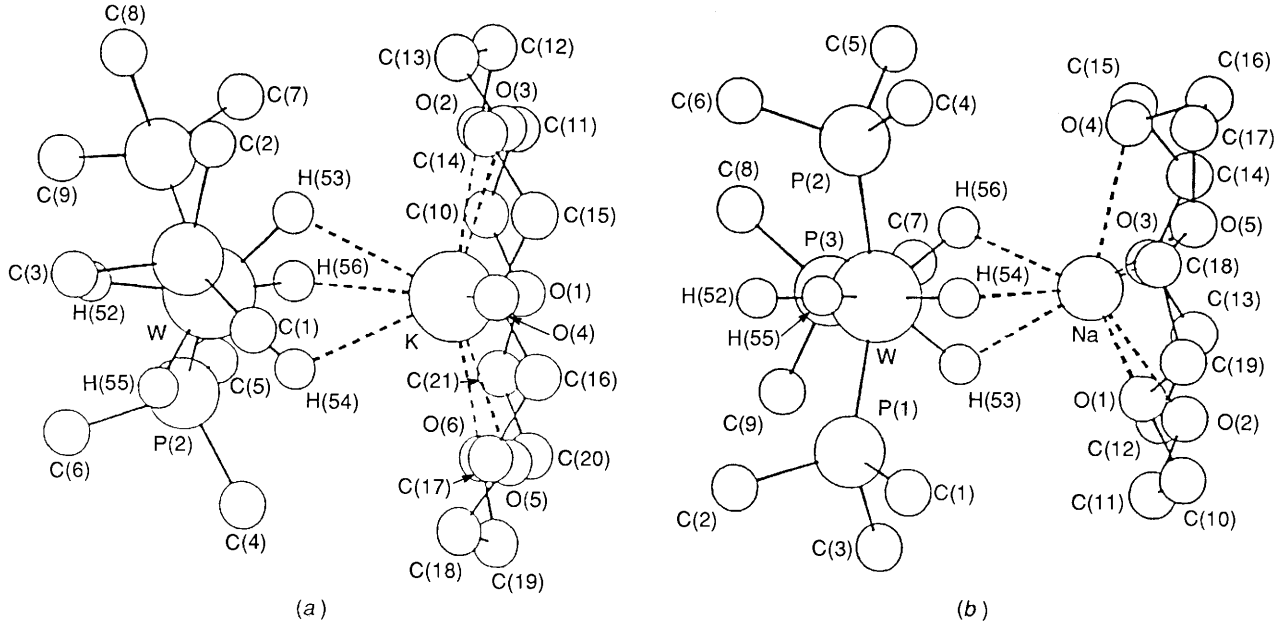


Fig. 1 Neutron diffraction structure analysis of (*a*) [K(18-crown-6)][$W(PMe_3)_3H_5$] **3** and (*b*) [Na(15-crown-5)][$W(PMe_3)_3H_5$] **5** looking parallel to the plane containing H(53), H(54) and H(56). In **3** the 18-crown-6 is somewhat bow shaped with the potassium out of the plane O(1)–O(6) but in **5** the 15-crown-5 is less regular in shape

decompose slowly. In order to maintain clean NMR spectra of **1**–**6** an excess of potassium hydride or sodium hydride, as appropriate, was added.

A preliminary single-crystal structure determination has been carried out on [$W(PMe_3)_3H_6$] **1**.[26] The geometry of the WP_3 skeleton is closely similar to that reported from the neutron diffraction structure of [$W(PPr^i_3)_3H_6$].[27] This neutron study located the tungsten-bound hydrogens and the co-ordination about tungsten was found to be best described as a tricapped trigonal prism in which the two phosphines with long W–P distances occupied eclipsed positions of a distorted trigonal prism which was then capped by two hydrogen atoms and one phosphine. The close similarity between the tungsten–phosphine geometries in [$W(PMe_3)_3H_6$] and [$W(PPhPr^i_2)_3H_6$] suggests that **1** has a similar disposition of the six hydrogens.

The molecular structures of compounds **3** and **5** have been determined by both X-ray and neutron diffraction. The overall views of the molecular structures as determined by the low-temperature neutron experiment are shown in Figs. 1(*a*) and (*b*) and are very similar to the room-temperature X-ray structures. The discussion and the dimensions quoted refer to the neutron diffraction analyses except where explicitly stated.

Table 1 Analytical and spectroscopic data[a]

Compound, colour, analysis	NMR data[b]
2 $K[W(PMe_3)_3H_5]$	^1H at 185 K: 1.50 (27 H, br s, $3PMe_3$), −4.74 (1 H, br m, WH), −5.74 [1 H, br m, WH], −5.51 [3 H, br q, J(P–H) 22, 3WH]
Pale yellow[c]	$^{31}P-\{^1H\}$: −25.61 [s, J(P–W) 167.8, $3PMe_3$]
C, 23.4 (23.7); H, 6.85 (7.0)[d]	$^{31}P-\{^1H$–Me$\}$: −25.61 [sxt, J(P–H) 26]
3 $[K(18\text{-crown-6})][W(PMe_3)_3H_5]$	^1H: 3.63 (24 H, s, 18-crown-6), 1.62 (27 H, s, $3PMe_3$), −5.16 (5 H, br m, 5WH); (at 203 K) 3.82 (24 H, s, 18-crown-6), 1.62 (27 H, s, $3PMe_3$), −4.32 [1 H, br t, J(P–H) 45, WH], −5.20 [3 H, br q, J(P–H) 23, 3WH], −6.21 [1 H, br dt, J(P–H) 63, J(P–H) 28, WH]
Orange[e]	$^{31}P-\{^1H\}$: −24.16 [s, J(P–W) 167.5, $3PMe_3$]
C, 34.3 (35.00); H, 7.6 (7.8)[f]	$^{31}P-\{^1H$–Me$\}$: −24.16 [sxt, J(P–H) 25.3]
4 $Na[W(PMe_3)_3H_5]$	^1H: 1.44 [27 H, vct, J(P–H) 5.6, $3PMe_3$], −5.3 (2 H, br s, 2WH), −6.1 (3 H, br s, 3WH); (at 200 K) 1.44 [27 H, vct, J(P–H) 5.6, $3PMe_3$], −4.3 (1 H, br m, WH), −5.8 (1 H, br m, WH), −6.1 (3 H, br q, 3WH)
Pale yellow[g]	$^{31}P-\{^1H\}$: −24.9 [s, J(P–W) 171.4, $3PMe_3$]
C, 22.1 (24.5); H, 6.4 (7.3)[h]	$^{31}P-\{^1H$–Me$\}$: −24.9 [sxt, J(P–H) 26]
5 $[Na(15\text{-crown-5})][W(PMe_3)_3H_5]$	^1H: 3.71 (20 H, s, 15-crown-5), 1.48 [27 H, vct, J(P–H) 5.6, $3PMe_3$], −5.14 [2 H, br q, J(P–H) 35.2, 2WH], −5.94 [3 H, br q, J(P–H) 20.7, 3 WH]
Yellow[i]	$^{31}P-\{^1H\}$: −24.3 [s, J(P–W) 172, $3PMe_3$]
C, 34.4 (34.5); H, 7.7 (7.9)[j]	$^{31}P-\{^1H$–Me$\}$: −24.3 [sxt, J(P–H) 25.9]
6 $[\{W(PMe_3)_3H_5Li\}_4]$	^1H: 1.52 [27 H, vct, J(P–H) 5.5, $3PMe_3$], −5.60 (5 H, vbr s, 5WH); (400 MHz at 138 K) 1.46 (27 H, br s, $3PMe_3$), −4.62 [1 H, br t, J(P–H) 44.3, WH_d], −6.00 [3 H, dt, J(P–H) 66, 26, and overlapping br s, $WH_{b,c,e}$], −7.10 (1 H, br s, WH_a)
Yellow[k]	$^{31}P-\{^1H\}$: −24.03 [s, J(P–W) 175.2, $3PMe_3$]
C, 25.5 (25.5); H, 7.5 (7.6)[l]	$^{31}P-\{^1H$–Me$\}$: −24.03 [sxt, J(P–H) 26]
7 $[W(PMe_3)_3H_5(SnBu^n_3)]$	^1H: 1.83 (6 H, m, $3CH_2$), 1.56 (6 H, m, $3CH_2$), 1.41 [27 H, vct, J(P–H) 3.6, $3PMe_3$], 1.05 (15 H, m, $3CH_2$ and $3CH_3$), −3.84 [5 H, q, J(P–H) 34.11, J(W–H) 24, 5WH][o]
White,[m] m.p. 27 °C	$^{31}P-\{^1H\}$: −31.54 [s, J(W–P) 106.23, $J(^{117}Sn$–P) 154.73, $J(^{119}Sn$–P) 161.54, $3PMe_3$][o]
C, 35.7 (35.6); H, 8.2 (8.3)[n]	$^{31}P-\{^1H$–Me$\}$: −31.54 [sxt, J(P–H) 26.6][o]
$Bu^n = C_aH_2C_bH_2C_cH_2C_dH_3$	$^{119}Sn-\{^1H\}$: 49.0 [q, $J(^{119}Sn$–W) 116, $J(^{119}Sn$–P) 162][p]
	$^{183}W-\{^1H\}$: −3715 [q, J(W–P) 106]
	^{13}C (62.89 MHz): 31.34 (t, $3C_b$ or $3C_c$), 29.43 (4 lines, $3PMe_3$), 28.67 (t, $3C_c$ or $3C_b$), 17.37 [t, $J(^{13}C$–$^{117}Sn)$ 186, $J(^{13}C$–$^{119}Sn)$ 192, $3C_a$], 14.35 (q, $3C_d$)[o]
8 $K[W(\eta\text{-}C_5H_5)(PMe_3)H_4]$	^1H: 3.76 [5 H, d, J(P–H) 3.0, η-C_5H_5], 1.50 [9 H, d, J(P–H) 7.0, PMe_3], −1.78 [1 H, vbr s, WH], −8.40 (2 H, vbr s, 2WH), −9.35 (1 H, vbr s, WH)
Yellow solution in thf	
9 $[K(18\text{-crown-6})][W(\eta\text{-}C_5H_5)(PMe_3)H_4]$	^1H: 3.73 [5 H, d, J(P–H) 2.8, η-C_5H_5], 3.66 (24 H, s, 18-crown-6), 1.52 [9 H, d, J(P–H) 7.1, PMe_3], −8.33 (2 H, vbr s, 4WH)
Yellow solution in thf	
10 $[K(18\text{-crown-6})][W(\eta\text{-}C_5H_4Et)(PMe_3)H_4]$	^1H: 3.96 (2 H, s, $2H_a$ or $2H_b$), 3.76 [s, 18-crown-6 (excess)], 3.29 (2 H, br s, $2H_b$ or $2H_a$), 2.40 [2 H, q, J(H–H) 6.8, $C_5H_4CH_2CH_3$], 1.60 [9 H, d, J(P–H) 7.6, PMe_3], 1.20 [3 H, t, J(H–H) 6.8, $C_5H_4CH_2CH_3$], −7.50 [2 H, vbr s, 4WH]; (at 250 MHz at 228 K)[q] −1.66 [1 H, br dq, J(P–H) 68.5, WH], −7.70 [2 H, dt, J(P–H) 15.9, J(H–H) 8.2, J(W–H) 63.9, 2WH], −8.27 [1 H, qnt, J(H–H) 7.0, J(P–H) 7.0, WH]
Yellow solution in thf	$^1H-\{^{31}P\}$ (at 250 MHz at 228 K)[r]: −1.66 [1 H, br q, J(H–H) 8.5, WH], −7.70 [2 H, t, J(H–H) 8.2, J(W–H) 63.9, 2WH], −8.27 [1 H, q, J(H–H) 7.0, WH]
	$^{31}P-\{^1H\}$: −25.22 [s, J(P–W) 226.4, PMe_3]
	$^{31}P-\{^1H$–Me$\}$: −25.22 (br s, PMe_3)
11 $[W(\eta\text{-}C_5H_5)(PMe_3)H_4(SnBu^n_3)]$	^1H (at 250 MHz): 4.53 [5 H, d, J(P–H) 2, η-C_5H_5], 1.81 (6 H, m, $3CH_2$), 1.57 [6 H, sxt, J(H–H) 7.1, $3CH_2$], 1.14 [9 H, d, J(P–H) 8.9, PMe_3], 1.08 [15 H, m, $3CH_2$ and $3CH_3$], −4.76 (1 H, vbr s, WH), −6.07 (3 H, br m, 3WH);[t] (at 250 MHz at 223 K)[r] −3.55 [1 H, br d, J(P–H) 50, WH], −5.80 [1 H, br d, J(P–H) 50], −5.92 (1 H, br s, WH), −6.40 [1 H, br d, J(P–H) 48, WH][t]
Brown oil[s]	$^1H-\{^{31}P\}$ (at 250 MHz at 223 K)[r]: −3.55 (1 H, br s, WH), −5.80 (1 H, br s, WH), −5.92 (1 H, br s, WH), −6.40 (1 H, br s, WH)[t]
	$^{31}P-\{^1H\}$ (at 223 K): −26.69 [s, J(P–W) 43.3, J(P–Sn)$_{av}$ 148, PMe_3][t]
	$^{31}P-\{^1H$–Me$\}$ (at 223 K): −26.69 [q, J(P–H) 46.5][t]
12 $[K(18\text{-crown-6})][cis\text{-}Re(PMe_3)_4H_2]$	^1H: 3.65 (24 H, s, 18-crown-6), 1.63 [18 H, s, $2(P_aMe_3)$], 1.51 [18 H, d, J(P–H) 4.6, $2(P_bMe_3)$], −8.66 (2 H, m, 14 lines, 2ReH)
	$^{31}P-\{^1H\}$: −48.6 [2P, br t, $2(P_aMe_3)$], −53.9 [2P, br t, $2(P_bMe_3)$]
13 $K[Re(PMe_3)_4H_2]$	^1H: 1.51 [18 H, s, $2(P_aMe_3)$], 1.43 [18 H, d, J(P–H) 4.5, $2(P_bMe_3)$], −9.34 (2 H, m, 14 lines, 2ReH)
Pale yellow	$^{31}P-\{^1H\}$: −45.8 [2P, br t, $2(P_aMe_3)$], −52.7 [2P, br m, $2(P_bMe_3)$]
	$^{31}P-\{^1H$–Me$\}$: −45.8 [2P, br m, $2(P_aMe_3)$], −52.7 [2P, br m, $2(P_bMe_3)$]
14 $[Re(PMe_3)_4H_2(SnBu^n_3)]$	^1H: 1.93 (6 H, m, $3CH_2$), 1.66 [6 H, sxt, J(H–H) 23, $3CH_2$], 1.38 [36 H, d, J(P–H) 5, $4PMe_3$], 1.15 (15 H, m, 3 CH_2 and $3CH_3$), −8.66 [2 H, qnt, J(P–H) 23.1, J(H–Sn)$_{av}$ 63, 2ReH][o]
White	$^{31}P-\{^1H\}$: −51.6 (br s, $4PMe_3$)[o]
C, 36.8 (37.3); H, 8.3 (7.2)	$^{31}P-\{^1H$–Me$\}$: −51.6 [br t, J(P–H) 22.1][o]
15 $[Cl(\eta\text{-}C_5H_5)_2ZrW(PMe_3)_3H_5]$	^1H: 6.17 [10 H, s, $2(\eta$-$C_5H_5)$], 1.57 [27 H, d, J(P–H) 7.24, $3PMe_3$], −2.19 [5 H, q, J(P–H) 25.3, J(W–H) 33.75, 5WH)][o]
Green	$^{31}P-\{^1H\}$: −20.36 [s, J(P–W) 195.5, $3PMe_3$][o]
C, 33.8 (33.9); H, 6.1 (6.2)[u]	$^{31}P-\{^1H$–Me$\}$: −20.36 [sxt, J(P–H) 22.0][o]
16 $[H(\eta\text{-}C_5H_5)_2ZrW(PMe_3)_3H_5]$	^1H: 5.93 [10 H, s, $2(\eta$-$C_5H_5)$], 5.25 (1 H, m, ZrH), 1.55 (18 H, $2PMe_3$), 1.53 (9 H, $1PMe_3$), −3.35 [5 H, dq, J(P–H) 25.8, J(H–H) 2.33 J(W–H) 37.5, 5WH][o]
Purple	$^{31}P-\{^1H\}$: −22.4 [s, J(P–W) 198.9, $3PMe_3$][o]
C, 35.5 (35.7); H, 6.6 (6.7)[v]	$^{31}P-\{^1H$–Me$\}$: −22.4 [sxt, J(P–H) 19.6][o]

Table 1 (*continued*)

Compound, colour, analysis	NMR data[b]
17 $[\{(Ph_3P)Au\}_3W(PMe_3)_3H_4]Cl\cdot 0.15CH_2Cl_2$ Orange-red[w] C, 40.7 (41.2); H, 4.2 (4.1)[x]	^{1}H: 7.60 [9 H, d, *J*(H–H) 8.1, 6 H_o or 6 H'_o], 7.56 [9 H, d, *J*(H–H) 7.9, 6 H'_o or 6 H_o], 7.37 [9 H, t, *J*(H–H) 7.3, 6 H_p], 7.16 [18 H, t, *J*(H–H) 7.1, 12 H_m], 2.12 [br s, CH_2Cl_2 and $CHDCl_2$ (solvent)], 1.67 [27 H, vct, *J*(P–H) 7.1, 3PMe_3], −0.18 [4 H, br m (12 lines), 4WH][y] ^{1}H-{^{31}P} (at 250 MHz)[r]: −0.18 (4 H, br s, 4WH)[y] ^{31}P-{^{1}H}: 55.67 (3P, s, 3PPh_3), −32.26 [3P, s, *J*(P–W) 144.5, 3PMe_3][y] ^{31}P-{^{1}H–Ph}: 55.67 [3P, br qnt, *J*(P–H) 7.9][y] ^{31}P-{^{1}H–Me}: −32.26 [3P, qnt, *J*(P–H) 19.5][y] ^{31}P-{^{1}H} (at 173K): 54.96 (2P, s, 2PPh_3), 49.72 (1P, s, 1PPh_3), −30.60 (3P, s, 3PMe_3)[y]

[a] Analytical data given as: found (required) in %. Ir data: KBr disc. [b] Unless otherwise stated, ^{1}H at 300, ^{13}C at 62.9, ^{31}P at 101.26 MHz, in [$^2H_8$]tetrahydrofuran at ambient temperature. Data given as chemical shift (δ) [relative integral, multiplicity, coupling constant *J*/Hz, assignment]. [c] ν(W–H) 1748s, 1660m, ν(P–C) 950s cm^{-1}. [d] K, 8.7 (8.8); W, 40.55 (40.1%). [e] ν(W–H) 1747s, 1682s and 1622s cm^{-1}. [f] K, 5.2 (5.4%). [g] ν(W–H) 1746s and 1640s cm^{-1}. [h] Na, 5.00 (5.2%). [i] ν(W–H) 1677s and 1625s cm^{-1}. [j] Na, 3.4 (3.5); W, 27.6 (27.8%). [k] ν(W–H) 1690s cm^{-1}. [l] Li, 1.6 (1.65%). [m] *m*/*z* 720 [P^+(^{184}W, ^{118}Sn) + O − 2H], 706 [P^+(^{184}W, ^{118}Sn)] and 649 [P^+(^{184}W, ^{118}Sn) − C_4H_9]. [n] W, 25.9 (26.0%). [o] In [$^2H_6$]benzene. [p] At 89.55 MHz in light petroleum (b.p. 40–60 °C). [q] As above except for WH signals. [r] Hydride resonances only. [s] *m*/*z* 562 [P^+(^{184}W, ^{118}Sn) − C_4H_9] and 505 [P^+(^{184}W, ^{118}Sn) − $2C_4H_9$]. [t] In [$^2H_8$]toluene. [u] Cl, 5.4 (5.3); Zr, 13.75 (13.5%). [v] W, 29.05 (28.8%). [w] ν(W–H) 2144m cm^{-1}. [x] Cl, 2.5 (2.5); Au, 30.5 (32.0%). [y] In [$^2H_2$]dichloromethane.

Table 2 Selected interatomic distances (Å) and interbond angles (°) with estimated standard deviations (e.s.d.s) in parentheses

(*a*) $[\{W(PMe_3)_3H_5Li\}_4]$

W(1)···Li(1)	2.76(1)	P(1)–W(1)–Li(1)	101.4(3)	P(5)–W(2)–Li(1)	177.6(2)
W(1)···Li(2)	2.92(1)	P(2)–W(1)–Li(1)	102.7(2)	P(5)–W(2)–Li(2)	100.1(3)
W(1)–P(1)	2.411(2)	P(2)–W(1)–P(1)	97.3(1)	P(5)–W(2)–P(4)	96.2(1)
W(1)–P(2)	2.421(2)	P(3)–W(1)–Li(1)	103.3(2)	P(6)–W(2)–Li(1)	81.6(2)
W(1)–P(3)	2.435(2)	P(3)–W(1)–P(1)	100.8(1)	P(6)–W(2)–Li(2)	105.0(3)
W(2)···Li(1)	2.94(1)	P(3)–W(1)–P(2)	144.5(1)	P(6)–W(2)–P(4)	143.2(1)
W(2)···Li(2)	2.78(1)	Li(2)–W(2)–Li(1)	80.0(3)	P(6)–W(2)–P(5)	100.6(1)
W(2)–P(4)	2.412(2)	P(4)–W(2)–Li(1)	81.5(2)	W(2)–Li(1)–W(1)	169.3(5)
W(2)–P(5)	2.424(2)	P(4)–W(2)–Li(2)	103.9(3)		
W(2)–P(6)	2.432(2)				

(*b*) $[Na(15\text{-crown-5})][W(PMe_3)_3H_5]$

W···Na	3.215(6)	Na–O(3)	2.46(3)	Na–O(14)	2.46(4)	P(2)–C(5)	1.83(2)
W–P(1)	2.415(4)	Na–O(4)	2.50(3)	Na–O(15)	2.58(4)	P(2)–C(6)	1.84(2)
W–P(2)	2.392(4)	Na–O(5)	2.52(3)	P(1)–C(1)	1.82(2)	P(3)–C(7)	1.84(2)
W–P(3)	2.392(4)	Na–O(11)	2.46(2)	P(1)–C(2)	1.88(2)	P(3)–C(8)	1.83(2)
Na–O(1)	2.48(2)	Na–O(12)	2.70(4)	P(1)–C(3)	1.81(2)	P(3)–C(9)	1.81(2)
Na–O(2)	2.66(4)	Na–O(13)	2.60(3)	P(2)–C(4)	1.78(2)		
P(1)–W–Na	99.9(1)	O(4)–Na–W	108.9(8)	O(12)–Na–O(11)	64.7(7)	C(3)–P(1)–C(1)	96.0(1)
P(2)–W–Na	97.4(1)	O(4)–Na–O(1)	127.0(9)	O(13)–Na–O(11)	129.3(9)	C(3)–P(1)–C(2)	103.0(1)
P(2)–W–P(1)	145.6(1)	O(4)–Na–O(2)	115.5(9)	O(13)–Na–O(12)	64.9(8)	C(4)–P(2)–W	116.6(7)
P(3)–W–Na	107.1(1)	O(4)–Na–O(3)	65.7(9)	O(14)–Na–O(11)	130.0(9)	C(5)–P(2)–W	121.1(8)
P(3)–W–P(1)	103.1(2)	O(5)–Na–W	126.0(7)	O(14)–Na–O(12)	110.9(9)	C(5)–P(2)–C(4)	99.0(1)
P(3)–W–P(2)	99.8(2)	O(5)–Na–O(1)	63.1(7)	O(14)–Na–O(13)	66.4(9)	C(6)–P(2)–W	118.1(6)
O(1)–Na–W	109.7(6)	O(5)–Na–O(2)	100.8(8)	O(15)–Na–O(11)	65.4(7)	C(6)–P(2)–C(4)	99.0(1)
O(2)–Na–W	125.7(5)	O(5)–Na–O(3)	111.0(1)	O(15)–Na–O(12)	101.6(8)	C(6)–P(2)–C(5)	99.0(1)
O(2)–Na–O(1)	65.4(7)	O(5)–Na–O(4)	65.1(8)	O(15)–Na–O(13)	121.4(9)	C(7)–P(3)–W	118.8(7)
O(3)–Na–W	112.7(9)	O(11)–Na–W	105.5(6)	O(15)–Na–O(14)	67.4(8)	C(8)–P(3)–W	119.9(7)
O(3)–Na–O(1)	126.2(9)	O(12)–Na–W	125.1(6)	C(1)–P(1)–W	115.1(7)	C(8)–P(3)–C(7)	98.0(1)
O(3)–Na–O(2)	63.5(8)	O(13)–Na–W	106.8(8)	C(2)–P(1)–W	116.7(8)	C(9)–P(3)–W	120.1(8)
		O(14)–Na–W	113.8(8)	C(2)–P(1)–C(1)	101.0(1)	C(9)–P(3)–C(7)	99.0(1)
		O(15)–Na–W	123.9(6)	C(3)–P(1)–W	121.3(8)	C(9)–P(3)–C(8)	96.0(1)

(*c*) $[Na(15\text{-crown-5})][W(PMe_3)_3H_5]$ (neutron diffraction data)

W–H(52)	1.778(3)	C(3)–H(8)	1.085(4)	C(8)–H(24)	1.081(3)	C(11)–H(30)	1.098(3)
W–H(53)	1.766(3)	C(3)–H(9)	1.067(4)	C(9)–H(25)	1.094(3)	C(11)–H(31)	1.107(3)
W–H(54)	1.793(3)	P(2)–C(4)	1.849(2)	C(9)–H(26)	1.083(3)	C(12)–C(13)	1.509(2)
W–H(55)	1.772(3)	P(2)–C(5)	1.829(2)	C(9)–H(27)	1.090(3)	C(12)–H(32)	1.108(3)
W–H(56)	1.750(3)	P(2)–C(6)	1.837(2)	Na–O(1)	2.497(3)	C(12)–H(33)	1.103(3)
W–P(1)	2.411(2)	C(4)–H(10)	1.093(3)	Na–O(2)	2.569(3)	C(13)–H(34)	1.108(3)
W–P(2)	2.393(2)	C(4)–H(11)	1.087(3)	Na–O(3)	2.469(3)	C(13)–H(35)	1.097(3)
W–P(3)	2.389(2)	C(4)–H(12)	1.084(3)	Na–O(4)	2.524(3)	C(14)–C(15)	1.524(2)
W···Na	3.204(3)	C(5)–H(13)	1.094(3)	Na–O(5)	2.502(3)	C(14)–H(36)	1.108(3)
H(53)–Na	2.413(4)	C(5)–H(14)	1.098(4)	O(1)–C(10)	1.412(2)	C(14)–H(37)	1.098(3)
H(54)–Na	2.283(4)	C(5)–H(15)	1.085(3)	O(1)–C(19)	1.424(2)	C(15)–H(38)	1.098(3)
H(56)–Na	2.316(4)	C(6)–H(16)	1.097(3)	O(2)–C(11)	1.413(2)	C(15)–H(39)	1.109(3)
P(1)–C(1)	1.842(2)	C(6)–H(17)	1.090(4)	O(2)–C(12)	1.422(2)	C(16)–C(17)	1.527(2)
P(1)–C(2)	1.837(2)	C(6)–H(18)	1.093(3)	O(3)–C(13)	1.416(2)	C(16)–H(40)	1.101(3)
P(1)–C(3)	1.849(2)	P(3)–C(7)	1.837(2)	O(3)–C(14)	1.416(2)	C(16)–H(41)	1.097(3)
C(1)–H(1)	1.094(3)	P(3)–C(8)	1.850(2)	O(4)–C(15)	1.416(2)	C(17)–H(42)	1.101(3)
C(1)–H(2)	1.082(4)	P(3)–C(9)	1.855(2)	O(4)–C(16)	1.417(2)	C(17)–H(43)	1.098(3)
C(1)–H(3)	1.084(3)	C(7)–H(19)	1.098(3)	O(5)–C(17)	1.405(2)	C(18)–C(19)	1.510(2)
C(2)–H(4)	1.092(3)	C(7)–H(20)	1.090(3)	O(5)–C(18)	1.427(2)	C(18)–H(44)	1.096(3)
C(2)–H(5)	1.091(4)	C(7)–H(21)	1.091(4)	C(10)–C(11)	1.522(2)	C(18)–H(45)	1.106(3)
C(2)–H(6)	1.093(4)	C(8)–H(22)	1.091(3)	C(10)–H(28)	1.098(3)	C(19)–H(46)	1.104(3)
C(3)–H(7)	1.090(3)	C(8)–H(23)	1.082(3)	C(10)–H(29)	1.098(3)	C(19)–H(47)	1.102(3)

Table 2 (*continued*)

(*c*) [Na(15-crown-5)][$W(PMe_3)_3H_5$] (neutron diffraction data)

H(53)–W–H(52)	130.4(2)	P(3)–W–H(52)	66.6(1)	C(6)–P(2)–C(5)	99.0(1)	O(5)–Na–O(2)	102.4(1)
H(54)–W–H(52)	140.5(2)	P(3)–W–H(53)	79.9(1)	C(7)–P(3)–W	118.2(1)	O(4)–Na–O(3)	67.8(1)
H(54)–W–H(53)	78.8(2)	P(3)–W–H(54)	152.9(1)	C(8)–P(3)–W	118.4(1)	O(5)–Na–O(3)	112.2(1)
H(55)–W–H(52)	69.7(2)	P(3)–W–H(55)	136.2(1)	C(8)–P(3)–C(7)	99.5(1)	O(5)–Na–O(4)	67.4(1)
H(55)–W–H(53)	134.3(2)	P(3)–W–H(56)	78.3(1)	C(9)–P(3)–W	120.5(1)	C(19)–O(1)–C(10)	114.5(1)
H(55)–W–H(54)	70.8(2)	P(3)–W–P(1)	103.0(1)	C(9)–P(3)–C(7)	98.0(1)	C(12)–O(2)–C(11)	114.1(1)
H(56)–W–H(52)	131.3(2)	P(3)–W–P(2)	99.6(1)	C(9)–P(3)–C(8)	97.9(1)	C(14)–O(3)–C(13)	113.2(1)
H(56)–W–H(53)	70.5(2)	Na–H(53)–W	99.0(2)	H(54)–Na–H(53)	57.4(1)	C(16)–O(4)–C(15)	114.1(1)
H(56)–W–H(54)	78.9(2)	Na–H(54)–W	103.0(2)	H(56)–Na–H(53)	50.8(1)	C(18)–O(5)–C(17)	114.6(1)
H(56)–W–H(55)	132.2(2)	Na–H(56)–W	103.1(2)	H(56)–Na–H(54)	58.6(1)	C(11)–C(10)–O(1)	107.8(1)
P(1)–W–H(52)	81.7(1)	C(1)–P(1)–W	115.5(1)	O(1)–Na–W	107.9(1)	C(10)–C(11)–O(2)	107.0(1)
P(1)–W–H(53)	71.0(1)	C(2)–P(1)–W	118.7(1)	O(2)–Na–W	119.6(1)	C(13)–C(12)–O(2)	106.8(1)
P(1)–W–H(54)	85.7(1)	C(2)–P(1)–C(1)	99.4(1)	O(2)–Na–O(1)	65.3(1)	C(12)–C(13)–O(3)	107.5(1)
P(1)–W–H(55)	73.5(1)	C(3)–P(1)–W	120.8(1)	O(3)–Na–W	108.7(1)	C(15)–C(14)–O(3)	106.8(1)
P(1)–W–H(56)	140.5(1)	C(3)–P(1)–C(1)	99.7(1)	O(3)–Na–O(1)	128.8(1)	C(14)–C(15)–O(4)	112.6(1)
P(2)–W–H(52)	84.8(1)	C(3)–P(1)–C(2)	98.9(1)	O(3)–Na–O(2)	66.0(1)	C(17)–C(16)–O(4)	106.9(1)
P(2)–W–H(53)	138.2(1)	C(4)–P(2)–W	116.4(1)	O(4)–Na–W	105.0(1)	C(16)–C(17)–O(5)	106.3(1)
P(2)–W–H(54)	85.4(1)	C(5)–P(2)–W	121.2(1)	O(4)–Na–O(1)	132.4(1)	C(19)–C(18)–O(5)	105.7(1)
P(2)–W–H(55)	72.9(1)	C(5)–P(2)–C(4)	97.9(1)	O(4)–Na–O(2)	123.3(1)	C(18)–C(19)–O(1)	107.4(1)
P(2)–W–H(56)	68.6(1)	C(6)–P(2)–W	118.4(1)	O(5)–Na–W	130.3(1)		
P(2)–W–P(1)	146.3(1)	C(6)–P(2)–C(4)	99.9(1)	O(5)–Na–O(1)	65.2(1)		

(*d*) [K(18-crown-6)][$W(PMe_3)_3H_5$]

W···K	3.660(1)	P(1)–C(1)	1.819(7)	P(1)–W–K	98.3(1)	O(4)–K–O(3)	57.9(1)
W–P(1)	2.406(1)	P(1)–C(2)	1.842(7)	P(2)–W–K	99.4(1)	O(5)–K–O(1)	109.2(2)
W–P(2)	2.394(1)	P(1)–C(3)	1.825(6)	P(2)–W–P(1)	146.5(1)	O(5)–K–O(2)	152.0(1)
W–P(3)	2.389(2)	P(2)–C(4)	1.832(7)	P(3)–W–K	107.7(1)	O(5)–K–O(3)	111.8(1)
K–O(1)	2.949(5)	P(2)–C(5)	1.832(6)	P(3)–W–P(1)	104.0(1)	O(5)–K–O(4)	58.2(1)
K–O(2)	2.812(5)	P(2)–C(6)	1.822(6)	P(3)–W–P(2)	97.3(1)	O(6)–K–O(1)	58.6(2)
K–O(3)	2.935(4)	P(3)–C(7)	1.839(6)	O(2)–K–O(1)	58.4(2)	O(6)–K–O(2)	116.9(2)
K–O(4)	2.872(4)	P(3)–C(8)	1.814(8)	O(3)–K–O(1)	108.2(2)	O(6)–K–O(3)	152.0(1)
K–O(5)	2.907(4)	P(3)–C(9)	1.850(7)	O(3)–K–O(2)	57.6(1)	O(6)–K–O(4)	116.4(1)
K–O(6)	2.820(4)			O(4)–K–O(1)	143.9(1)	O(6)–K–O(5)	58.6(1)
				O(4)–K–O(2)	115.2(1)		

(*e*) [K(18-crown-6)][$W(PMe_3)_3H_5$] (neutron diffraction data)

W–K	3.655(4)	P(3)–C(7)	1.848(3)	C(8)–H(22)	1.082(6)	C(15)–O(4)	1.422(3)
W–P(1)	2.411(3)	P(3)–C(8)	1.851(3)	C(8)–H(23)	1.103(7)	C(15)–H(38)	1.104(5)
W–P(2)	2.394(3)	P(3)–C(9)	1.838(3)	C(8)–H(24)	1.082(7)	C(15)–H(39)	1.102(5)
W–P(3)	2.398(4)	C(1)–H(1)	1.084(6)	C(9)–H(25)	1.084(6)	C(16)–C(17)	1.504(3)
W–H(52)	1.767(5)	C(1)–H(2)	1.087(6)	C(9)–H(26)	1.087(6)	C(16)–O(4)	1.412(3)
W–H(53)	1.781(5)	C(1)–H(3)	1.095(7)	C(9)–H(27)	1.093(6)	C(16)–H(40)	1.090(5)
W–H(54)	1.784(5)	C(2)–H(4)	1.093(6)	C(10)–C(11)	1.511(4)	C(16)–H(41)	1.120(5)
W–H(55)	1.756(5)	C(2)–H(5)	1.075(7)	C(10)–O(1)	1.418(4)	C(17)–O(5)	1.421(3)
W–H(56)	1.766(5)	C(2)–H(6)	1.077(6)	C(10)–H(28)	1.111(5)	C(17)–H(42)	1.120(5)
K–C(18)	3.480(4)	C(3)–H(7)	1.092(5)	C(10)–H(29)	1.093(7)	C(17)–H(43)	1.088(6)
K–O(1)	2.950(4)	C(3)–H(8)	1.077(6)	C(11)–O(2)	1.411(4)	C(18)–C(19)	1.492(3)
K–O(2)	2.821(4)	C(3)–H(9)	1.076(6)	C(11)–H(30)	1.092(6)	C(18)–O(5)	1.423(3)
K–O(3)	2.923(4)	C(4)–H(10)	1.097(5)	C(11)–H(31)	1.114(6)	C(18)–H(44)	1.109(5)
K–O(4)	2.867(4)	C(4)–H(11)	1.081(5)	C(12)–C(13)	1.512(3)	C(18)–H(45)	1.102(5)
K–O(5)	2.893(4)	C(4)–H(12)	1.081(6)	C(12)–O(2)	1.415(4)	C(19)–O(6)	1.423(4)
K–O(6)	2.827(4)	C(5)–H(13)	1.085(5)	C(12)–H(32)	1.095(5)	C(19)–H(46)	1.108(6)
K–H(53)	2.750(6)	C(5)–H(14)	1.083(6)	C(12)–H(33)	1.117(5)	C(19)–H(47)	1.098(5)
K–H(54)	2.684(6)	C(5)–H(15)	1.079(6)	C(13)–O(3)	1.419(3)	C(20)–C(21)	1.514(4)
K–H(56)	2.708(6)	C(6)–H(16)	1.085(5)	C(13)–H(34)	1.099(5)	C(20)–O(6)	1.405(3)
P(1)–C(1)	1.837(3)	C(6)–H(17)	1.103(6)	C(13)–H(35)	1.108(5)	C(20)–H(48)	1.093(6)
P(1)–C(2)	1.845(3)	C(6)–H(18)	1.086(6)	C(14)–C(15)	1.502(3)	C(20)–H(49)	1.105(5)
P(1)–C(3)	1.835(3)	C(7)–H(19)	1.086(5)	C(14)–O(3)	1.405(3)	C(21)–O(1)	1.414(4)
P(2)–C(4)	1.845(3)	C(7)–H(20)	1.094(5)	C(14)–H(36)	1.095(5)	C(21)–H(50)	1.096(6)
P(2)–C(5)	1.836(3)	C(7)–H(21)	1.100(5)	C(14)–H(37)	1.101(5)	C(21)–H(51)	1.111(6)
P(2)–C(6)	1.843(3)						

P(2)–W–P(1)	147.8(1)	H(54)–W–H(52)	140.2(3)	H(56)–W–H(54)	77.2(2)	O(6)–K–O(2)	116.6(1)
P(3)–W–P(1)	103.8(1)	H(54)–W–H(53)	79.5(2)	H(56)–W–H(55)	132.4(3)	O(6)–K–O(3)	155.1(2)
P(3)–W–P(2)	96.7(1)	H(55)–W–P(1)	72.6(2)	O(2)–K–O(1)	58.5(1)	O(6)–K–O(4)	117.7(1)
H(52)–W–P(1)	82.0(2)	H(55)–W–P(2)	75.4(2)	O(3)–K–O(1)	109.1(1)	O(6)–K–O(5)	58.8(1)
H(52)–W–P(2)	83.4(2)	H(55)–W–P(3)	136.4(2)	O(3)–K–O(2)	57.8(1)	K–H(53)–W	105.5(2)
H(52)–W–P(3)	67.2(2)	H(55)–W–H(52)	69.3(2)	O(4)–K–O(1)	145.3(2)	K–H(54)–W	108.1(2)
H(53)–W–P(1)	70.4(2)	H(55)–W–H(53)	133.9(3)	O(4)–K–O(2)	116.1(1)	K–H(56)–W	107.7(2)
H(53)–W–P(2)	138.8(2)	H(56)–W–P(1)	138.9(2)	O(4)–K–O(3)	58.59(9)	C(1)–P(1)–W	115.8(2)
H(53)–W–P(3)	79.3(2)	H(56)–W–P(2)	68.9(2)	O(5)–K–O(1)	109.2(1)	C(2)–P(1)–W	122.4(2)
H(53)–W–H(52)	129.6(3)	H(56)–W–P(3)	79.4(2)	O(5)–K–O(2)	154.0(2)	C(2)–P(1)–C(1)	99.0(2)
H(54)–W–P(1)	85.1(2)	H(56)–W–H(52)	133.5(3)	O(5)–K–O(3)	114.1(1)	C(3)–P(1)–W	118.2(1)
H(54)–W–P(2)	87.9(2)	H(56)–W–H(53)	70.0(2)	O(5)–K–O(4)	59.2(1)	C(3)–P(1)–C(1)	99.6(2)
H(54)–W–P(3)	152.7(2)	H(55)–W–H(54)	70.9(2)	O(6)–K–O(1)	58.3(1)	C(3)–P(1)–C(2)	97.7(2)

Table 2 (*continued*)

(*e*) [K(18-crown-6)][$W(PMe_3)_3H_5$] (neutron diffraction data)

C(4)–P(2)–W	116.2(1)	C(8)–P(3)–C(7)	98.4(2)	O(3)–C(14)–C(15)	108.2(2)	C(21)–O(1)–C(10)	110.9(2)
C(5)–P(2)–W	120.7(1)	C(9)–P(3)–W	119.4(2)	O(4)–C(15)–C(14)	108.7(2)	C(12)–O(2)–C(11)	112.9(2)
C(5)–P(2)–C(4)	98.3(2)	C(9)–P(3)–C(7)	99.2(2)	O(4)–C(16)–C(17)	108.6(2)	C(14)–O(3)–K	110.8(2)
C(6)–P(2)–W	119.1(1)	C(9)–P(3)–C(8)	96.5(2)	O(5)–C(17)–C(16)	108.2(2)	C(14)–O(3)–C(13)	113.1(2)
C(6)–P(2)–C(4)	99.7(2)	O(1)–C(10)–C(11)	109.3(2)	O(5)–C(18)–C(19)	107.8(2)	C(16)–O(4)–C(15)	112.8(2)
C(6)–P(2)–C(5)	98.6(2)	O(2)–C(11)–C(10)	108.4(2)	O(6)–C(19)–C(18)	109.0(2)	C(18)–O(5)–C(17)	112.3(2)
C(7)–P(3)–W	117.7(2)	O(2)–C(12)–C(13)	108.3(2)	O(6)–C(20)–C(21)	108.5(2)	C(20)–O(6)–C(19)	112.8(2)
C(8)–P(3)–W	121.0(2)	O(3)–C(13)–C(12)	107.6(2)	O(1)–C(21)–C(20)	109.5(2)		

(*f*) [K(18-crown-6)][$Mo(\eta\text{-}C_5H_5)_2H$]

Mo–C(1)	2.289(4)	C(1)–C(2)	1.402(6)	O(1)–C(11)	1.357(7)	O(5)–C(19)	1.382(8)
Mo–C(2)	2.305(5)	C(1)–C(5)	1.398(8)	O(1)–C(22)	1.426(7)	O(6)–C(20)	1.416(7)
Mo–C(3)	2.284(5)	C(2)–C(3)	1.401(7)	O(2)–C(12)	1.429(8)	O(6)–C(21)	1.374(7)
Mo–C(4)	2.257(5)	C(3)–C(4)	1.401(7)	O(2)–C(13)	1.353(9)	C(11)–C(12)	1.50(1)
Mo–C(5)	2.249(5)	C(4)–C(5)	1.420(8)	O(3)–C(14)	1.43(1)	C(13)–C(14)	1.51(1)
Mo–C(6)	2.266(5)	C(6)–C(7)	1.417(8)	O(3)–C(15)	1.348(9)	C(15)–C(16)	1.50(1)
Mo–C(7)	2.233(5)	C(6)–C(10)	1.396(8)	O(4)–C(16)	1.419(9)	C(17)–C(18)	1.50(1)
Mo–C(8)	2.243(5)	C(7)–C(8)	1.411(7)	O(4)–C(17)	1.39(1)	C(19)–C(20)	1.48(1)
Mo–C(9)	2.292(5)	C(8)–C(9)	1.405(8)	O(5)–C(18)	1.400(9)	C(21)–C(22)	1.49(1)
Mo–C(10)	2.293(5)	C(9)–C(10)	1.420(7)				
C(5)–C(1)–C(2)	107.4(4)	C(9)–C(8)–C(7)	109.4(4)	C(19)–O(5)–C(18)	110.9(6)	C(15)–C(16)–O(4)	110.9(6)
C(3)–C(2)–C(1)	109.1(4)	C(10)–C(9)–C(8)	106.3(5)	C(21)–O(6)–C(20)	112.3(5)	C(18)–C(17)–O(4)	107.4(7)
C(4)–C(3)–C(2)	107.5(4)	C(9)–C(10)–C(6)	109.3(5)	C(12)–C(11)–O(1)	109.5(6)	C(17)–C(18)–O(5)	110.2(6)
C(5)–C(4)–C(3)	107.8(5)	C(22)–O(1)–C(11)	112.0(5)	C(11)–C(12)–O(2)	108.7(5)	C(20)–C(19)–O(5)	108.7(5)
C(4)–C(5)–C(1)	108.1(4)	C(13)–O(2)–C(12)	113.0(6)	C(14)–C(13)–O(2)	110.8(6)	C(19)–C(20)–O(6)	109.7(5)
C(10)–C(6)–C(7)	107.8(4)	C(15)–O(3)–C(14)	111.6(6)	C(13)–C(14)–O(3)	108.8(5)	C(22)–C(21)–O(6)	108.7(5)
C(8)–C(7)–C(6)	107.2(5)	C(17)–O(4)–C(16)	112.3(7)	C(16)–C(15)–O(3)	108.5(6)	C(21)–C(22)–O(1)	109.7(4)

(*g*) [K(18-crown-6)][*cis*-$Re(PMe_3)_4H_2$]

Re–P(1)	2.323(4)	P(3)–C(7)	1.812(9)	K(1)–O(5)	2.86(1)	C(21)–O(5)	1.42(1)
Re–P(2)	2.311(4)	P(3)–C(8)	1.818(9)	K(1)–O(6)	2.92(1)	C(22)–O(6)	1.42(1)
Re–P(3)	2.304(4)	P(3)–C(9)	1.826(9)	C(13)–O(1)	1.41(1)	C(23)–O(6)	1.42(1)
Re–P(4)	2.307(4)	P(4)–C(10)	1.823(9)	C(14)–O(2)	1.42(1)	C(24)–O(1)	1.42(1)
Re · · · K	3.784(3)	P(4)–C(11)	1.825(9)	C(15)–O(2)	1.41(1)	C(13)–C(14)	1.51(1)
P(1)–C(1)	1.831(9)	P(4)–C(12)	1.818(9)	C(16)–O(3)	1.42(1)	C(15)–C(16)	1.50(1)
P(1)–C(2)	1.826(9)	K–O(1)	2.93(1)	C(17)–O(3)	1.42(1)	C(17)–C(18)	1.51(1)
P(1)–C(3)	1.831(9)	K–O(2)	2.85(1)	C(18)–O(4)	1.42(1)	C(19)–C(20)	1.50(1)
P(2)–C(4)	1.828(9)	K–O(3)	2.99(1)	C(19)–O(4)	1.41(1)	C(21)–C(22)	1.50(1)
P(2)–C(5)	1.826(9)	K–O(4)	2.92(1)	C(20)–O(5)	1.42(1)	C(23)–C(24)	1.50(1)
P(2)–C(6)	1.824(9)						
P(2)–Re–P(1)	162.0(1)	K–Re–P(2)	78.8(1)	O(4)–K–O(1)	141.0(4)	O(5)–K–O(4)	58.1(4)
P(3)–Re–P(1)	96.6(1)	K–Re–P(3)	121.9(1)	O(4)–K–O(2)	110.1(5)	O(6)–K–O(1)	55.6(4)
P(3)–Re–P(2)	96.5(1)	K–Re–P(4)	138.6(1)	O(4)–K–O(3)	55.1(4)	O(6)–K–O(2)	107.6(4)
P(4)–Re–P(1)	95.4(1)	O(2)–K–O(1)	57.7(4)	O(5)–K–O(1)	113.9(5)	O(6)–K–O(3)	108.2(4)
P(4)–Re–P(2)	94.6(2)	O(3)–K–O(1)	96.8(4)	O(5)–K–O(2)	152.7(4)	O(6)–K–O(4)	104.1(4)
P(4)–Re–P(3)	99.4(1)	O(3)–K–O(2)	56.2(4)	O(5)–K–O(3)	103.4(4)	O(6)–K–O(5)	58.3(4)
K–Re–P(1)	83.8(1)						

(*h*) [$\{(Ph_3P)Au\}_3W(PMe_3)_3H_4]Cl\cdot 0.15CH_2Cl_2$

W–Au(1)	2.806(1)	W–P(3)	2.498(4)	P(1)–C(3)	1.85(3)	P(4)–C(16)	1.82(1)
W–Au(2)	2.793(1)	Au(1)–P(2)	3.292(4)	P(2)–C(4)	1.83(2)	P(4)–C(22)	1.82(1)
W–Au(3)	2.812(1)	Au(1)–P(4)	2.287(3)	P(2)–C(5)	1.83(2)	P(5)–C(28)	1.80(1)
Au(1)–Au(2)	2.881(1)	Au(2)–P(3)	3.239(4)	P(2)–C(6)	1.81(2)	P(5)–C(34)	1.80(1)
Au(1)–Au(3)	2.858(1)	Au(2)–P(6)	2.292(4)	P(3)–C(7)	1.86(2)	P(5)–C(40)	1.84(1)
Au(2)–Au(3)	2.796(1)	Au(3)–P(5)	2.284(4)	P(3)–C(8)	1.79(2)	P(6)–C(46)	1.80(1)
W–P(1)	2.435(4)	P(1)–C(1)	1.81(2)	P(3)–C(9)	1.75(3)	P(6)–C(52)	1.82(1)
W–P(2)	2.507(4)	P(1)–C(2)	1.82(3)	P(4)–C(10)	1.81(1)	P(6)–C(58)	1.83(1)
Au(1)–W–P(1)	113.9(1)	P(3)–W–P(2)	138.6(2)	Au(3)–P(5)–C(34)	113.1(5)	Au(2)–Au(3)–W	59.73(2)
Au(1)–W–P(2)	76.4(1)	C(1)–P(1)–W	121.9(8)	Au(3)–P(5)–C(40)	108.3(3)	Au(2)–Au(3)–Au(1)	61.24(2)
Au(1)–W–P(3)	136.1(1)	C(2)–P(1)–W	121.1(10)	Au(2)–P(6)–C(46)	112.5(4)	Au(2)–Au(1)–P(4)	128.9(1)
Au(2)–W–P(1)	117.2(1)	C(3)–P(1)–W	115.8(9)	Au(2)–P(6)–C(52)	111.0(3)	Au(3)–Au(1)–P(4)	134.2(1)
Au(2)–W–P(2)	135.2(1)	C(4)–P(2)–W	114.6(8)	Au(2)–P(6)–C(58)	117.1(4)	P(6)–Au(2)–W	171.3(1)
Au(2)–W–P(3)	75.3(1)	C(5)–P(2)–W	117.8(8)	P(4)–Au(1)–W	165.6(1)	P(6)–Au(2)–P(3)	127.3(1)
Au(2)–W–Au(1)	61.9(1)	C(6)–P(2)–W	120.5(7)	P(4)–Au(1)–P(2)	126.2(1)	Au(1)–Au(2)–P(3)	106.9(1)
Au(3)–W–P(1)	174.9(1)	C(7)–P(3)–W	119.0(8)	Au(2)–Au(1)–W	58.82(2)	Au(1)–Au(2)–P(6)	125.7(1)
Au(3)–W–P(2)	87.0(1)	C(8)–P(3)–W	117.2(8)	Au(3)–Au(1)–W	59.53(2)	Au(3)–Au(2)–P(3)	76.9(1)
Au(3)–W–P(3)	90.2(1)	C(9)–P(3)–W	117.5(9)	Au(3)–Au(1)–Au(2)	58.33(2)	Au(3)–Au(2)–P(6)	127.8(1)
Au(3)–W–Au(1)	61.2(1)	Au(1)–P(4)–C(10)	110.0(4)	Au(1)–Au(2)–W	59.27(2)	P(5)–Au(3)–W	162.7(1)
Au(3)–W–Au(2)	59.9(1)	Au(1)–P(4)–C(16)	117.6(4)	Au(3)–Au(2)–W	60.42(2)	Au(1)–Au(3)–P(5)	137.0(1)
P(2)–W–P(1)	93.3(2)	Au(1)–P(4)–C(22)	113.5(4)	Au(3)–Au(2)–Au(1)	60.44(2)	Au(2)–Au(3)–P(5)	128.8(1)
P(3)–W–P(1)	93.1(2)	Au(3)–P(5)–C(28)	118.4(4)	Au(1)–Au(3)–W	59.32(2)		

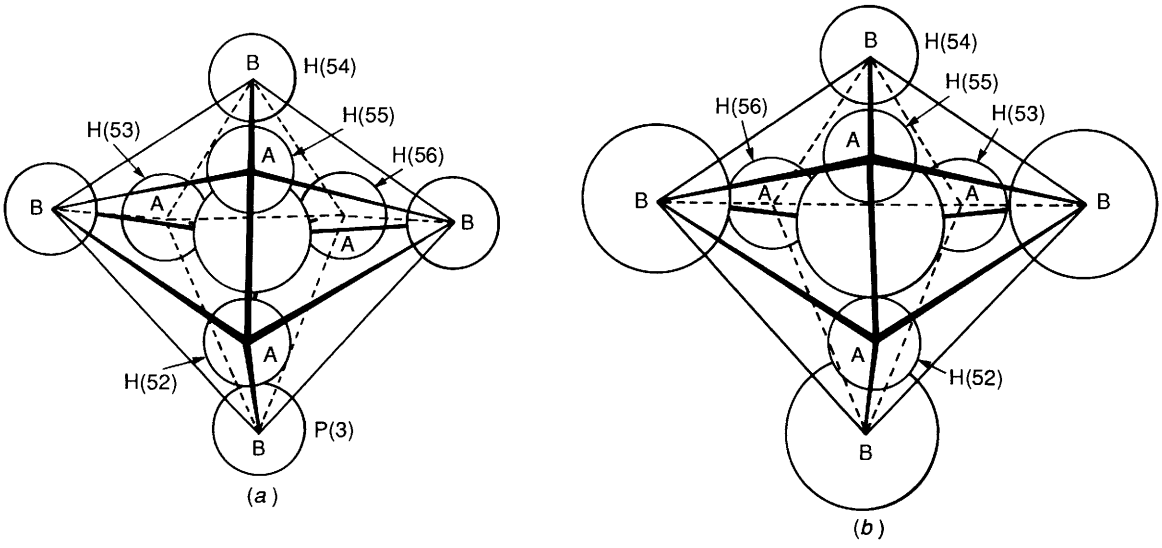


Fig. 2 The WP_3H_5 group in (*a*) compound **3** and (*b*) **5** viewed close to the pseudo-S_4 axis of the D_{2h} triangulated dodecahedron; H(52), H(53), H(55) and H(56) form the elongated tetrahedron A and H(54), P(1), P(2) and P(3) the flattened tetrahedron B. The WP_3H_5 groups in the two compounds are virtually indistinguishable

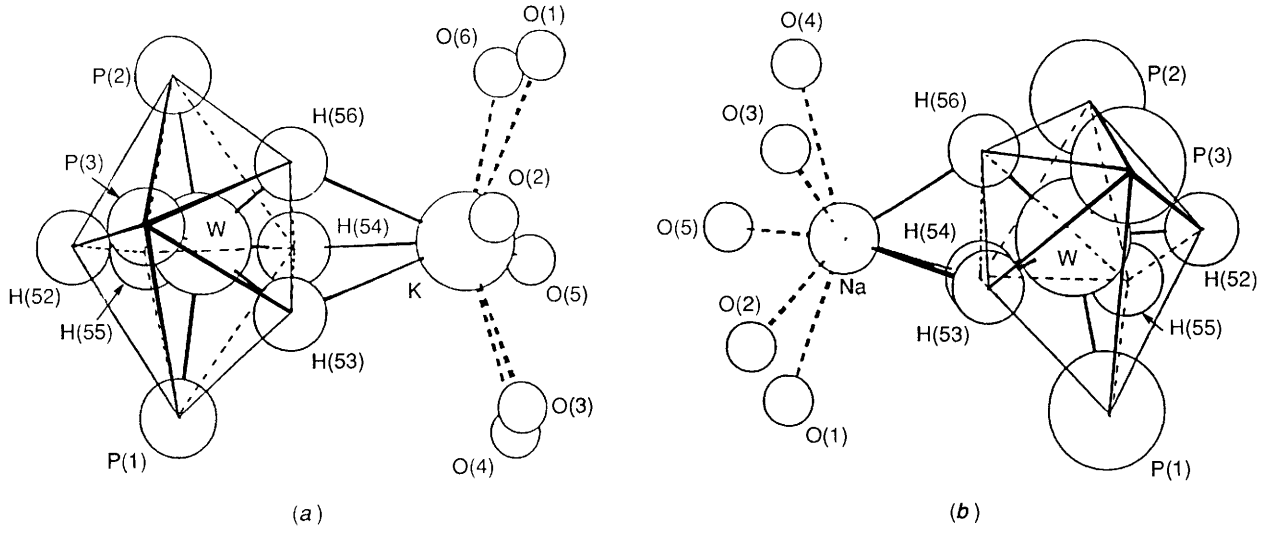


Fig. 3 (*a*) The potassium ion K of compound **3** and (*b*) the sodium ion Na of **5** interacting with the triangular face H(53), H(54), H(56) and the WP_3H_5 triangulated dodecahedron with the oxygen atoms of the crown ether completing the alkali-metal co-ordination

The geometries about the tungsten atoms in compounds **3** and **5** are remarkably similar and are essentially distorted D_{2d} (triangulated) dodecahedra. The D_{2d} dodecahedron may be considered to consist of two interpenetrating tetrahedra, one of which is elongated (A) and the other flattened (B).[28] The vertices of the elongated tetrahedron have four neighbours but those of the flattened tetrahedra have five neighbours. There is no single idealised D_{2d} dodecahedral geometry and it is defined in terms of shape parameters θ_A and θ_B which are the tetrahedral half angles and take the values θ_A 37–38° and θ_B 71–72° for a dodecahedron with equilateral triangular faces.[29–31]

Figs. 2(*a*) and (*b*), in which the $[W(PMe_3)_3H_5]$ units are drawn viewed down the very approximate S_4 axes, illustrates the assignment of each $[W(PMe_3)_3H_5]$ unit to dodecahedral geometry. Hydrogen atoms H(52), H(53), H(55) and H(56) form the elongated tetrahedron occupying the A sites, whilst H(54) and the three phosphine ligands form the flattened tetrahedron and occupy the B sites. For the elongated tetrahedron, the angles H(53)–W–H(56) (**3**, 70.0; **5**, 70.5°) and H(52)–W–H(55) (**3**, 69.3; **5**, 69.7°) give an average shape parameter, θ_A, of 34.8 for **3** and 35.0° for **5**, whilst for the flattened tetrahedron the angles P(1)–W–P(2) (**3**, 147.8; **5**, 146.3°) and P(3)–W–H(54) (**3**, 152.7; **5**, 152.9°) give θ_B = 74.9 for **3** and 74.8° for **5**. Comparison of θ_A and θ_B for $[W(PMe_3)_3H_5]$ in **3** and **5** with values of θ_A and θ_B for other dodecahedral structures shows that θ_A is smaller and θ_B is larger than those found in complexes with eight equivalent ligands. This reflects the large steric bulk of PMe_3 relative to hydrogen since the former are distorted towards the hydride ligands. Three other eight-co-ordinate transition-metal tertiary phosphine polyhydride complexes have been crystallographically characterised. A neutron diffraction study has been carried out on $[Re(PPh_2Me)_3H_5]$[32] and X-ray diffraction studies have been carried out on $[\{Re(PPh_2Me)_3H_5\}_2Cu]^+PF_6^-$[33] and $[Mo(PPh_2Me)_4H_4]$.[34] Each of these compounds displays distorted D_{2d} dodecahedral geometry about the metal centre with phosphine ligands on B sites. The geometry about the rhenium centre in the $Re(PPh_2Me)_3H_5$ and in $[\{Re(PPh_2Me)_3H_5\}_2Cu]^+$ moieties was found to be closely similar to that about tungsten in $W(PMe_3)_3H_5$ in **3** and **5**.

The tungsten–hydrogen bond distances in compound **3** lie in the range 1.756–1.784 Å and are somewhat longer than the only other terminal W–H bonds determined by neutron diffraction {1.728 Å for $W-H_{average}$ in $[W(PPhPr^i_2)_3H_6]$[27]}. They are, however, significantly shorter than the hydride bridge bonds $W-H_{bridge}$ 1.88 Å (average) in $[W_2(CO)_9H(NO)]$[35] and $[W_2(CO)_8H(NO)\{P(OMe)_3\}]$.[36] The average W–P bond length in **3** (2.401 Å) and in **5** (2.398 Å) is shorter than that in $[W(PMe_3)_3H_6]$ (2.447 Å). This can be discussed in terms either of the lower co-ordination number in **3** and **5** compared to $[W(PMe_3)_3H_6]$, or of increased π-back bonding to the

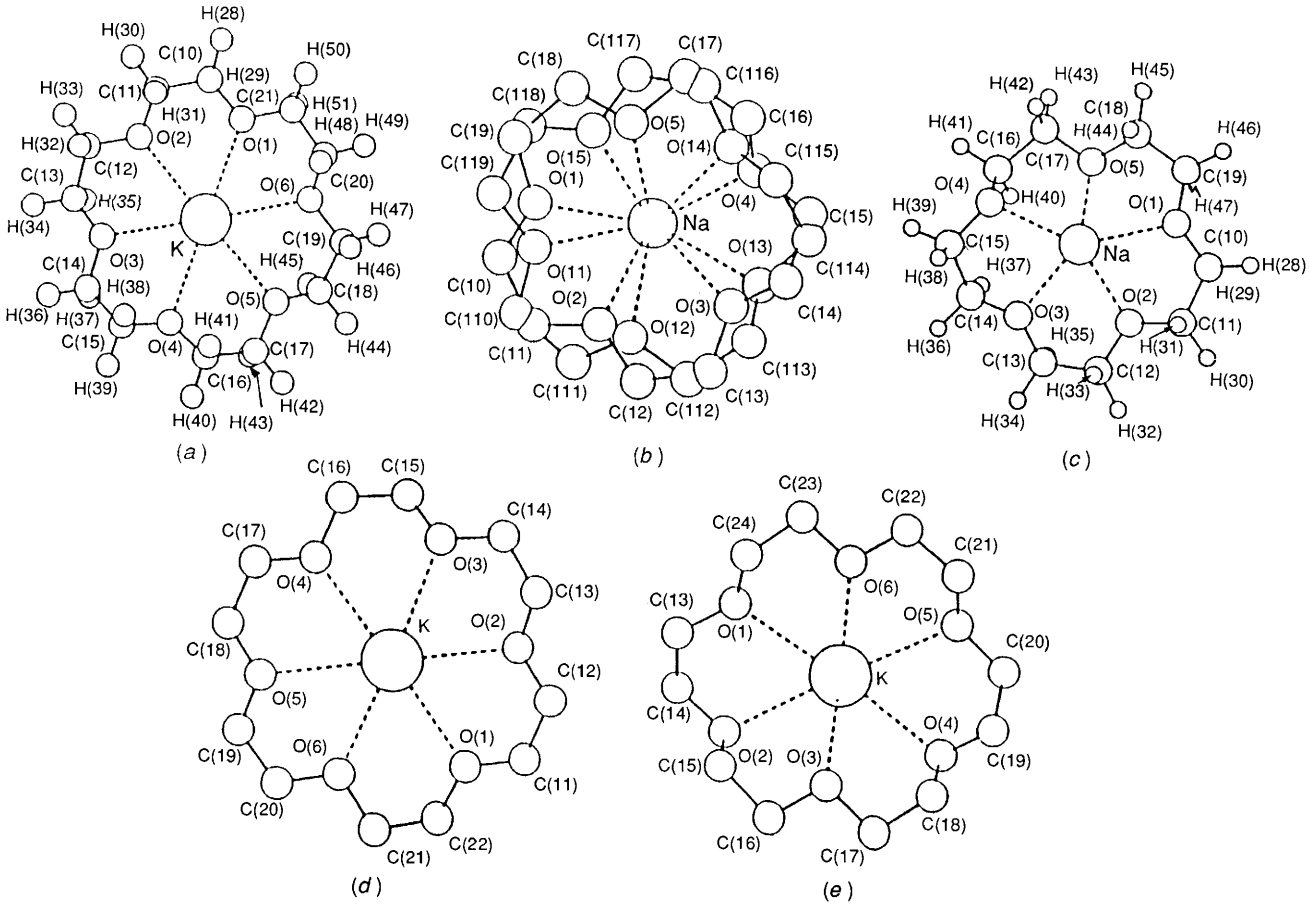


Fig. 4 The alkali metal–crown ether co-ordination viewed perpendicular to the plane of the ether oxygen atoms: (*a*) 18-crown-6 in compound **3** from neutron diffraction at 98.8 K; (*b*) disorder of 15-crown-5 in **5** at room temperature according to X-ray diffraction and (*c*) the same system at 30 K according to neutron diffraction; (*d*) conformation of 18-crown-6 in **18** which is very similar to that in **3** [K lies 0.87 Å out of the plane O(1)–O(6)]; (*e*) 18-crown-6 in **12**. In **12** the crown has a markedly different conformation to that in **3** with C(15), C(18), C(12) and C(24) all above the plane of O(1), O(2), O(4) and O(5). The atom K lies 0.82 Å above this plane and O(3) and O(6) 1.09 and 0.72 Å above the plane

phosphine ligands in the highly electron-rich anionic systems in **3** and **5**.

The interaction between the $W(PMe_3)_3H_5$ unit and the K(18-crown-6) or Na(15-crown-5) unit occurs at the triangular face presented by atoms H(53), H(54) and H(56), Fig. 3(*a*) and (*b*), that is two A-site and one B-site hydrogen atoms. In compound **3** this interaction pulls the potassium ion out of the best plane defined by the six crown ether oxygens by 0.755 Å (in contrast to the potassium thiocyanate complex of 18-crown-6 in which the potassium lies in the plane of the six oxygen atoms of the crown)[37] but has no significant effect on the length of the tungsten–hydride bonds [W–$H_{terminal}$ (average) 1.762, W–H_{bridge} (average) 1.777 Å]. In **5** this interaction pulls the sodium ion out of the best plane defined by the five crown ether oxygens by 1.10 Å but again the effect on the length of the tungsten–hydrogen bonds is not significant [W–$H_{terminal}$ (average) 1.775, W–H_{bridge} (average) 1.770 Å]. Very similar bridging interactions have recently been observed at triangular metal hydride faces in other compounds.[25]

It is interesting to consider whether the bonding between the tungsten and potassium centres in compound **3** is mainly ionic or substantially covalent, *i.e. via* two-electron, three-centre W–H–K bonds. Potassium usually occurs in essentially ionic lattices, however electron-rich ligands could encourage covalency, and dimeric K_2, for example, has a K–K covalent bond.[38]

The molecular structures of compounds **3** and **5** show that the alkali-metal atoms do not occupy a direct co-ordination site at tungsten as indicated by the W ··· K distance 3.665 Å and the W ··· Na distance, 3.204 Å, compared to the sums of the covalent radii, 3.56 Å for tungsten and potassium and 3.14 Å for sodium and tungsten (W 1.6 Å, approximately from W–W single bonds;[39] K 1.96 Å derived spectroscopically[38]). However, there appears to be some interaction attracting the potassium out of the best plane of the six oxygen atoms of the crown ether ligand and towards the tungsten. Further, the average K–H_{bridge} distance in **3** is 2.715 Å compared to a value of 2.854 Å in potassium hydride[40] and the average Na–H_{bridge} distance in **5** is 2.337 Å compared to a value of 2.44 Å in sodium hydride.[40] This suggests that there is some degree of covalent W–H–K interaction. Caulton and co-workers[25] have reported K–H distances as short as 2.52 Å in dimeric $[\{KOs(PPhMe_2)_3H_4\}_2]$ so it would seem that the perturbation of the K–H distances in compound **3** from those in potassium hydride is relatively small.

It is noted that these compounds exhibit the side-on pairing interaction between an alkali-metal cation and the M–H bond of an electron-rich metal hydride predicted by Darensbourg and co-workers[41] from studies on $Na[M(CO)_4L(H)]$ (M = Cr, Mo or Co; L = CO or PR_3). Further evidence for covalency in W–H–K bonds is provided by IR and NMR data, see below.

The pseudo-D_{2d} symmetrical conformation of the 18-crown-6, Fig. 4(*a*), in compound **3** demonstrated by the torsion angles in Table 3, is not significantly different from those previously observed in MNCS complexes (M = NH_4, K, Rb or Cs). The conformation at 193 K is not significantly different from that at 98.8 K but the atoms do have large thermal parameters. The mean C–C bond length at 98.8 K of 1.506 Å, and rather high thermal motion indicates that there may be some residual disordering of the crown at this temperature. The 15-crown-5, Fig. 4(*b*), in **5** is disordered at 293 K (X-ray structure analysis) with two positions of the crown clearly discernible. This

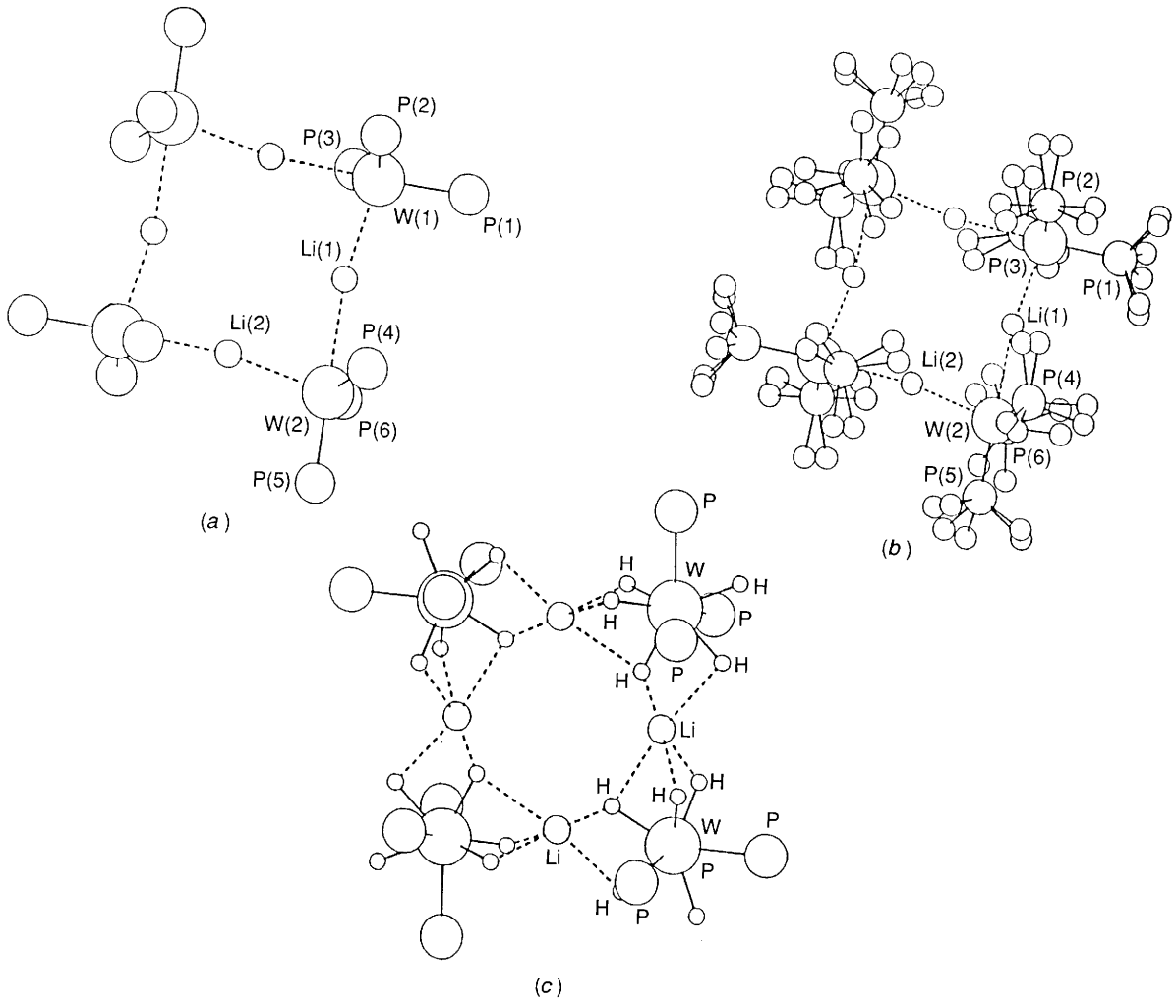


Fig. 5 (*a*) The $(P_3WLi)_4$ skeleton of $[\{W(PMe_3)_3H_5Li\}_4]$ **6** from the X-ray structure analysis and (*b*) with the disordered methyl carbons added. (*c*) The P_3W groups in the X-ray structure have been replaced by the WP_3H_5 groups from the neutron diffraction structure of **3** using a least-squares best fit to the positions of W and P and showing the proposed hydrogen bridges

disorder has disappeared at 30 K, Fig. 4(*c*), as evidenced by the mean C–C bond length, 1.518 Å, and the very small thermal parameters. The conformation of the 15-crown-5 is effectively the same in the disordered structure at 293 K and in the ordered low-temperature structure.

The tetrameric nature of compound **6** provides an interesting contrast to the structures of **3** and **5**, Fig. 5(*a*). In the crystal there are two crystallographically independent $Li[W(PMe_3)_3H_5]$ monomers at W(1) and W(2) that together form half the tetramer the other half of which is generated by the crystallographic inversion centre at $0,\frac{1}{2},\frac{1}{2}$. The arrangement of the PMe_3 ligands about each tungsten atom is very similar to that in **3** and **5** but the methyl groups are disordered, Fig. 5(*b*). The central W_4Li_4 core is essentially planar with alternating W–Li bond lengths. The similarity of the tungsten–phosphine geometry in **6**, **3** and **5** suggests that the tungsten-bound hydrogen atoms occupy positions in **6** closely analogous to those found in the neutron diffraction structures of **3** and **5**, Fig. 5(*c*). The tetramer has approximate four-fold symmetry. Each lithium atom forms one triple hydrogen bridge to tungsten corresponding to the shorter Li–W contact and one double hydrogen bridge corresponding to the longer Li–W contact. Thus each tungsten has four bridging and one terminal hydrogen atom and one hydrogen bridge is bifurcated.

During the course of this work Wilkinson and co-workers[20] also described $[\{W(PMe_3)_3H_5Li\}_4]$, prepared by treating $[\{(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)\}_2]$ with lithium alkyls. They reported the crystal structure and claimed to locate most of the tungsten-bound hydrogens.[24] Other structures in which polar covalent bonds between transition metals and lithium have been postulated are $[\{(\eta\text{-}C_5H_5)_2MHLi\}_4]$ (M = Mo or W),[1,2] some lithium-bridged dinuclear platinum(II) complexes[12] and several nickel–olefin derivatives.[13]

The solution structures of compounds **2**–**6** have been investigated using variable-temperature NMR spectroscopy. The degree of aggregation of **6** in tetrahydrofuran (thf) solutions cannot be established conclusively. However, the ^1H and ^{31}P NMR spectra of **2**–**6** in $[^2H_8]$tetrahydrofuran are very similar, suggesting that their solution structures are closely related. The observation that crystalline $[\{W(PMe_3)_3H_5Li\}_4]$ could not be obtained from thf solutions suggests that **6** is monomeric in such solutions. It is reasonable to assume that the geometry about the tungsten centre in **2**–**6** in solution is essentially pseudo-dodecahedral, as determined in the neutron diffraction study of **3**. However, the chemical shifts of the tungsten-bound hydrides vary between compounds **2**–**6**, which presumably reflects the effect of different cations.

The ^1H NMR spectra of compound **6** over the temperature range 323–138 K (Fig. 6) identified three fluxional processes. The spectrum at 138 K, the lowest recorded, shows three signals, whose assignments are proposed in Table 1. This spectrum and its variable-temperature behaviour are consistent with a pseudo-dodecahedral monomeric structure in solution, analogous to that depicted for compound **4** in Scheme 1. Based on the assignments in Table 1, the lowest-energy process (process 3) is the exchange between the three hydrogens H_a, H_b and H_c which are bridging between the tungsten and lithium centres. The fast-exchange limit is observed at 193 K, where the integrals of the

Table 3 Torsion angles (°) (anticlockwise Newman projection) for the crown ethers in compounds **3**, **5**, **12** and **18**. The carbon atoms of the 18-crown-6 in **12** are numbered C(13)–C(24) and correspond exactly to C(10)–C(21) in the other 18-crown-6 ligands. The numbers in italics refer to the 15-crown-5 ligands in **5** where it differs from that of the 18-crown-6. For all analyses the crystallographic e.s.d.s are about 1° but much larger differences are required for chemical significance in these very flexible systems

	3	**3** (neutron)	**18**	**12**	**5**	**5**	**5** (neutron)
O(1)–C(10)–C(11)–O(2)	−64.8	−65.4	−64.4	63.3	59.1	61.7	60.9
C(10)–C(11)–O(2)–C(12)	−174.4	−172.4	177.7	*67.5**	−177.9	−172.4	−177.8
C(11)–O(2)–C(12)–C(13)	−176.9	−176.4	177.4	171.9	165.9	172.0	176.9
O(2)–C(12)–C(13)–O(3)	63.6	63.9	67.4	63.4	−67.2	−51.3	−63.3
C(12)–C(13)–O(3)–C(14)	171.9	169.7	−173.3	−176.8	169.9	156.5	167.2
C(13)–O(3)–C(14)–C(15)	177.4	175.7	−175.4	−169.2	−96.3	174.6	−180.0
O(3)–C(14)–C(15)–O(4)	−70.0	−68.6	−66.9	−66.9	−58.3	48.0	56.8
C(14)–C(15)–O(4)–C(16)	−178.0	−178.9	178.6	175.7	−173.8	102.7	77.3
C(15)–O(4)–C(16)–C(17)	178.1	−178.2	170.4	−165.3	−150.5	−176.3	−176.5
O(4)–C(16)–C(17)–O(5)	69.6	69.4	64.1	61.8	61.8	51.4	68.6
C(16)–C(17)–O(5)–C(18)	−174.1	−172.0	−176.7	*89.7**	−176.4	−172.2	−165.4
C(17)–O(5)–C(18)–C(19)	−169.3	−169.2	176.6	177.4	168.7	−169.3	−166.8
O(5)–C(18)–C(19)–O(6)	−66.4	−65.8	−60.0	67.7	−54.2	−43.8	−59.9
O(5)–C(18)–C(19)–O(1)							
C(18)–C(19)–O(6)–C(20)	169.8	167.7	166.0	168.6	161.1	152.3	159.9
C(18)–C(19)–O(1)–C(10)							
C(19)–O(6)–C(20)–C(21)	173.0	171.5	174.0	−175.2	−161.8	−169.3	−162.8
C(19)–O(1)–C(10)–C(11)							
O(6)–C(20)–C(21)–O(1)	64.4	64.5	61.3	−62.2			
C(20)–C(21)–O(1)–C(10)	−173.5	173.8	172.5	−171.3			
C(21)–O(1)–C(10)–C(11)	−178.2	−176.4	173.2	−170.4			

* Note the substantial difference between compound **12** and **3**, **5** and **18**.

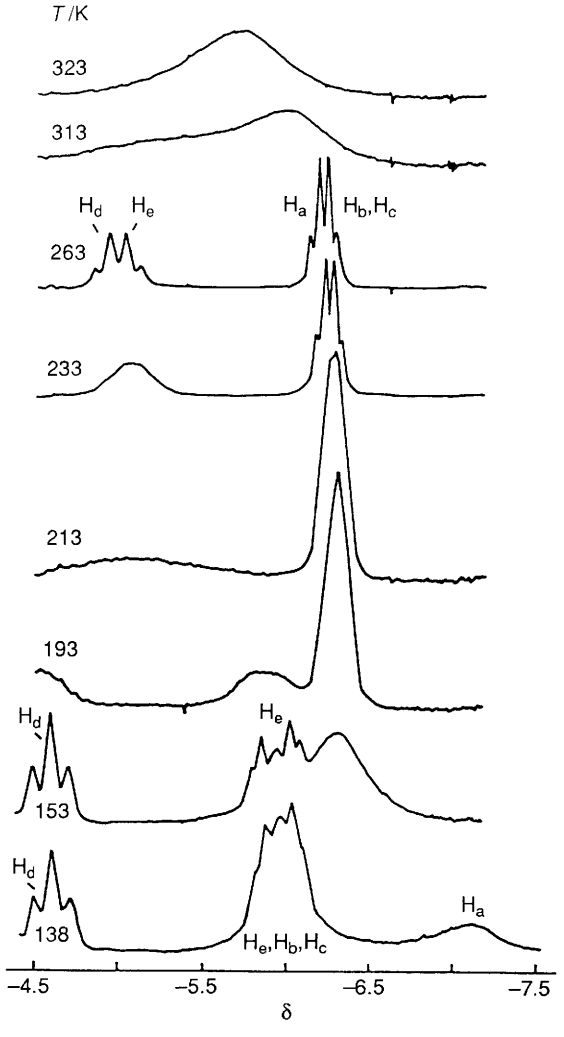


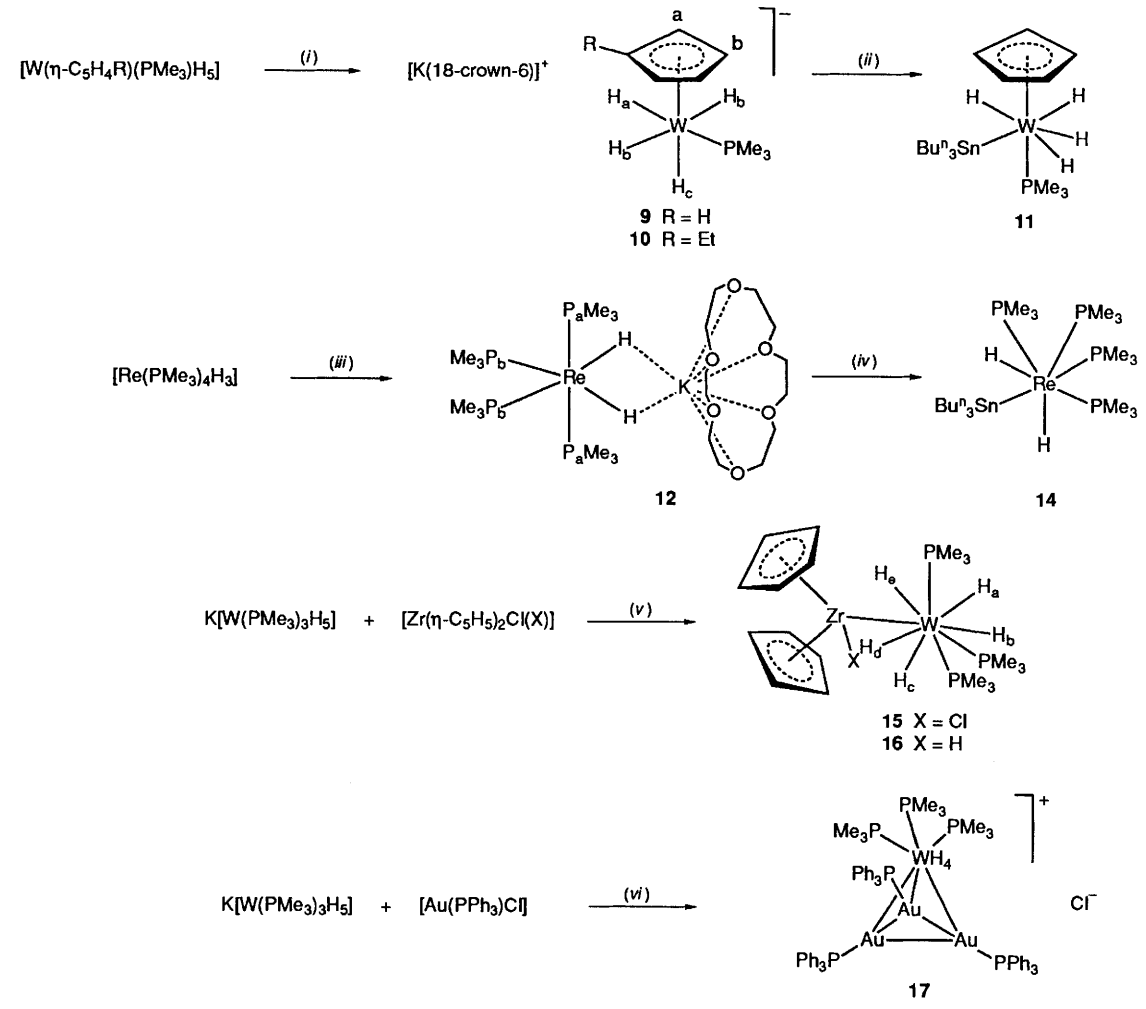
Fig. 6 The variable-temperature ^{1}H NMR spectra of compound **6**, showing the high-field hydride bands only

Table 4 Rate constants and activation energies for dynamic hydride-exchange processes in $M[W(PMe_3)_3H_5]$

Compound	Process	Δν/Hz	T_c/K	k_{av}/s^{-1}	$\Delta G^{\ddagger}_{av}$/kJ mol^{-1}
2	1	175	280 ± 5	291.1	55.2 ± 1
	2	483	222 ± 5	1073.0	40.9 ± 1
3	1	43	335 ± 10	71.3	70.5 ± 4
	2	567	243 ± 5	1260.0	44.7 ± 1
4	1	313	310 ± 5	521.2	59.9 ± 1
	2	445	220 ± 3	988.7	40.7 ± 0.7
6	1	472	318 ± 3	785.1	60.4 ± 0.7
	2	520	210 ± 3	1155.1	38.5 ± 0.7
	3	480	145 ± 3	724.1	26.7 ± 0.7

resonances assigned to H_d, H_e and (H_a, H_b, H_c) are in the expected ratio of 1:1:3. Upon warming from 193 K the resonances assigned to H_d and H_e coalesce (process 2, T_c *ca.* 213 K), and the fast-exchange-limit spectrum is observed at 263 K. Further warming to 323 K results in the formation of a broad singlet corresponding to all five tungsten-bound hydrogens moving towards fast-exchange conditions (process 1). It is reasonable to propose that processes 2 and 3 should have lower activation energies than for process 1 because the first two processes do not require the substantial skeletal rearrangement (that is, bridge-terminal exchange) necessary for process 1. Evidence that the fluxional processes in compounds **2**–**6** are intramolecular comes from the observation of coupling between the hydrogens and the three ^{31}P nuclei of the PMe_3 ligands. For example, the 500 MHz ^{1}H NMR spectrum of **2** at 215 K shows the resonance assigned to H_a, H_b, H_c to be coupled to both the three phosphorus nuclei and to H_d, H_e [J(H–H) = 4 Hz (average)].

The lowest-energy process 3 has only been observed for compound **6**; the magnitudes of $\Delta G^{\ddagger}$ for the various exchange processes for compounds **2**–**4** and **6** are given in Table 4. The values of $\Delta G^{\ddagger}$ for process 1 in compounds **2**–**6** are comparable with values obtained for the eight-co-ordinate tungsten complexes $[W(PR_3)_4H_4]$.[34] The variance of the values of $\Delta G^{\ddagger}$ may be associated with cation–anion interactions in solution. The particularly high value observed for compound **3** suggests that the cation–anion interaction may be intimate enough to lead to steric interaction between the 18-crown-6 ring and the



Scheme 2 (*i*) KH and 18-crown-6 in thf, yield 79%; (*ii*) $SnBu^n_3Cl$ in thf at r.t. for 10 min, 60%; (*iii*) KH and 18-crown-6 in thf at 60 °C for 24 h, 89%; (*iv*) $SnBu^n_3Cl$ in thf at r.t. for 30 min, 45%; (*v*) X = Cl, in thf at − 80 °C, warm to r.t., 63%; X = H, in thf at −20 °C, warm to r.t., 15 min, 83%; (*vi*) in thf at −78 °C, warm to r.t. for 1 h, 77%

tungsten-bound trimethylphosphine ligands. The infrared spectra of **2–6** have been recorded using mulls and bands assigned to ν(W–H) are given in Table 1. Absorptions assignable to ν(W–H) occur in the region 1690–1750 cm^{-1} and there are also lower broad bands at 1600–1660 cm^{-1}; it is tempting to assign the latter to bridging W–H–M′ systems.

We conclude that combined structural and spectroscopic evidence mitigates in favour of the presence of strong covalent W–H–Li bonds in **6**, and a fair degree of covalent M–H–M′ bonding in the sodium and potassium compounds **2–5**.

Tetrahydrofuran solutions of $K[W(PMe_3)_3H_5]$ and [K-(18-crown-6)][$W(PMe_3)_3H_5$] were found to react instantly with $SnBu^n_3Cl$ giving the new compound $[W(PMe_3)_3H_5(SnBu^n_3)]$ **7** in approximately 50% yields as pentane-soluble, white, air-sensitive crystals (m.p. 27 °C). Treatment of $[\{W(PMe_3)_3H_5Li\}_4]$ with $SnBu^n_3Cl$ also gave **7**, but in lower yields. The ^1H NMR spectrum of **7** at ambient temperatures shows it to be fluxional since the hydride resonances occur as a quartet. Also, the ^{31}P-$\{^1H\}$ NMR spectrum shows a sharp singlet at δ −31.54 due to the three PMe_3 groups. The ^{31}P-$\{^1H$–Me$\}$ NMR spectrum shows a binominal sextet coupling pattern for the main resonance which confirms the presence of five hydrogens attached to the tungsten. Closer examination of the ^{31}P-$\{^1H\}$ NMR spectrum reveals satellite peaks due to molecules containing all combinations of stable NMR-active isotopes of tungsten and tin. The structure proposed for **7** is shown in Scheme 1.

We have explored the reactions of the tungsten pentahydrides $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$ and $[W(\eta\text{-}C_5H_4Et)(PMe_3)H_5]$[42] with KH, and with KH and 18-crown-6. The reactions were monitored by ^1H NMR spectroscopy and took 3 d or 12 h, respectively, at 60 °C. During this time the initially pale brown solutions became orange. Difficulty in obtaining sufficient amounts of the parent pentahydrides coupled with the extreme sensitivity of the products to moisture prevented satisfactory elemental analysis of the orange powders. However, the ^1H and ^1H-$\{^{31}P\}$ NMR spectra were entirely consistent with the presence in solution of the compounds $K[W(\eta\text{-}C_5H_5)(PMe_3)H_4]$ **8**, [K(18-crown-6)][$W(\eta\text{-}C_5H_5)(PMe_3)H_4$] **9** and [K(18-crown-6)][$W(\eta\text{-}C_5H_4Et)(PMe_3)H_4$] **10**, each being formed by deprotonation of the parent tungsten pentahydrido species.

The ^1H NMR spectrum of compound **10** at 228 K showed three signals in the high-field region of relative intensity 1:2:1 at δ −1.66 a 'doublet of quartets' assignable to coupling to the ^{31}P nucleus of a *trans* PMe_3 ligand [J(P–H) 68.5 Hz] together with further coupling to the three other hydride ligands [$J(H–H)_{average}$ = 7.9 Hz]; at δ −7.70 a doublet of triplets [$J(P–H)_{cis}$ 15.9, $J(H–H)_{average}$ = 8.2, $J(^{183}W–H)$ 63.9 Hz]; and at δ −8.27 a quintet assignable on the basis of J(H–H) = $J(P–H)_{cis}$ = 7.0 Hz. Further support for the structures proposed for **8–10** is provided by the product of the reaction of [K(18-crown-6)][$W(\eta\text{-}C_5H_5)(PMe_3)H_4$] **9** with $SnBu^n_3Cl$ which gave $[W(\eta\text{-}C_5H_5)(PMe_3)H_4(SnBu^n_3)]$ **11** as a brown oil. The ^1H NMR spectrum at −50 °C showed four high-field resonances assignable to tungsten hydrides. Three of the resonances were doublets [at δ −3.55, J(P–H) 50; δ −5.80, J(P–H) 50; and δ −6.40, J(P–H) 48 Hz] whilst the fourth was a singlet at δ −5.92. Confirmation that the doublet splittings arose from coupling to the ^{31}P nucleus was obtained from the ^1H-$\{^{31}P\}$ NMR

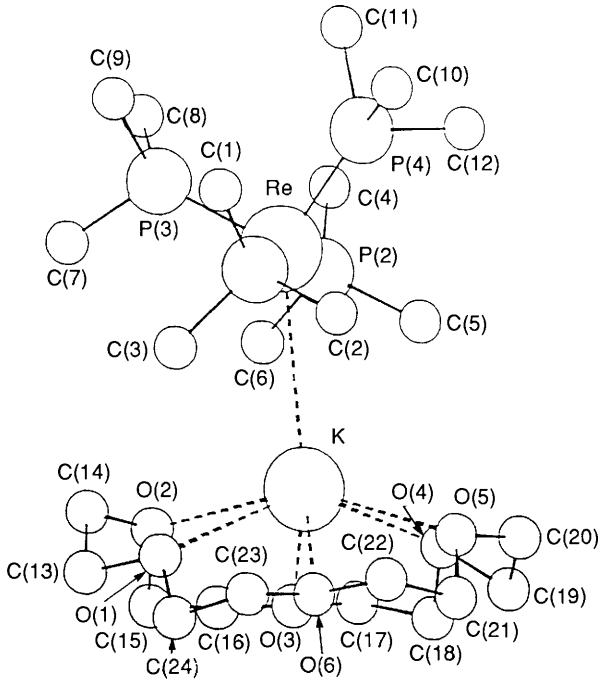


Fig. 7 General view of the structure of [K(18-crown-6)][*cis*-$Re(PMe_3)_4H_2$] **12** parallel to the plane of the crown ether oxygen atoms

spectrum at −50 °C in which each of the three doublets collapsed to a singlet. At ambient temperature the ^{31}P-$\{^1H$–Me$\}$ NMR spectrum showed one broad resonance at δ −26.7 whilst at −50 °C a binomial quartet was observed with J(P–H) 46.5 Hz. This is consistent with the low-temperature ^1H NMR spectrum and it would appear that for one of the four hydrides J(P–H) is close to zero. These observations can be accounted for by a capped octahedral structure for **11** in which the PMe_3 ligand is *trans* to either the $SnBu^n_3$ group or to the η-C_5H_5 ligand. Scheme 2 illustrates one of these structures, in which PMe_3 is *trans* to the sterically demanding η-C_5H_5 ligand which, therefore, seems a more likely geometry.

The compound $[Re(PMe_3)_4H_3]$ was treated with an excess of KH and 18-crown-6 giving red crystals of [K(18-crown-6)][*cis*-$Re(PMe_3)_4H_2$] **12**, the crystal structure of which has been determined (Fig. 7). The phosphorus atoms of the phosphine ligands occupy four of the six sites of a distorted octahedron leaving two *cis* sites for the hydrido ligands. The phosphorus atoms are displaced towards the hydrogen sites by the mutual repulsion of the four bulky phosphine ligands. The *trans* pair of phosphorus ligands, P(1) and P(2), form rather longer Re–P bonds than do the remaining pair, P(3) and P(4), but the differences are on the margin of significance. The atoms P(3), P(4), Re and K are coplanar with Re • • • K 3.784 Å, longer than the sum of covalent radii and longer than the W • • • K distance in **3**. However, there does appear to be a significant K • • • Re interaction both from the positioning of the potassium and the effect of this position on the conformation of the 18-crown-6. The potassium is exactly where it would be expected if there were a double hydrido bridge from potassium to rhenium. However to accommodate the bulky *trans* PMe_3 groups attached to the rhenium the 18-crown-6 has to take up a new conformation with the four oxygen atoms O(1), O(2), O(5) and O(6), almost coplanar and the remaining two, O(3) and O(4), out of the plane away from Re, see Fig. 7. Table 3 shows that this apparently large change in conformation requires two significant changes in torsion angle and is therefore unlikely to require a large increase in the conformational energy. There was no evidence on the positioning of the bridging hydrogen atoms from the difference electron-density map. The ambient temperature ^1H and ^{31}P NMR spectra of **12** (Table 1) are entirely consistent with the presence of the anion [*cis*-$Re(PMe_3)_4H_2]^-$ in solution.

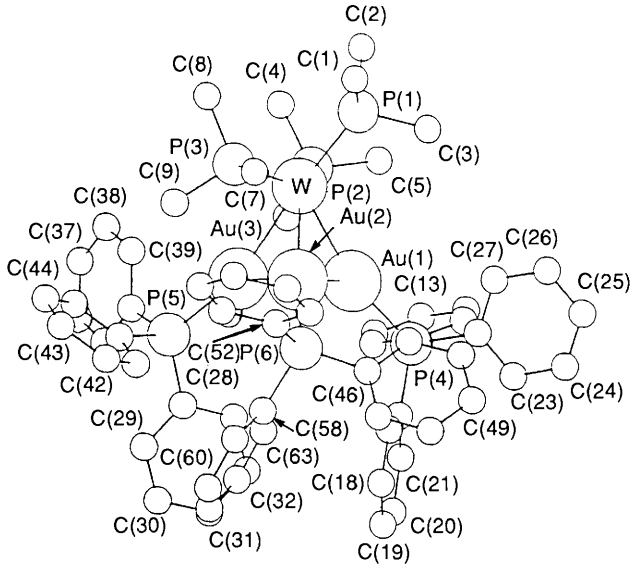


Fig. 8 General view of the structure of $[\{(Ph_3P)Au\}_3W(PMe_3)_3H_4]$-$Cl\cdot 0.15CH_2Cl_2$ **17**

The reaction between $[Re(PMe_3)_4H_3]$ and an excess of KH at 60 °C gave a pale yellow, pyrophoric, microcrystalline solid **13** in good yield. Compound **13** is exceptionally sensitive to moisture and satisfactory elemental analysis was not obtained. The ^1H, ^{31}P-$\{^1H$–Me$\}$ and ^{31}P-$\{^1H\}$ NMR spectra are, however, entirely consistent with the presence in solution of K[*cis*-$Re(PMe_3)_4H_2$] **13**, since they are closely similar to those of **12**. Compound **13** was treated, at −78 °C, with an excess of $[^2H_4]$methanol giving $[Re(PMe_3)_4H_2D]$ in reasonable yield. This provides further evidence for the stoichiometry $K[Re(PMe_3)_4H_2]$ proposed for **13**. Similarly, treatment of **13** in tetrahydrofuran with $SnBu^n_3Cl$ gave white crystals of $[Re(PMe_3)_4H_2(SnBu^n_3)]$ **14** which ^1H NMR spectroscopy shows to be fluxional at ambient temperature.

Treatment of compound **2** in tetrahydrofuran at −80 °C with $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ gave $[Cl(\eta\text{-}C_5H_5)_2ZrW(PMe_3)_3H_5]$ **15** as dark green needles. Compound **15** is mildly air sensitive and soluble in non-polar solvents giving green–red dichroic solutions that appear indefinitely stable at ambient temperature. Addition of **2** in tetrahydrofuran to 1 equivalent of $[Zr(\eta\text{-}C_5H_5)_2Cl(H)]$ gave dark purple, crystalline $[H(\eta\text{-}C_5H_5)_2Zr$-$W(PMe_3)_3H_5]$, **16** in 83% yield. Compound **16** is moderately air-sensitive, and soluble in non-polar solvents.

The ^1H and ^{31}P NMR spectra of compounds **15** and **16** show both molecules to be fluxional. The stoichiometry of the $W(PMe_3)_3H_5$ moiety is clearly established by the binomial quartets for the hydride resonances in the ^1H NMR spectra, and binomial sextets in the ^{31}P-$\{^1H$–Me$\}$ NMR spectra. The NMR data indicate that, for **16**, the zirconium-bound hydride (at δ 5.25) does not exchange with the tungsten-bound hydride ligands, and resolution of a 2.3 Hz coupling between the two types of hydrides rules out the possibility of any form of dissociative equilibrium. The variable-temperature ^1H NMR spectra of **16** showed changes for the tungsten-bound hydride resonances which were somewhat reminiscent of those observed for **2**–**6**. Thus the binomial doublet of quartets pattern of integral five hydrogens centred at δ −3.35 $\{J_q$(P–H) 25.8, J_d[(W–H)–(Zr–H)] 2.3 Hz$\}$ observed at 298 K changes to an unsymmetrical pattern at 253 K. On cooling to 183 K this pattern reverts to a broad, symmetrical quartet (at δ −3.35) of integral three hydrogens for which the J(P–H) coupling constant (14.5 Hz) is lower than that for the quartet at 298 K. At 173 K two new broad resonances of unit intensity appear at δ 1.8 and 5.6, and the broad quartet at δ −3.35 became a broad singlet. The data can be interpreted on the basis of a tricapped pseudo-octahedral structure for **16**. This structure (see Scheme 2) is proposed by analogy with the work by Caulton

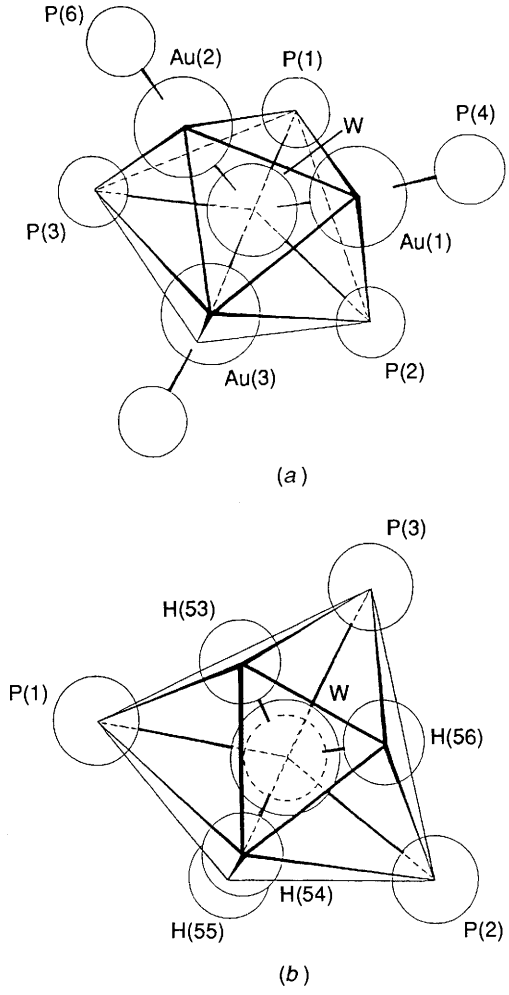


Fig. 9 (*a*) The WAu_3P_6 group in compound **17** projected on to the plane of the gold atoms and showing the relation of the WAu_3P_3 co-ordination to that of the WP_3H_5 of dodecahedron **3** seen in the analogous projection in (*b*)

and co-workers[43] in which $K[OsH_3(PMe_2Ph)_3]$ and $K[ReH_6(PMePh_2)_2]$ were treated with $[Zn(\eta\text{-}C_5H_5)_2Cl(X)]$ (X = H, Cl or Me), giving compounds of the type $[X(\eta\text{-}C_5H_5)_2ZrM(PR_3)_yH_x]$. The crystal structure of $[Cl(\eta\text{-}C_5H_5)_2\text{-}ZrOs(PMe_2Ph)_3H_3]$ showed that the $(\eta\text{-}C_5H_5)_2ZrCl$ moiety essentially caps the triangular face presented by the three osmium-bound hydride ligands in the pseudo-octahedral unit [*fac*-$Os(PMe_2Ph)_3H_3$]. The three hydrides H_c, H_d, H_e in the *fac*-$W(PMe_3)_3H_3$ core in **16** presumably undergo fast exchange at all temperatures studied. The resonances of the other two tungsten-bound hydrides (H_a and H_b, at δ 1.8 and δ 5.6 at 173 K) are presumably in the baseline due to exchange broadening at 183 K. The J(P–H) coupling constant of 14.5 Hz at 183 K is therefore assigned to $J(P\text{–}H_{c,d,e})$, whereas the value of 25.8 Hz at 298 K is an exchange-averaged value. This gives rise to $J(P\text{–}H_a) + J(P\text{–}H_b) = 85.5$ Hz. The spectra at temperatures above 183 K are deceptively simple because the exchange-averaged chemical shift of the resonances due to H_a and H_b is very close to that of H_c, H_d and H_e.

Treatment of $K[W(PMe_3)_3H_5]$ with $[Au(PPh_3)Cl]$ gave orange crystals of $[\{(Ph_3P)Au\}_3W(PMe_3)_3H_4]Cl\cdot xCH_2Cl_2$ **17**. Solutions of **17** in CH_2Cl_2 decomposed slowly at ambient temperature giving a gold mirror. The crystal structure of **17** has been determined. (Figs. 8 and 9). The tetrahydride **17** is isoelectronic with the known rhenium–gold cluster cation $[(PhMe_2P)_3ReH_3(AuPPh_3)_3]^+$[44] and structurally related to the compound $[(Ph_3P)_3AuV(CO)_5]$.[44] The WP_3 group is similar in shape to that found in **3** and **5** but the P–W–P angles are about 8° smaller, possibly due to the bulk of the Au atoms.

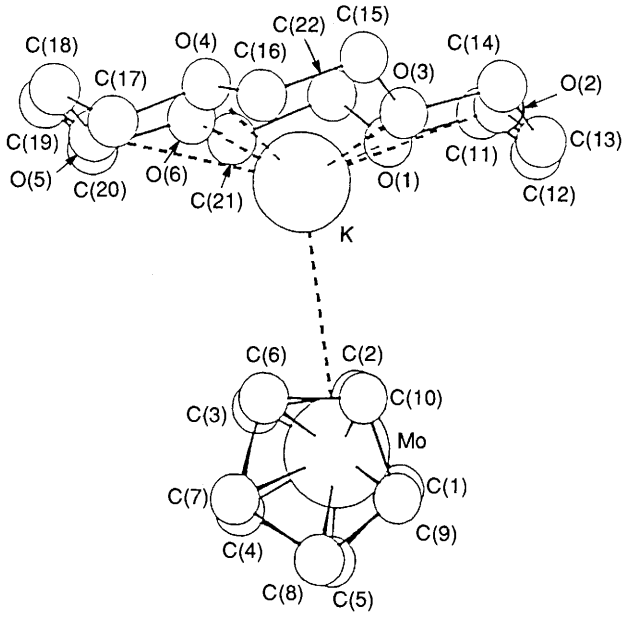


Fig. 10 General view of the structure of $[K(18\text{-crown-6})][Mo(\eta\text{-}C_5H_5)_2H]$ **18** seen 10° from the plane O(1)–O(6)

The hydrido ligands of **17** could not be located in the difference electron-density map.

We propose that the three hydrogen atoms in the co-ordination polyhedron corresponding to H(53), H(54) and H(56) in compounds **3** and **5** point at the three Au atoms forming non-linear W–H–Au bridges with the B-site hydrogen H(56) bridging to Au(2), Fig. 9. The W–Au (mean 2.804 Å) and the Au–Au (mean 2.845 Å) distances are sensibly equal so that the metal atoms are at the corners of a slightly distorted equilateral triangle. The co-ordination sphere of the gold atoms is completed by one phosphorus atom of a Ph_3P ligand so that W–Au–P is nearly linear (mean 166.5°). The Ph_3P ligands themselves have the familiar propeller conformation.

Finally, we report the reaction between $[Mo(\eta\text{-}C_5H_5)_2H_2]$ and potassium hydride in the presence of 18-crown-6. This gave the expected compound $[K(18\text{-crown-6})][Mo(\eta\text{-}C_5H_5)_2H]$ **18** in excellent yield as highly sensitive yellow-orange crystals. The molecular structure of **18** is shown in Fig. 10. The torsion angles in Table 3 show that the 18-crown-6 has the same configuration as in **3**. The atoms of the crown ether show large thermal motion and consequent bond-length shortening. The potassium ion lies 0.87 Å out of the plane of the six crown ether oxygen atoms towards the molybdenum atom of the $Mo(\eta\text{-}C_5H_5)_2$ moiety and this together with the observed Mo ··· K contact distance of 3.614 Å is highly suggestive of the existence of a covalent Mo–H–K bridge. There is a significant peak, a possible hydrogen atom, in the residual electron density at $R = 0.041$ a distance of 1.71 Å from Mo and 2.80 Å from K. These distances agree fairly well with the observed Mo–H distance, 1.685 Å for Mo–H in $[Mo(\eta\text{-}C_5H_5)_2H_2]$[45] and the mean H–K distance, 2.714 Å, in **3**. The planes of the C_5H_5 groups are not parallel but are inclined at an angle of 153.3° {*cf* 145.8° in $[Mo(\eta\text{-}C_5H_5)_2H_2]$}. The possible hydrogen atom lies 0.2 Å from the plane defined by the vectors from Mo to the centroids X and Y of the C_5H_5 rings and in the plane containing the midpoint of the XY vector, Mo and K. If the hydrogen assignment is correct the Mo–H–K bridge is non-linear, as would be expected. The hydrogen position is speculative and must await conformation by neutron diffraction, but so far we have been unable to obtain sufficiently large crystals.

In conclusion we have presented evidence for a degree of covalent bonding in bent M–H–K and M–H–Na bonds: the first bonds of this type to be described. These bonds may be compared to the two-electron three-centre agostic M–H–C bonds.[46] It is apparent from this work and from previous work

referred to above that M–H–M′ bonds, where M is a transition metal and M′ is a highly electropositive element, are likely to occur widely.

Experimental

All preparations and reactions described were carried out under an atmosphere of argon or dinitrogen (< 10 ppm oxygen or water) using standard Schlenk-vessel and vacuum-line techniques or in a dry-box. Argon and nitrogen were purified by passage through a gas-drying column containing BTS catalyst and 5Å molecular sieves.

Solvents were pre-dried over activated molecular sieves and then distilled from potassium (toluene, benzene, tetrahydrofuran, cyclohexane), sodium–potassium alloy [pentane, light petroleum (b.p. 40–60 °C throughout), diethyl ether] or phosphorus pentaoxide (dichloromethane), under an inert atmosphere of nitrogen. Deuteriated solvents for NMR samples were stored in ampoules over activated molecular sieves or a potassium film and transferred by vacuum distillation.

Elemental analyses were performed by Analytische Laboratorien, Elbach, Germany, or the Analytical Laboratory in this Department.

Infrared spectra were recorded on a Perkin-Elmer 1510 FT interferometer or on a Philips Analytical SP2000 double-beam grating spectrophotometer. The NMR spectra were recorded on the following instruments: ^{1}H (250 MHz, Bruker AM-250; 300 MHz, WH-300; 400 MHz, WH-400 and 500 MHz, AM-500), ^{13}C (62.9 MHz, Bruker AM-250), ^{31}P (101.2 MHz, Bruker AM-250), ^{2}H (38.4 MHz, Bruker AM-250), ^{183}W (3.7 MHz, JEOL 90) and ^{119}Sn (33.6 MHz, JEOL 90). Abbreviations used for multiplicities are s = singlet, d = doublet, t = triplet, q = quartet, qnt = quintet, sxt = sextet, m = multiplet, vct = virtually coupled triplet and br = broad. Spectra were referenced internally using the residual protio solvent resonance (^{1}H) or solvent resonance (^{13}C) relative to tetramethylsilane (δ 0), or externally using trimethyl phosphate in D_2O (^{31}P). All chemical shifts are quoted in δ (ppm), and coupling constants in Hz.

Low-resolution mass spectra were recorded on an AEI M.S. 902 spectrometer, updated by a data-handling system supplied by Mass Spectroscopy Services Ltd.

Reactions of $[W(PMe_3)_3H_6]$.—*With* KH: *Formation of* $K[W(PMe_3)_3H_5]$ **2**. The compound $[W(PMe_3)_3H_6]$ (2.0 g, 4.78 mmol) in tetrahydrofuran (30 cm^3) was transferred onto an excess of KH (0.5 g, 12.5 mmol) in a glass ampoule equipped with a glass-coated magnetic follower. The slurry was stirred at 50 °C for 5 d whereupon an orange colouration appeared. The solution was filtered through a flame-dried glass filter paper into a flame-dried Schlenk vessel. It was then concentrated under reduced pressure to the point where orange crystals just started to precipitate, warmed slightly to redissolve all solid, and then cooled slowly to −80 °C. Yellow crystals precipitated which were isolated by filtration, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*. On drying *in vacuo*, the crystals changed to powdered $K[W(PMe_3)_3H_5]$ (2.07 g, 4.54 mmol, 95%).

With KH *and* 18-crown-6: *Formation of* [K(18-crown-6)][$W(PMe_3)_3H_5$] **3**. The compound $[W(PMe_3)_3H_6]$ (2.0 g, 4.78 mmol) in tetrahydrofuran (30 cm^3) was transferred onto an excess of KH (*ca.* 0.5 g, 12.5 mmol) and an excess of 18-crown-6 (*ca.* 1.3 g, 4.92 mmol). An immediate colour change from green to orange was observed. The reaction mixture was stirred at ambient temperature for 2 d, filtered, concentrated under reduced pressure to the point where orange crystals started to precipitate, warmed slightly to redissolve all solid, and then cooled slowly to −10 °C. Large orange crystals of [K(18-crown-6)][$W(PMe_3)_3H_5$] formed which were isolated by filtration, washed with cold diethyl ether (2 × 5 cm^3) and dried *in vacuo*. The mother-liquor was further concentrated and cooled to −30 °C, whereupon more orange, crystalline [K(18-crown-6)][$W(PMe_3)_3H_5$] precipitated. Total yield: 2.88 g, 84%.

With NaH: *Formation of* $Na[W(PMe_3)_3H_5]$ **4**. The compound $[W(PMe_3)_3H_6]$ (2.0 g, 4.78 mmol) in tetrahydrofuran (30 cm^3) was transferred onto an excess of NaH (*ca.* 0.5 g, 20.8 mmol). The mixture was stirred at 60 °C for 4 d whereupon the solution became yellow and a fine black suspension formed. The solution was filtered free of excess of NaH and black solid, concentrated under reduced pressure to the point where yellow crystals started to precipitate, warmed slightly to redissolve all solid, and finally cooled to −80 °C. Yellow crystals precipitated which were isolated by filtration, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*. On drying the crystals changed to powdered $Na[W(PMe_3)_3H_5]$. Yield 1.99 g, 95%.

With NaH *and* 15-crown-5: *Formation of* [Na(15-crown-5)][$W(PMe_3)_3H_5$] **5**. The compound $[W(PMe_3)_3H_6]$ (2.0 g, 4.78 mmol) in tetrahydrofuran (30 cm^3) was transferred onto an excess of NaH (0.5 g, 20.8 mmol) and 15-crown-5 (1.10 g, 5.00 mmol). The mixture was stirred at 60 °C for 3 d whereupon an orange colouration appeared. The solution was filtered, concentrated under reduced pressure to the point where yellow crystals just started to form, warmed to redissolve all solid and cooled slowly to −10 °C. Very large yellow crystals precipitated which were isolated by filtration, washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*. The mother-liquor was concentrated to approximately 5 cm^3 and cooled to −80 °C whereupon more yellow crystals precipitated which were isolated by filtration, washed with diethyl ether (2 × 5 cm^3) and dried *in vacuo*. Yield, 2.80 g, 89%.

With $LiBu^n$: *Formation of* $[\{W(PMe_3)_3H_5Li\}_4]$ **6**. The compound $[W(PMe_3)_3H_6]$ (1.5 g, 3.58 mmol), freshly extracted into light petroleum (50 cm^3), was treated with an excess of a solution of *n*-butyllithium in hexane (5 cm^3 of a 2.5 mol dm^{-3} solution, 12.5 mmol). An immediate yellow colouration occurred and yellow crystals precipitated over 15–24 h. These were isolated by filtration, washed with light petroleum (2 × 10 cm^3) and dried *in vacuo*. Yield of $[\{W(PMe_3)_3H_5Li\}_4]$ 1.5 g (0.88 mmol, 99%).

Reaction of $K[W(PMe_3)_3H_5]$ *with* $SnBu^n_3Cl$: *Formation of* $[W(PMe_3)_3H_5(SnBu^n_3)]$ **7**.—The compound $K[W(PMe_3)_3H_5]$ (0.57 g, 1.25 mmol) in tetrahydrofuran (15 cm^3) was treated with $SnBu^n_3Cl$ (0.41 g, 1.25 mmol) in tetrahydrofuran (5 cm^3) over 3 min at ambient temperature. The initial orange solution became pale brown and a suspension of white powder appeared. Solvent was removed under reduced pressure and the residue was extracted into light petroleum (15 cm^3). The resulting pale brown solution was filtered, concentrated under reduced pressure to approximately 1.5 cm^3 and cooled to −80 °C giving white crystals. These were isolated by filtration, washed with cold pentane (0.2 cm^3, −80 °C) and dried *in vacuo*. Yield 0.26 g, 30%.

Reaction of [K(18-crown-6)][$W(PMe_3)_3H_5$] *with* $SnBu^n_3Cl$: *Formation of* $[W(PMe_3)_3H_5(SnBu^n_3)]$ **7**.—The compound [K(18-crown-6)][$W(PMe_3)_3H_5$] (0.65 g, 0.90 mmol) in tetrahydrofuran (15 cm^3) was treated at ambient temperature with $SnBu^n_3Cl$ (0.29 g, 0.9 mmol) in tetrahydrofuran (5 cm^3). The mixture was stirred for 3 h. The resulting brown solution and white solid was taken to dryness under reduced pressure and extracted with pentane (20 cm^3). The pale brown extract was filtered and the filtrate was taken to dryness under reduced pressure. White solid 18-crown-6 was removed by sublimation at 50 °C and 8 × 10^{-5} mmHg for 2 h. The residual brown oil was dissolved in pentane (5 cm^3) and the solution was filtered, concentrated to 0.5 cm^3 under reduced pressure, and cooled to −80 °C. White crystals of $[W(PMe_3)_3H_5(SnBu^n_3)]$ precipitated which were isolated by filtration, washed with cold pentane (0.2 cm^3 at −80 °C) and dried *in vacuo*. Yield 0.16 g, 27%.

Reaction of $[\{W(PMe_3)_3H_5Li\}_4]$ *with* $SnBu^n_3Cl$: *Formation of*

$[W(PMe_3)_3H_5(SnBu^n_3)]$ **7**.—The compound $[\{W(PMe_3)_3H_5Li\}_4]$ (0.7 g, 0.42 mmol) in tetrahydrofuran (15 cm^3) was treated dropwise with $SnBu^n_3Cl$ (0.55 g, 1.68 mmol) in tetrahydrofuran (20 cm^3). The addition was made at −22 °C with stirring, over a period of 10 min. A subtle colour change occurred from orange to orange-green to golden brown. Solvent was removed *in vacuo* giving a brown oil which was extracted with light petroleum (20 cm^3). The brown extract was filtered from a white solid, and the filtrate was concentrated giving a brown oil. Attempts to obtain crystals were unsuccessful.

Reactions of $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$ *with* KH: *Formation of* $K[W(\eta\text{-}C_5H_5)(PMe_3)H_4]$ **8**.—The compound $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$ (0.1 g, 0.3 mmol) in a 5 mm NMR tube was treated with an excess of KH (*ca.* 30 mg, 0.75 mmol) and with $[^2H_8]$tetrahydrofuran as solvent. The tube was immersed in an oil-bath at 60 °C for 3 d whereupon a colour change from pale brown to orange was observed. A 300 MHz ^1H NMR spectrum recorded at this stage showed the reaction to be complete.

With KH *and* 18-crown-6: *Formation of* $[K(18\text{-crown-6})][W(\eta\text{-}C_5H_5)(PMe_3)H_4]$ **9**. The compound $[W(\eta\text{-}C_5H_5)(PMe_3)H_5]$ (0.15 g, 0.45 mmol) in a 5 mm NMR tube was treated with an excess of KH (*ca.* 30 mg, 0.75 mmol) and a slight excess of 18-crown-6 (0.13 g, 0.5 mmol). $[^2H_8]$Tetrahydrofuran was the solvent. The tube was warmed to 60 °C in an oil-bath and the initially pale brown solution became orange-red after 12 h. A ^1H NMR spectrum showed that the reaction was complete and only one product was formed.

Reaction of $[W(\eta\text{-}C_5H_4Et)(PMe_3)H_5]$ *with* KH *and* 18-crown-6: *Formation of* $[K(18\text{-crown-6})][W(\eta\text{-}C_5H_4Et)(PMe_3)H_4]$ **10**.—The compound $[W(\eta\text{-}C_5H_4Et)(PMe_3)H_5]$ (0.1 g, 0.28 mmol) in a 5 mm NMR tube was treated with an excess of KH (*ca.* 30 mg, 0.75 mmol) and a slight excess of 18-crown-6 (80 mg, 0.3 mmol) and with $[^2H_8]$tetrahydrofuran as solvent. The tube was warmed to 60 °C in an oil-bath for 12 h resulting in a colour change from pale brown to orange. The ^1H NMR spectrum confirmed that the reaction was complete.

Reaction of $K[W(\eta\text{-}C_5H_5)(PMe_3)H_4]$ *with* $SnBu^n_3Cl$: *Formation of* $[W(\eta\text{-}C_5H_5)(PMe_3)H_4(SnBu^n_3)]$ **11**.—The compound $K[W(\eta\text{-}C_5H_5)(PMe_3)H_4]$ (*ca.* 0.1 g, 0.16 mmol) in tetrahydrofuran (5 cm^3) was added dropwise with stirring to $SnBu^n_3Cl$ (75 mg, 0.23 mmol) in tetrahydrofuran (3 cm^3) at ambient temperature. The solution changed from orange-brown to pale brown and a fine white solid precipitated. Solvent was removed under reduced pressure and the pale brown oily residue was extracted into light petroleum (10 cm^3). A pale brown solution was obtained which was filtered and taken to dryness under reduced pressure. The oily residue thus obtained was dissolved in $[^2H_6]$benzene and characterised by NMR spectroscopy. Yield 60%.

Reaction of $[Re(PMe_3)_5H]$ *with Hydrogen: Preparation of* $[Re(PMe_3)_4H_3]$.—The compound $[Re(PMe_3)_5H]$ (2.4 g, 4.23 mmol) in light petroleum (b.p. 100–120 °C) (15 cm^3) was stirred under hydrogen (2 atm, *ca.* 2×10^5 Pa) at 60 °C for 3 d. The solvent was removed from the resulting green solution under reduced pressure. The residue was extracted into light petroleum (30 cm^3) and the green solution was filtered, concentrated under reduced pressure, and cooled to −80 °C. White crystals of $[Re(PMe_3)_4H_3]$ precipitated which were isolated by filtration, and dried *in vacuo*. The mother-liquor was further concentrated under reduced pressure and cooled to −80 °C whereupon more white, crystalline $[Re(PMe_3)_4H_3]$ precipitated. Combined yield 2.0 g, 4.05 mmol, 96%.

Reaction of $K[Re(PMe_3)_4H_2]$ *with* 18-crown-6: *Formation of* $[K(18\text{-crown-6})][Re(PMe_3)_4H_2]$ **12**.—The compound $K[Re(PMe_3)_4H_2]$ (*ca.* 1.5 g, 2.8 mmol) in tetrahydrofuran (20 cm^3) was decanted onto a mixture of 18-crown-6 (0.8 g, 3.0 mmol) and KH (*ca.* 0.8 g, 20 mmol). A colour change from orange to orange-red was observed. The reaction mixture was heated to 40 °C overnight, then left to settle for 12 h. The orange-red solution thus obtained was decanted into a flame-dried Schlenk tube, concentrated under reduced pressure to the point where orange crystalline solid just started to precipitate (*ca.* 5 cm^3), warmed slightly (to redissolve all solid), and left to stand under partial vacuum at ambient temperature. After 2 h, crystalline $[K(18\text{-crown-6})][Re(PMe_3)_4H_2]$ precipitated. This was isolated by filtration, washed with diethyl ether–tetrahydrofuran (5:1 v/v) (2×5 cm^3) and dried *in vacuo*. The mother-liquor was further concentrated under reduced pressure and cooled to −80 °C whereupon more microcrystalline $[K(18\text{-crown-6})][Re(PMe_3)_4H_2]$ precipitated. This was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Yield 1.3 g, 2.44 mol, 89%.

Reaction of $[Re(PMe_3)_4H_3]$ *with* KH: *Formation of* $K[Re(PMe_3)_4H_2]$ **13**.—The compound $[Re(PMe_3)_4H_3]$ (2.0 g, 4.05 mmol) in tetrahydrofuran (20 cm^3) was stirred over an excess of KH (0.5 g, 12.5 mmol) at 60 °C for 6 weeks whereupon the colour changed from green to orange. The solution was decanted into a flame-dried Schlenk vessel, concentrated under reduced pressure (*ca.* 5 cm^3) and cooled to −80 °C. Yellow microcrystalline $K[Re(PMe_3)_4H_2]$ precipitated overnight and the crystals were isolated by filtration, washed with diethyl ether (2×10 cm^3) and dried *in vacuo*. The product was a semicrystalline cream coloured powder which became pale green on standing in dry argon. Yield 1.8 g, 3.38 mmol, 83.5%.

Reactions of $K[Re(PMe_3)_4H_2]$.—*With methanol.* A tetrahydrofuran solution of $K[Re(PMe_3)_4H_2]$ (*ca.* 2 cm^3 of a 0.06 mol dm^{-3} solution; 65 mg, 0.12 mmol) was added at −78 °C dropwise and with stirring to an excess of methanol (*ca.* 0.2 g, 6.4 mmol, 52 equivalents) in tetrahydrofuran (10 cm^3). A blue-green colour appeared as the orange $K[Re(PMe_3)_4H_2]$ solution was added. After the addition was complete the reaction mixture was allowed to reach ambient temperature and solvent was removed under reduced pressure. A blue-green solid residue remained which was extracted into light petroleum (15 cm^3) to give a blue-green solution. This was filtered, taken to dryness under reduced pressure, and dissolved in $[^2H_6]$benzene. The product was shown by ^1H NMR spectroscopy to be pure $[Re(PMe_3)_4]H_3]$.

With $[^2H_4]$*methanol: Formation of* $[Re(PMe_3)_4H_2D]$. The compound $K[Re(PMe_3)_4H_2]$ (*ca.* 2 cm^3 of a 0.06 mol dm^{-3} solution; 65 mg, 0.12 mmol) in tetrahydrofuran was added at −78 °C dropwise and with stirring to an excess of $[^2H_4]$methanol (*ca.* 0.1 g, 3.2 mmol, 26 equivalents) in tetrahydrofuran (3 cm^3). A turquoise colour developed and, after complete addition, the reaction mixture was allowed to reach ambient temperature before solvent was removed under reduced pressure. The residue was extracted into light petroleum giving a turquoise solution which was filtered and taken to dryness under reduced pressure. A blue-green crystalline residue remained, part of which was dissolved in $[^2H_6]$benzene and used to record a 300 MHz ^1H NMR spectrum and part of which was dissolved in benzene and used to record a ^2H NMR spectrum.

With $SnBu^n_3Cl$: *Formation of* $[Re(PMe_3)_4H_2(SnBu^n_3)]$ **14**. The compound $SnBu^n_3Cl$ (25 mg, 0.08 mmol) in tetrahydrofuran (3 cm^3) was treated dropwise with stirring at ambient temperature with $K[Re(PMe_3)_4H_2]$ in tetrahydrofuran (*ca.* 2 cm^3 of a 0.06 mol dm^{-3} solution, 0.13 mmol, *ca.* 1.6 molar equivalents). As the orange $K[Re(PMe_3)_4H_2]$ solution was added an immediate colour change to blue-green was observed. After complete addition the reaction mixture was taken to dryness under reduced pressure and the resulting blue-green solid was extracted into light petroleum (10 cm^3). A pale blue solution formed which was filtered from a white solid and the filtrate was concentrated to an oil under reduced pressure. The

compound $[Re(PMe_3)_4H_3]$ was sublimed out of this oil at 75 °C and 8×10^{-4} mmHg for 1 h. A green oily residue was dried *in vacuo* (8×10^{-4} mmHg) for 2 h whereupon white crystals separated which were washed and dried *in vacuo*. Yield 27 mg, 45% based on $SnBu^n_3Cl$.

Reactions of $K[W(PMe_3)_3H_5]$.—*With* $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$: *Formation of* $[Cl(\eta\text{-}C_5H_5)_2ZrW(PMe_3)_3H_5]$ **15**. The compound $K[W(PMe_3)_3H_5]$ (0.30 g, 0.66 mmol) in tetrahydrofuran (5 cm^3) was added dropwise to a stirred solution of $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ (0.20 g, 0.68 mmol) in tetrahydrofuran (10 cm^3) at −80 °C. As the orange $K[W(PMe_3)_3H_5]$ solution entered the colourless $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ solution a green colour formed and, after complete addition, a green-red dichroic solution was obtained (red by transmitted light). The reaction mixture was allowed to warm to ambient temperature, then the solvent was removed under reduced pressure and the residue was extracted into light petroleum (2×15 cm^3). A green-red dichroic extract was separated from a white powder by filtration. The filtrate was concentrated to *ca.* 15 cm^3 under reduced pressure, and cooled to −30 °C. Green needles precipitated which were isolated by filtration, washed with cold light petroleum (2×3 cm^3) and dried *in vacuo*. The mother-liquor was further concentrated to *ca.* 5 cm^3 and cooled to −30 °C whereupon more green needles precipitated which were isolated by filtration and dried *in vacuo*. Yield 0.28 g, 63%.

With $[Zr(\eta\text{-}C_5H_5)_2Cl(H)]$: *Formation of* $[H(\eta\text{-}C_5H_5)_2ZrW(PMe_3)_3H_5]$ **16**. The compound $K[W(PMe_3)_3H_5]$ (0.30 g, 0.66 mmol) in tetrahydrofuran (8 cm^3) was added dropwise at −20 °C, to a stirred slurry of $[Zr(\eta\text{-}C_5H_5)_2Cl(H)]$ (0.17 g, 0.67 mmol) in tetrahydrofuran (10 cm^3). A colour change from orange to red-brown developed over *ca.* 10 min. The solution was stirred at ambient temperature for 15 min whereupon the colour changed to red-purple. Solvent was removed under reduced pressure, and the residue was extracted into light petroleum (25 cm^3) giving a purple solution with some white powder. The solution was filtered, and the filtrate was concentrated under reduced pressure to *ca.* 10 cm^3 and cooled slowly to −10 °C. Purple crystals precipitated which were isolated by filtration, washed with diethyl ether (2.2 cm^3) and dried *in vacuo*. Yield 0.35 g, 0.55 mmol, 83%.

With $[Au(PPh_3)Cl]$: *Formation of* $[\{(Ph_3P)Au\}_3W(PMe_3)_3H_4]Cl\cdot 0.15CH_2Cl_2$ **17**. A stirred slurry of $[Au(PPh_3)Cl]$ (0.50 g, 1.01 mmol) in tetrahydrofuran (10 cm^3) was treated dropwise at −78 °C with $K[W(PMe_3)_3H_5]$ (0.46 g, 1.01 mmol) in tetrahydrofuran (10 cm^3). An immediate colour change from yellow to red was observed, and an orange-red precipitate formed. As the addition was completed the precipitate redissolved and a clear red solution remained. The reaction mixture was allowed to warm to ambient temperature (no further colour change) and solvent was removed under reduced pressure leaving an orange solid. This was washed with light petroleum (2×20 cm^3), toluene (20 cm^3) and diethyl ether (20 cm^3). It was recrystallised from a mixture of dichloromethane (5 cm^3) and diethyl ether (3 cm^3). The orange crystalline plates which precipitated were isolated by filtration and dried *in vacuo*. Yield 0.48 g, 77% based on $[Au(PPh_3)Cl]$.

Synthesis of $[K(18\text{-crown-}6)][Mo(\eta\text{-}C_5H_5)_2H]$ **18**.—The compound $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (1.5 g, 6.6 mmol) in tetrahydrofuran (220 cm^3) was treated with potassium hydride (300 mg, 7.5 mmol) and 18-crown-6 (2.5 g, 9.5 mmol) in benzene (25 cm^3). The mixture was stirred for 7 d during which time large red crystals deposited. The red thf solution was decanted and discarded and the crystals washed twice with toluene (20 cm^3) and dried *in vacuo*. Yield 1.75 g, 50% (Found: C, 49.8; H, 6.65. Calc. C, 49.7; H, 6.6%).

Crystal Structure Determinations.—For the structure analyses the crystal data and some experimental details are recorded in Table 5, the atomic parameters in Table 6, selected interatomic distances and interbond angles in Table 2, and crown ether torsion angles in Table 3.

(*a*) *Neutron diffraction.* Neutron diffraction data were collected at the Institute Laue-Langevin (I.L.L.) in Grenoble on the D10 triple-axis instrument fitted with a helium cryostat; an instrument in the guide hall not normally used for single-crystal analysis. The reflections were sharp with intensities comparable with those expected from instruments using shorter wavelengths on the reactor face. For each compound the crystals were mounted in evacuated sealed glass tubes.

A crystal of $[Na(15\text{-crown-}5)][W(PMe_3)_3H_5]$ was mounted on D10 in a random orientation and cautiously cooled to 30 K. The orientation matrix and unit-cell dimensions were determined from 55 well centred reflections. The unit-cell dimensions at 30 K were all shorter than at 293 K and the unit-cell volume was 184 $Å^3$ less. The X-ray parameters with (*i*) the disordered model for the 15-crown-5 system, (*ii*) the one, then (*iii*) the other 15-crown-5 site were all tried as starting models for the refinement and gave $R \approx 0.3$ after scaling and isotropic refinement. The structure was then considered as two rigid groups $W(PMe_3)_3H_5Na$ and the 15-crown-5 without hydrogen atoms. The positions of the rigid groups each with an overall isotropic thermal parameter were refined and the hydrogen atoms found from a Fourier difference synthesis at $R \approx 0.16$. The structure was then further refined with geometric restraints and anisotropic thermal parameters with soft vibrational restraints to $R = 0.037$. The restraints were then relaxed and the final refinement converged at $R = 0.036$ with anisotropic thermal parameters for all atoms. The final position of the 15-crown-5 was very significantly different from that in the disordered structure at room temperature. The observed contraction in the unit cell is consistent with the loss of the room-temperature disorder on cooling.

For the potassium compound a similar procedure was followed. A crystal was mounted about the [010] axis. The intention was to cool to about 30 K, however during the cooling process the crystal orientation began to change rapidly at about 90 K with some irreversible loss in intensity, indicating a possible phase change. It was decided to proceed with a second crystal (sealed in a thin-walled silica capillary under nitrogen using an epoxy resin to secure the crystal) at a temperature of ≈100 K (the average temperature was in fact 98.9 K with a fluctuation of about 1 K). In the analysis of the neutron data the chosen model was the X-ray structure at room temperature including all hydrogen atoms. The initial agreement was good and the parameter shifts in the least-squares refinement were relatively small, indicating that the X-ray positions for all atoms were essentially correct.

The refinement used a large-block approximation to the normal matrix and converged, with all atoms anisotropic and an isotropic extinction correction, at $R = 0.065$ using all observed data. The final Fourier difference map was featureless, however the thermal parameters calculated from these data at 98.8 K still showed considerable thermal anisotropy. A VAX computer was used with the I.L.L. program COLL5P for data reduction, a Busing and Levy analytical absorption correction,[47] CHEMGRAF[48] for graphics, and CRYSTALS[49] for all other crystallographic calculations.

(*b*) *X-Ray diffraction.* For each compound the crystals were mounted under argon in 0.7 mm Lindemann glass capillaries and data were collected using an Enraf-Nonius CAD-4F diffractometer with graphite-monochromated Mo-Kα radiation {except $[K(18\text{-crown-}6)][cis\text{-}Re(PMe_3)_4H_2]$ for which Cu-Kα was used}. The orientation matrix and unit-cell dimensions were determined from a least-squares best fit to 25 carefully centred reflections following the manufacturer's recommended procedures. All intensity data were collected by ω–2θ scans, corrected for Lorentz and polarisation effects and an empirical absorption correction applied. A VAX 11/750 computer was used with MULTAN[50] for direct methods, CHEMGRAF for graphics, and CRYSTALS for all other crystallographic

Table 5 Crystal data and some details of experimental conditions

	6	**5**	**5** (neutron)	**3**
	$C_{36}H_{128}Li_4P_{12}W_4$	$C_{19}H_{52}NaO_5P_3W$	$C_{19}H_{52}NaO_5P_3W$	$C_{21}H_{56}KO_6P_3W$
M	1 696.3	660.4	660.4	720.55
a/Å	14.472(2)	11.943(2)	11.773(7)	10.362(3)
b/Å	14.561	15.273(8)	15.005(10)	16.168(4)
c/Å	10.813(4)	16.878(3)	16.388(12)	20.480(4)
α/°	104.40(3)	90	90	90
β/°	114.64(2)	90.04(2)	90.52(3)	98.66(2)
γ/°	102.55(2)	90	90	90
U/Å^3	1 868	3 079	2 895	3 392
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	1	4	4	4
D_c/Mg m^{-3}	1.51	1.43	1.52	1.42
F(000)	832	1 344	—	1472
μ/cm^{-1}	67.77	41.78	4.04	38.89
T/K	r.t.	r.t.	30	r.t.
Radiation	Mo-Kα	Mo-Kα	Thermal neutrons	Mo-Kα
λ/Å	0.7107	0.7107	1.2602	0.7107
$\theta_{min,max}$/°	2, 26	1, 25	5, 55	1, 26
ω scan angle/° min^{-1}	1.0 + 0.35 tan θ	1.2 + 0.35 tan θ	—	0.85 + 0.35 tan θ
Horizontal aperture/mm	3.5	4.0	Aperture 6 × 12 mm	3.5
Scan speed$_{min,max}$/° min^{-1}	3, 17	3, 18	—	3, 21
Crystal size/mm	0.225 × 0.4 × 0.75	0.425 × 0.625 × 0.85	2.6 × 2.0 × 1.1	0.1 × 0.22 × 0.3
Total data	9 006	7 865	6 744	9 492
Unique data	7 335	5 399	4 170	6 649
Observed data [$I > 3\sigma(I)$]	5 598	3 884	4 170 [$I > 2\sigma(I)$]	3 966
R_m	2.39	3.61	—	2.34
Maximum, minimum absorption correction	2.06, 1.0	1.41, 1.0		1.42, 1.0
R	3.30	5.75	4.98	2.33
R'	3.84	8.46	4.34	2.51

	3 (neutron)	**18**	**12**	**17**
	$C_{21}H_{56}KO_6P_3W$	$C_{22}H_{35}KMoO_6$	$C_{25}H_{62}KO_6P_4Re$	$C_{64}H_{78}Au_3Cl_2P_6W$
M	720.55	530.50	796.1	1 874.7
a/Å	10.154(5)	16.777(3)	13.083(2)	12.844(3)
b/Å	15.914(6)	11.910(2)	16.701(2)	22.959(5)
c/Å	20.449(10)	24.917(4)	10.042(6)	13.046(3)
α/°	90	90	94.35(3)	90
β/°	98.43(4)	101.85(1)	119.35(3)	116.97(2)
γ/°	90	90	94.49(1)	90
U/Å^3	3 269	4 873	1 890	3 429
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$I2/c$	$P\bar{1}$	$P2_1$
Z	4	8	2	2
D_c/Mg m^{-3}	1.46	1.45	1.40	1.82
F(000)	—	2 208	816	1 786
μ/cm^{-1}	3.45	7.32	89.4	83.7
T/K	98.8	r.t.	r.t.	r.t.
Radiation	Thermal neutrons	Mo-Kα	Cu-Kα	Mo-Kα
λ/Å	1.2604	0.7107	1.5418	0.7107
$\theta_{min,max}$/°	5, 55	1, 27	1, 50	1, 25
ω scan angle/°	—	0.8 + 0.35 tan θ	1.0 + 0.14 tan θ	1.0 + 0.35 tan θ
Horizontal aperture/mm	Aperture 6 × 12 mm	4.0	3.5 mm	4.0
Scan speed$_{min,max}$/° min^{-1}	—	3, 21	3, 17	3, 17
Crystal size/mm	2.77 × 0.65 × 0.65	0.35 × 0.4 × 0.5	0.2 × 0.275 × 0.75	0.65 × 0.43 × 0.23
Total data		10 278	4 820	10 419
Unique data	4 583	7 082	3 007	6 969
Observed data [$I > 3\sigma(I)$]	4 583	3 760	2 974	6 088
R_m	—	1.35	2.76	3.12
Maximum, minimum absorption correction		1.11, 1.0	5.0, 1.0	3.8, 1.0
R	6.54	3.84	5.97	3.24
R'	6.58	4.99	6.86	4.17

r.t. = Room temperature.

calculations. Scattering factors and anomalous dispersion corrections were taken from ref. 51. In the final anisotropic refinements a large-block approximation to the normal matrix was used with the scale, extinction, and dummy overall thermal parameters in a separate block. Soft restraints were those of Waser as implemented by Rollett and Watkin.[52] The least-squares weighting function was a truncated Chebyshev polynomial.

[{W(PMe$_3$)$_3$H$_5$Li}$_4$] **6**. A yellow crystal precipitated from the reaction between [W(PMe$_3$)$_3$H$_6$] and LiBu^n was used for the analysis. The structure was solved by Patterson and Fourier methods, and refinement converged to an R value of 0.036 (R' 0.046). The six crystallographically independent trimethylphosphine groups were found to be rotationally disordered *in* contrast with the ordered structure proposed by Barron *et al.*[24] The refinement of the model with rotational disorder and, for

Table 6 Fractional atomic coordinates with e.s.d.s in parentheses together with equivalent isotropic thermal parameters *without* e.s.d.s for neutron diffraction data

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
(*a*) [{W(PMe$_3$)$_3$H$_5$Li}$_4$]							
W(1)	−0.291 16(2)	0.326 72(2)	0.420 40(3)	C(14)	0.322 4(9)	0.285 5(8)	0.402(1)
W(2)	0.086 38(2)	0.255 20(2)	0.451 48(2)	C(15)	0.345 2(9)	0.208(1)	0.617(1)
Li(1)	−0.100 0(9)	0.310 9(9)	0.438(1)	C(16)	0.051(1)	0.329(1)	0.767(2)
Li(2)	0.171(1)	0.462 6(8)	0.516(1)	C(17)	0.023(1)	0.125 5(8)	0.673(2)
P(1)	−0.398 2(2)	0.151 6(2)	0.350 1(3)	C(18)	0.203 1(9)	0.273(1)	0.842(1)
P(2)	−0.383 8(2)	0.337 2(2)	0.182 2(2)	C(101)	−0.435(2)	0.115(2)	0.478(3)
P(3)	−0.243 9(2)	0.397 1(2)	0.677 3(2)	C(102)	−0.341(2)	0.055(1)	0.308(2)
P(4)	−0.031 1(2)	0.182 3(1)	0.187 7(2)	C(103)	−0.535(1)	0.093(2)	0.185(2)
P(5)	0.236 8(2)	0.207 4(2)	0.451 9(3)	C(104)	−0.469(2)	0.415(2)	0.166(3)
P(6)	0.101 7(2)	0.243 9(2)	0.679 5(2)	C(105)	−0.477(2)	0.226(1)	0.011(2)
C(1)	−0.386(2)	0.099(1)	0.492(2)	C(106)	−0.294(2)	0.401(2)	0.125(3)
C(2)	−0.368(1)	0.059(1)	0.238(1)	C(107)	−0.311(2)	0.482(2)	0.725(3)
C(3)	−0.546 6(7)	0.102(1)	0.237(2)	C(108)	−0.255(2)	0.320(2)	0.784(3)
C(4)	−0.506 9(9)	0.368(1)	0.141(2)	C(109)	−0.101(1)	0.484(2)	0.802(2)
C(5)	−0.438(1)	0.225 3(9)	0.012(1)	C(110)	−0.095(2)	0.043 5(7)	0.111(2)
C(6)	−0.311(1)	0.431 5(9)	0.138(2)	C(111)	−0.153(1)	0.211(2)	0.096(2)
C(7)	−0.343 9(9)	0.439 1(9)	0.713(2)	C(112)	0.025(2)	0.196(2)	0.067(2)
C(8)	−0.212(1)	0.325 3(9)	0.798(1)	C(113)	0.229(2)	0.077(1)	0.392(3)
C(9)	−0.123 5(7)	0.513 9(7)	0.797(1)	C(114)	0.284(3)	0.248(2)	0.335(3)
C(10)	−0.131 9(8)	0.053 3(6)	0.107(1)	C(115)	0.368(2)	0.261(2)	0.622(2)
C(11)	−0.122 5(8)	0.246 8(8)	0.111(1)	C(116)	0.118(2)	0.349(1)	0.828(2)
C(12)	0.022(1)	0.167 4(9)	0.061(1)	C(117)	−0.018(1)	0.149(1)	0.653(2)
C(13)	0.206 9(9)	0.082 2(6)	0.325(1)	C(118)	0.206(1)	0.201(2)	0.789(2)
(*b*) [Na(15-crown-5)][W(PMe$_3$)$_3$H$_5$]							
W	0.172 34(5)	0.231 95(4)	0.458 52(3)	C(9)	0.269(2)	0.456(1)	0.489(2)
Na	−0.029 7(5)	0.218 1(4)	0.333 1(3)	C(10)	−0.291(2)	0.252(1)	0.405(2)
P(1)	0.069 3(3)	0.275 8(3)	0.575 0(2)	C(11)	−0.238(3)	0.339(1)	0.388(2)
P(2)	0.290 4(3)	0.122 7(3)	0.401 0(2)	C(12)	−0.125(3)	0.413(2)	0.294(2)
P(3)	0.277 0(3)	0.360 5(3)	0.425 8(3)	C(13)	−0.065(4)	0.399(2)	0.217(2)
O(1)	−0.207(2)	0.187(1)	0.404(2)	C(14)	0.015(4)	0.283(2)	0.143(2)
O(2)	−0.190(3)	0.337(2)	0.312(1)	C(15)	0.087(3)	0.201(2)	0.151(2)
O(3)	−0.006(3)	0.318(2)	0.220(1)	C(16)	−0.020(3)	0.074(2)	0.178(1)
O(4)	0.041(3)	0.146(2)	0.210(2)	C(17)	−0.071(4)	0.022(2)	0.245(2)
O(5)	−0.132(3)	0.080(1)	0.295(2)	C(18)	−0.171(3)	0.040(1)	0.365(2)
O(11)	−0.201(2)	0.245(1)	0.410(2)	C(19)	−0.252(2)	0.101(1)	0.405(2)
O(12)	−0.156(3)	0.354(2)	0.283(2)	C(110)	−0.260(2)	0.324(1)	0.400(2)
O(13)	0.039(3)	0.293(2)	0.203(2)	C(111)	−0.187(3)	0.389(1)	0.358(2)
O(14)	0.006(3)	0.115(2)	0.224(2)	C(112)	−0.084(3)	0.409(2)	0.240(2)
O(15)	−0.172(3)	0.091(2)	0.330(1)	C(113)	−0.033(3)	0.358(2)	0.172(2)
C(2)	0.146(2)	0.270(2)	0.672(1)	C(114)	0.075(3)	0.233(2)	0.145(2)
C(3)	−0.001(2)	0.381(2)	0.580(2)	C(115)	0.001(4)	0.153(2)	0.148(2)
C(4)	0.228(2)	0.019(1)	0.381(1)	C(116)	−0.052(3)	0.034(2)	0.229(2)
C(5)	0.359(2)	0.141(2)	0.306(1)	C(117)	−0.096(3)	0.022(2)	0.313(2)
C(6)	0.413(2)	0.086(1)	0.458(1)	C(118)	−0.213(3)	0.088(1)	0.409(2)
C(7)	0.251(2)	0.414(2)	0.330(1)	C(119)	−0.273(2)	0.173(1)	0.427(2)
C(8)	0.430(1)	0.356(1)	0.421(1)				
(*c*) [Na(15-crown-5)][W(PMe$_3$)$_3$H$_5$] (neutron diffraction data)							
				U(iso)/Å^2					*U*(iso)/Å^2
W	0.170 1(1)	0.230 7(1)	0.460 59(9)	0.002 2	H(10)	0.284 8(3)	−0.039 8(2)	0.360 6(2)	0.028 7
H(52)	0.286 3(3)	0.248 4(2)	0.528 7(2)	0.023 0	H(11)	0.186 6(3)	−0.014 4(2)	0.440 7(2)	0.030 1
H(53)	0.059 9(3)	0.303 4(2)	0.429 6(2)	0.023 6	H(12)	0.154 9(3)	0.017 1(2)	0.341 1(2)	0.027 6
H(54)	0.056 5(3)	0.153 5(2)	0.442 0(2)	0.022 6	C(5)	0.349 3(1)	0.134 69(9)	0.299 44(8)	0.009 7
H(55)	0.180 3(3)	0.141 8(2)	0.531 4(2)	0.025 0	H(13)	0.406 2(3)	0.080 0(3)	0.283 0(2)	0.029 4
H(56)	0.161 6(3)	0.233 0(2)	0.353 9(2)	0.021 7	H(14)	0.395 1(3)	0.198 4(2)	0.296 5(2)	0.032 1
P(1)	0.063 9(1)	0.275 5(1)	0.578 80(9)	0.005 2	H(15)	0.280 0(3)	0.136 7(3)	0.255 4(2)	0.027 4
C(1)	−0.060 6(1)	0.206 10(9)	0.602 33(9)	0.010 6	C(6)	0.419 1(1)	0.086 68(9)	0.456 35(8)	0.009 6
H(1)	−0.105 5(3)	0.229 1(3)	0.656 5(2)	0.028 5	H(16)	0.461 5(3)	0.029 4(3)	0.428 3(2)	0.028 8
H(3)	−0.117 1(3)	0.205 4(3)	0.549 7(2)	0.030 6	H(17)	0.477 0(3)	0.143 3(2)	0.458 6(2)	0.028 9
C(2)	0.134 9(1)	0.274 1(1)	0.679 06(8)	0.010 3	H(18)	0.397 4(3)	0.070 3(3)	0.519 3(2)	0.028 0
H(4)	0.076 2(3)	0.291 5(3)	0.727 8(2)	0.031 5	P(3)	0.278 2(1)	0.361 0(1)	0.429 6(1)	0.006 5
H(5)	0.206 2(3)	0.320 5(3)	0.680 1(2)	0.032 5	C(7)	0.253 2(1)	0.415 90(9)	0.330 85(8)	0.009 6
H(6)	0.169 4(4)	0.207 7(3)	0.691 2(2)	0.033 7	H(19)	0.299 4(3)	0.479 1(2)	0.324 3(2)	0.025 4
C(3)	−0.001 8(1)	0.387 31(9)	0.584 25(9)	0.011 5	H(20)	0.162 5(3)	0.428 4(3)	0.323 4(2)	0.027 6
H(7)	−0.056 2(3)	0.394 2(3)	0.637 4(2)	0.028 3	H(21)	0.278 5(4)	0.370 6(3)	0.282 2(2)	0.031 4
H(8)	0.064 9(3)	0.437 1(2)	0.588 0(3)	0.034 6	C(8)	0.434 8(1)	0.351 48(9)	0.426 80(8)	0.009 8
H(9)	−0.049 5(4)	0.399 8(3)	0.529 8(2)	0.031 5	H(22)	0.477 5(3)	0.415 2(2)	0.417 7(2)	0.027 2
P(2)	0.289 3(1)	0.119 7(1)	0.401 1(1)	0.005 8	H(23)	0.464 1(3)	0.321 7(3)	0.483 3(2)	0.029 3
C(4)	0.224 5(1)	0.008 90(9)	0.384 27(9)	0.010 1	H(24)	0.458 0(3)	0.306 8(3)	0.377 9(2)	0.029 0

Table 6 (*continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*U*(iso)/Å²	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*U*(iso)/Å²
(*c*) [Na(15-crown-5)][W(PMe$_3$)$_3$H$_5$] (neutron diffraction data)									
C(9)	0.269 5(1)	0.461 26(9)	0.495 38(8)	0.010 5	H(28)	−0.331 2(3)	0.224 7(2)	0.471 6(2)	0.027 4
H(25)	0.330 6(3)	0.512 8(2)	0.478 6(2)	0.029 2	H(29)	−0.357 9(3)	0.222 9(2)	0.365 0(2)	0.024 5
H(26)	0.283 2(3)	0.442 0(2)	0.558 4(2)	0.029 5	H(30)	−0.297 9(3)	0.374 8(2)	0.412 9(2)	0.027 5
H(27)	0.183 9(3)	0.488 5(2)	0.489 7(2)	0.025 5	H(31)	−0.165 6(3)	0.328 2(2)	0.447 6(2)	0.025 9
Na	−0.029 8(2)	0.210 0(2)	0.328 0(1)	0.008 8	H(32)	−0.189 4(3)	0.464 3(2)	0.308 5(2)	0.026 5
O(1)	−0.206 0(1)	0.165 4(1)	0.401 2(1)	0.011 2	H(33)	−0.062 4(3)	0.415 6(2)	0.350 0(2)	0.023 8
O(2)	−0.190 7(1)	0.325 6(1)	0.322 79(9)	0.011 4	H(34)	−0.043 0(3)	0.459 3(2)	0.201 5(2)	0.027 6
O(3)	−0.005 8(1)	0.325 3(1)	0.222 0(1)	0.010 7	H(35)	−0.153 5(3)	0.381 6(2)	0.176 8(2)	0.025 4
O(4)	0.065 7(1)	0.149 8(1)	0.202 16(9)	0.009 2	H(36)	0.069 0(3)	0.351 4(2)	0.109 9(2)	0.024 6
O(5)	−0.125 0(1)	0.073 1(1)	0.273 35(9)	0.009 8	H(37)	−0.048 8(3)	0.277 0(2)	0.107 6(2)	0.023 7
C(10)	−0.291 0(1)	0.230 7(1)	0.411 60(8)	0.011 0	H(38)	0.184 3(3)	0.245 4(2)	0.190 2(2)	0.025 4
C(11)	−0.235 5(1)	0.321 7(1)	0.402 42(8)	0.011 5	H(39)	0.140 0(3)	0.196 1(2)	0.095 2(2)	0.028 0
C(12)	−0.131 8(1)	0.406 02(9)	0.305 23(9)	0.012 2	H(40)	−0.081 5(3)	0.132 2(2)	0.132 5(2)	0.021 7
C(13)	−0.084 7(1)	0.396 44(9)	0.220 35(9)	0.011 9	H(41)	0.033 0(3)	0.059 8(2)	0.108 3(2)	0.023 7
C(14)	0.026 6(1)	0.296 62(9)	0.143 25(8)	0.010 3	H(42)	0.015 6(3)	−0.006 3(2)	0.251 8(2)	0.024 4
C(15)	0.110 8(1)	0.220 50(9)	0.155 32(8)	0.010 8	H(43)	−0.104 4(3)	−0.026 7(2)	0.187 6(2)	0.024 4
C(16)	−0.010 2(1)	0.093 72(9)	0.158 48(8)	0.009 2	H(44)	−0.079 0(3)	0.022 3(2)	0.386 8(2)	0.024 1
C(17)	−0.055 7(1)	0.025 62(9)	0.219 22(9)	0.009 9	H(45)	−0.181 5(3)	−0.042 8(2)	0.332 9(2)	0.025 1
C(18)	−0.153 1(1)	0.026 0(1)	0.346 06(8)	0.011 2	H(46)	−0.276 4(3)	0.045 0(2)	0.441 1(2)	0.025 8
C(19)	−0.248 1(1)	0.078 2(1)	0.384 68(9)	0.012 2	H(47)	−0.320 6(3)	0.082 5(2)	0.341 8(2)	0.023 3
(*d*) [K(18-crown-6)][W(PMe$_3$)$_3$H$_5$]									
W	0.205 04(2)	0.233 96(1)	0.353 01(1)		C(12)	0.631 4(7)	0.448 8(4)	0.438 3(4)	
K	0.539 8(1)	0.271 26(8)	0.323 50(5)		C(13)	0.622 6(8)	0.372 7(4)	0.478 6(4)	
P(1)	0.251 9(1)	0.136 22(9)	0.441 98(7)		C(14)	0.705 8(7)	0.237 8(5)	0.492 3(3)	
P(2)	0.091 5(1)	0.259 8(1)	0.244 23(6)		C(15)	0.775 9(7)	0.174 6(4)	0.458 2(4)	
P(3)	0.133 5(2)	0.354 60(9)	0.404 58(8)		C(16)	0.749 1(7)	0.085 8(4)	0.367 8(4)	
C(1)	0.355 6(8)	0.049 4(5)	0.427 7(4)		C(17)	0.652 0(8)	0.059 1(4)	0.310 2(4)	
C(2)	0.334 5(8)	0.166 3(5)	0.524 6(3)		C(18)	0.538 9(8)	0.110 4(5)	0.210 8(4)	
C(3)	0.115 6(6)	0.080 3(4)	0.468 3(3)		C(19)	0.546 3(8)	0.173 5(6)	0.159 5(4)	
C(4)	0.153 4(7)	0.205 4(5)	0.176 8(3)		C(20)	0.539 3(9)	0.317 7(6)	0.145 8(4)	
C(5)	0.085 2(8)	0.364 4(4)	0.209 5(4)		C(21)	0.488 3(9)	0.395 0(6)	0.171 7(5)	
C(6)	−0.081 0(6)	0.233 1(5)	0.226 0(3)		O(1)	0.555 9(5)	0.414 4(3)	0.235 9(3)	
C(7)	0.217 3(7)	0.452 9(4)	0.393 9(4)		O(2)	0.569 8(4)	0.433 3(3)	0.373 2(3)	
C(8)	0.136(1)	0.359 4(5)	0.493 2(4)		O(3)	0.693 0(4)	0.309 2(3)	0.452 5(2)	
C(9)	−0.037 1(7)	0.389 7(4)	0.381 0(5)		O(4)	0.691 4(4)	0.147 8(3)	0.401 5(2)	
C(10)	0.501(1)	0.482 4(5)	0.265 1(5)		O(5)	0.637 0(4)	0.125 0(3)	0.264 1(2)	
C(11)	0.579(1)	0.500 2(5)	0.330 4(5)		O(6)	0.514 3(4)	0.252 5(3)	0.185 3(2)	
(*e*) [K(18-crown-6)][W(PMe$_3$)$_3$H$_5$] (neutron diffraction data)									
W	0.203 7(4)	0.236 3(2)	0.354 0(2)	0.010 5	H(1)	0.379 1(9)	0.009 4(5)	0.474 1(4)	0.043 3
K	0.545 9(5)	0.274 2(3)	0.325 9(3)	0.015 3	H(2)	0.462 7(7)	0.080 8(6)	0.426 9(4)	0.044 0
P(1)	0.251 3(4)	0.139 2(2)	0.445 0(2)	0.013 3	H(3)	0.327(1)	0.021 3(5)	0.386 8(4)	0.052 5
P(2)	0.092 1(4)	0.261 9(2)	0.244 2(2)	0.013 6	H(4)	0.350 9(9)	0.119 4(6)	0.561 3(4)	0.049 6
P(3)	0.124 6(4)	0.359 5(2)	0.403 8(2)	0.015 9	H(5)	0.259 4(9)	0.214 6(6)	0.548 8(4)	0.046 8
C(1)	0.365 2(4)	0.052 8(2)	0.432 7(2)	0.024 8	H(6)	0.417 2(9)	0.208 5(7)	0.524 6(4)	0.047 3
C(2)	0.327 7(3)	0.173 1(2)	0.528 1(2)	0.022 7	H(7)	0.148 5(8)	0.029 3(5)	0.505 2(4)	0.040 9
C(3)	0.113 4(3)	0.078 3(2)	0.469 5(2)	0.019 4	H(8)	0.048 9(8)	0.120 0(5)	0.492 1(4)	0.044 0
C(4)	0.156 4(3)	0.204 7(2)	0.177 2(1)	0.021 8	H(9)	0.054 4(9)	0.052 8(6)	0.425 8(4)	0.046 9
C(5)	0.088 2(3)	0.367 9(2)	0.208 4(2)	0.023 6	H(10)	0.095 1(8)	0.215 9(6)	0.129 1(3)	0.040 0
C(6)	−0.086 1(3)	0.236 4(2)	0.224 0(2)	0.019 7	H(11)	0.257 7(7)	0.226 1(5)	0.175 4(4)	0.039 9
C(7)	0.211 5(3)	0.459 5(2)	0.394 2(2)	0.021 4	H(12)	0.160 2(8)	0.138 6(5)	0.188 7(4)	0.046 0
C(8)	0.120 9(4)	0.364 8(2)	0.493 8(2)	0.028 8	H(13)	0.037 3(9)	0.369 5(5)	0.157 8(4)	0.044 2
C(9)	−0.047 7(3)	0.394 4(2)	0.378 2(2)	0.024 2	H(14)	0.038(1)	0.411 0(5)	0.237 6(5)	0.050 0
C(10)	0.504 7(4)	0.489 9(2)	0.267 0(2)	0.027 4	H(15)	0.189 6(8)	0.388 8(5)	0.210 0(4)	0.045 7
C(11)	0.585 4(4)	0.508 1(2)	0.333 6(2)	0.026 9	H(16)	−0.121 5(7)	0.243 8(6)	0.171 7(4)	0.040 7
C(12)	0.629 5(3)	0.455 0(2)	0.442 2(2)	0.020 3	H(17)	−0.144 1(7)	0.279 2(5)	0.251 7(4)	0.044 1
C(13)	0.616 9(3)	0.376 0(2)	0.481 9(2)	0.020 0	H(18)	−0.105 7(8)	0.172 7(5)	0.239 9(4)	0.041 0
C(14)	0.707 9(3)	0.239 8(2)	0.496 1(1)	0.019 6	H(19)	0.173 3(9)	0.511 1(5)	0.420 7(4)	0.043 7
C(15)	0.780 3(3)	0.174 9(2)	0.461 7(2)	0.020 1	H(20)	0.318 7(7)	0.450 8(5)	0.411 5(4)	0.038 8
C(16)	0.754 4(3)	0.084 8(2)	0.369 1(2)	0.022 0	H(21)	0.200 2(8)	0.475 0(5)	0.341 4(4)	0.039 1
C(17)	0.655 0(3)	0.058 1(2)	0.310 6(2)	0.022 1	H(22)	0.080(1)	0.422 6(5)	0.509 4(4)	0.048 9
C(18)	0.532 5(3)	0.110 9(2)	0.211 9(2)	0.021 3	H(23)	0.224 5(9)	0.358 2(6)	0.520 0(4)	0.050 9
C(19)	0.540 4(3)	0.176 7(2)	0.160 5(2)	0.023 4	H(24)	0.063(1)	0.311 2(6)	0.507 6(4)	0.049 4
C(20)	0.544 8(4)	0.323 9(2)	0.147 3(2)	0.024 9	H(25)	−0.068 8(8)	0.454 1(5)	0.399 9(4)	0.045 0
C(21)	0.492 6(3)	0.404 0(2)	0.173 8(2)	0.026 5	H(26)	−0.116 8(8)	0.347 4(5)	0.392 2(5)	0.044 6
O(1)	0.560 6(4)	0.420 0(2)	0.238 0(2)	0.023 9	H(27)	−0.068 9(8)	0.401 1(5)	0.324 4(4)	0.044 6
O(2)	0.571 7(4)	0.439 5(2)	0.375 9(2)	0.021 9	H(28)	0.505(1)	0.546 3(5)	0.235 1(4)	0.044 1
O(3)	0.692 9(3)	0.312 4(2)	0.456 5(2)	0.017 8	H(29)	0.402 3(8)	0.475 8(6)	0.273 4(4)	0.047 4
O(4)	0.695 2(3)	0.147 3(2)	0.404 2(2)	0.018 9	H(30)	0.550(1)	0.565 9(5)	0.353 5(4)	0.046 8
O(5)	0.638 0(4)	0.125 8(2)	0.264 8(2)	0.019 6	H(31)	0.692 2(8)	0.516 6(5)	0.327 9(4)	0.046 2
O(6)	0.513 1(4)	0.256 4(2)	0.186 9(2)	0.022 4	H(32)	0.734 6(7)	0.471 1(5)	0.444 3(4)	0.035 8

Table 6 (*continued*)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*U*(iso)/Å²	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*U*(iso)/Å²
(*e*) [K(18-crown-6)][$W(PMe_3)_3H_5$] (neutron diffraction data)									
H(33)	0.576 7(8)	0.507 7(4)	0.462 9(4)	0.033 1	H(45)	0.436 0(7)	0.113 8(5)	0.230 1(4)	0.038 0
H(34)	0.655 4(8)	0.388 4(5)	0.533 9(3)	0.040 5	H(46)	0.642 0(7)	0.178 1(5)	0.146 5(4)	0.041 2
H(35)	0.511 2(7)	0.356 2(5)	0.476 7(4)	0.034 9	H(47)	0.467 1(8)	0.164 3(6)	0.116 7(4)	0.043 3
H(36)	0.765 1(8)	0.254 2(5)	0.544 6(3)	0.036 1	H(48)	0.652 3(8)	0.327 4(6)	0.147 6(4)	0.045 7
H(37)	0.609 9(7)	0.215 7(5)	0.503 7(4)	0.037 7	H(49)	0.496 9(9)	0.314 8(6)	0.095 7(3)	0.043 5
H(38)	0.873 2(6)	0.200 9(4)	0.447 3(3)	0.033 0	H(50)	0.508 7(9)	0.455 9(6)	0.140 8(4)	0.049 5
H(39)	0.806 5(7)	0.121 1(5)	0.494 7(4)	0.037 0	H(51)	0.384 5(7)	0.397 2(5)	0.175 1(4)	0.045 8
H(40)	0.780 7(8)	0.030 7(5)	0.400 6(4)	0.041 7	H(52)	0.039 3(6)	0.224 7(4)	0.372 2(3)	0.031 0
H(41)	0.846 2(7)	0.110 0(5)	0.352 2(4)	0.035 2	H(53)	0.351 1(6)	0.268 1(4)	0.406 0(3)	0.031 3
H(42)	0.694 1(9)	0.001 9(5)	0.286 9(4)	0.041 7	H(54)	0.326 4(6)	0.179 1(4)	0.318 3(3)	0.030 6
H(43)	0.560 8(8)	0.043 1(5)	0.326 5(4)	0.040 7	H(55)	0.136 8(7)	0.138 4(4)	0.326 6(3)	0.033 0
H(44)	0.543 6(8)	0.048 1(5)	0.190 2(4)	0.039 0	H(56)	0.284 8(6)	0.315 6(4)	0.314 6(3)	0.027 5
(*f*) [K(18-crown-6)][$Mo(\eta\text{-}C_5H_5)_2H$]									
Mo	0.045 12(2)	0.151 24(3)	0.109 96(1)		C(8)	0.040 5(3)	0.288 5(5)	0.047 7(2)	
K	0.199 27(5)	−0.613 6(7)	0.150 97(4)		C(9)	0.105 4(4)	0.315 2(4)	0.091 1(2)	
O(1)	0.147 0(2)	−0.141 6(4)	0.246 0(1)		C(10)	0.163 3(3)	0.227 4(5)	0.093 4(2)	
O(2)	0.275 4(3)	0.012 2(3)	0.262 1(2)		C(11)	0.179 6(4)	−0.100 4(8)	0.296 5(3)	
O(3)	0.347 1(2)	0.063 2(4)	0.170 7(2)		C(12)	0.210 3(5)	0.016 9(7)	0.291 1(3)	
O(4)	0.324 8(4)	−0.090 9(4)	0.085 5(2)		C(13)	0.305 2(6)	0.114 7(6)	0.253 5(3)	
O(5)	0.189 1(3)	−0.230 6(4)	0.064 2(2)		C(14)	0.376 2(5)	0.104 6(7)	0.225 1(4)	
O(6)	0.129 7(2)	−0.281 6(3)	0.155 7(2)		C(15)	0.408 8(4)	0.040 9(7)	0.145 3(5)	
C(1)	−0.416(3)	0.130 1(4)	0.169 2(2)		C(16)	0.373 4(5)	0.007 0(7)	0.087 1(4)	
C(2)	0.002 0(3)	0.029 5(4)	0.170 0(2)		C(17)	0.289 6(7)	−0.122 9(9)	0.032 3(4)	
C(3)	−0.015 1(3)	−0.018 4(4)	0.117 6(2)		C(18)	0.252 2(7)	−0.236 7(8)	0.035 3(3)	
C(4)	−0.071 0(3)	0.051 9(5)	0.083 8(2)		C(19)	0.157 0(5)	−0.335 7(6)	0.069 9(3)	
C(5)	−0.086 8(3)	0.144 7(4)	0.115 8(3)		C(20)	0.094 3(4)	−0.325 4(5)	0.103 5(3)	
C(6)	0.134 0(4)	0.148 5(5)	0.052 7(2)		C(21)	0.079 9(3)	−0.293 9(6)	0.192 7(3)	
C(7)	0.056 9(4)	0.185 9(5)	0.023 9(2)		C(22)	0.125 3(4)	−0.257 1(6)	0.247 9(3)	
(*g*) [K(18-crown-6)][*cis*-$Re(PMe_3)_4H_2$]									
Re	0.262 76(5)	0.255 62(3)	0.283 7(7)		C(13)	−0.128 9(21)	0.142 2(10)	−0.624 3(27)	
P(1)	0.293 9(3)	0.328 1(2)	−0.140 0(4)		C(14)	−0.078 9(20)	0.095 4(13)	−0.488 0(26)	
P(2)	0.174 2(4)	0.196 8(2)	0.153 9(5)		C(15)	−0.250 4(14)	0.074 3(12)	−0.456 0(27)	
P(3)	0.351 4(4)	0.145 6(2)	0.005 4(5)		C(16)	−0.284 8(25)	0.080 6(11)	−0.333 5(30)	
P(4)	0.419 0(3)	0.327 6(2)	0.249 8(5)		C(17)	−0.297 0(21)	0.174 8(13)	−0.164 8(22)	
K	−0.599(3)	0.269 5(2)	−0.246 3(4)		C(18)	−0.305 4(17)	0.263 7(13)	−0.142 7(27)	
C(1)	0.433 3(13)	0.352 7(14)	−0.138 6(28)		C(19)	−0.239 3(25)	0.378 8(11)	−0.095 3(37)	
C(2)	0.254 1(22)	0.430 7(8)	−0.158 2(26)		C(20)	−0.141 0(25)	0.437 8(16)	−0.081 4(29)	
C(3)	0.209 9(20)	0.289 0(17)	−0 345 5(13)		C(21)	−0.164 1(17)	0.471 7(10)	−0.325 8(22)	
C(4)	0.253 5(17)	0.151 0(11)	0.330 8(16)		C(22)	−0.109 5(18)	0.457 9(10)	−0.425 7(23)	
C(5)	0.090 2(17)	0.257 5(11)	0.214 2(23)		C(23)	−0.110 0(25)	0.362 9(15)	−0.605 3(27)	
C(6)	0.060 1(18)	0.109 7(11)	0.052 4(23)		C(24)	−0.155 7(17)	0.275 3(15)	−0.669 8(23)	
C(7)	0.268 4(23)	0.062 3(14)	−0.147 9(31)		O(1)	−0.097 8(12)	0.224 1(9)	−0.556 3(16)	
C(8)	0.403 4(25)	0.073 6(13)	0.144 3(26)		O(2)	−0.130 5(12)	0.106 1(8)	−0.393 4(17)	
C(9)	0.492 2(16)	0.155 8(14)	0.007 5(36)		O(3)	−0.272 0(13)	0.164 8(9)	−0.286 9(17)	
C(10)	0.512 2(25)	0.416 2(14)	0.255 0(30)		O(4)	−0.190 7(15)	0.305 4(9)	−0.086 9(18)	
C(11)	0.537 1(17)	0.279 6(12)	0.395 9(22)		O(5)	−0.106 6(14)	0.430 2(8)	−0.195 5(19)	
C(12)	0.395 2(24)	0.378 2(17)	0.397 1(26)		O(6)	−0.139 6(11)	0.374 8(9)	−0.487 7(16)	
(*h*) [$\{(Ph_3P)Au\}_3W(PMe_3)_3H_4$]Cl·*x*$CH_2Cl_2$									
W	0.283 28(5)	0.337 1(1)	0.220 17(5)		C(12)	0.286(1)	0.415 6(6)	0.737(1)	
Au(1)	0.171 66(5)	0.321 1(1)	0.359 80(5)		C(13)	0.228(1)	0.467 1(7)	0.734(1)	
Au(2)	0.176 08(5)	0.229 9(1)	0.210 20(5)		C(14)	0.115(1)	0.475 6(7)	0.648(1)	
Au(3)	0.381 31(5)	0.259 1(1)	0.406 18(5)		C(15)	0.062(1)	0.432 8(6)	0.565(1)	
P(1)	0.182 3(4)	0.404 2(3)	0.060 9(4)		C(16)	0.028 9(8)	0.263 2(6)	0.512(1)	
P(2)	0.364 0(4)	0.417 4(2)	0.365 3(4)		C(17)	−0.009 9(9)	0.215 2(6)	0.441(1)	
P(3)	0.348 2(5)	0.273 1(2)	0.105 2(4)		C(18)	−0.037 1(9)	0.163 0(7)	0.475(1)	
P(4)	0.056 9(3)	0.329 1(2)	0.451 4(3)		C(19)	−0.023 9(9)	0.159 0(7)	0.586(1)	
P(5)	0.508 6(3)	0.199 4(2)	0.547 5(3)		C(20)	0.015 1(9)	0.206 8(7)	0.660(1)	
P(6)	0.073 7(3)	0.144 3(2)	0.172 4(3)		C(21)	0.042 1(8)	0.258 8(7)	0.624(1)	
C(1)	0.142(2)	0.384(1)	−0.086(2)		C(22)	−0.089(1)	0.355 6(5)	0.359(1)	
C(2)	0.246(3)	0.474(1)	0.056(3)		C(23)	−0.186(1)	0.339 2(6)	0.374(1)	
C(3)	0.036(2)	0.428(1)	0.038(3)		C(24)	−0.294(1)	0.362 8(6)	0.308(1)	
C(4)	0.478(2)	0.461(1)	0.355(2)		C(25)	−0.309(1)	0.403 6(6)	0.226(1)	
C(5)	0.263(2)	0.474(1)	0.363(2)		C(26)	−0.214(1)	0.420 3(6)	0.210(1)	
C(6)	0.435(2)	0.401 2(9)	0.518(2)		C(27)	−0.103(1)	0.396 2(5)	0.276(1)	
C(7)	0.236(2)	0.234(1)	−0.022(2)		C(28)	0.463 1(9)	0.167 8(5)	0.647 0(9)	
C(8)	0.432(2)	0.306(1)	0.043(2)		C(29)	0.512(1)	0.117 1(6)	0.709(1)	
C(9)	0.439(2)	0.214(1)	0.176(2)		C(30)	0.475(1)	0.096 8(6)	0.788(1)	
C(10)	0.120(1)	0.381 2(5)	0.568(1)		C(31)	0.391(1)	0.126 2(6)	0.805(1)	
C(11)	0.232(1)	0.373 4(6)	0.654(1)		C(32)	0.341(1)	0.176 4(6)	0.743(1)	

Table 6 (*continued*)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
(*h*) $[\{(Ph_3P)Au\}_3W(PMe_3)_3H_4]Cl\cdot xCH_2Cl_2$							
C(33)	0.378(1)	0.196 9(6)	0.665(1)	C(51)	−0.152(1)	0.109 6(7)	0.127 1(8)
C(34)	0.646(1)	0.233 9(5)	0.637(1)	C(52)	0.071(1)	0.108 2(4)	0.047(1)
C(35)	0.716(1)	0.219 6(6)	0.753(1)	C(53)	−0.029(1)	0.106 7(4)	−0.058(1)
C(36)	0.819(1)	0.250 4(7)	0.817(2)	C(54)	−0.019(2)	0.083 2(5)	−0.152(1)
C(37)	0.851(2)	0.294 7(7)	0.765(2)	C(55)	0.086(1)	0.062 0(5)	−0.143(1)
C(38)	0.783(1)	0.309 4(7)	0.650(2)	C(56)	0.186(2)	0.063 9(5)	−0.039(1)
C(39)	0.681(1)	0.279 0(6)	0.586(1)	C(57)	0.177(1)	0.086 9(4)	0.055(1)
C(40)	0.545(1)	0.137 9(5)	0.478 7(9)	C(58)	0.127 1(8)	0.088 8(6)	0.285(1)
C(41)	0.456(1)	0.098 3(5)	0.418 7(9)	C(59)	0.128 0(9)	0.029 8(6)	0.262(1)
C(42)	0.468(1)	0.057 1(6)	0.347(1)	C(60)	0.166 9(9)	−0.010 6(8)	0.352(1)
C(43)	0.570(1)	0.055 9(6)	0.334(1)	C(61)	0.204 8(9)	0.008 5(7)	0.464(1)
C(44)	0.659(1)	0.096 0(6)	0.394(1)	C(62)	0.204 0(9)	0.067 3(7)	0.486(1)
C(45)	0.647(1)	0.137 2(6)	0.467(1)	C(63)	0.165 9(8)	0.107 1(7)	0.396(1)
C(46)	−0.077(1)	0.155 1(6)	0.1381(7)	Cl(1)	0.492 0(6)	−0.000 3(3)	0.017 2(5)
C(47)	−0.124(1)	0.210 4(6)	0.117 3(8)	Cl(2)	0.558 6(8)	0.329 0(4)	0.826 3(8)
C(48)	−0.239(1)	0.221 5(8)	0.085 8(9)	Cl(3)	0.716(1)	0.424 2(6)	0.841(1)
C(49)	−0.314(2)	0.175 8(8)	0.074 2(9)	C(64)	0.634(4)	0.391(1)	0.900(3)
C(50)	−0.271(1)	0.119 6(8)	0.094 9(8)				

the disordered methyl groups, with riding hydrogen atoms and isotropic thermal parameters converged at $R = 0.033$ with satisfactory values for the thermal parameters of all atoms except perhaps C(101). A refinement of an ordered model with anisotropic thermal parameters converged at a slightly lower $R(0.032)$ but the anisotropic thermal parameter ellipsoids had unreasonable shapes. There were indications of the metal hydrido hydrogen atoms in chemically reasonable positions but there were many more peaks of comparable height in the vicinity of the tungsten atoms. No metal hydride hydrogen atoms were included in the refinement.

$[Na(15\text{-crown-}5)][W(PMe_3)_3H_5]$ **5**. The Laue symmetry of both the X-ray and neutron diffraction patterns confirm that compound **5** crystallises from tetrahydrofuran in the monoclinic system, space group $P2_1/n$, with the monoclinic angle very close to 90°. The structure was solved using Patterson and Fourier techniques. The 15-crown-5 was found to be disordered and was refined with the constraints that C–C 1.51, C–O 1.42 Å, C–C–O 109, C–O–C 113° All the ring non-hydrogen atoms were given anisotropic thermal parameters. The refinement converged at $R = 0.058$. The occupancies of the two contributing conformations of the crown ether refined to 0.505 and 0.495. Tungsten-bound hydrides were not located.

$[K(18\text{-crown-}6)][W(PMe_3)_3H_5]$ **3**. A crystal recrystallised from tetrahydrofuran was used for the analysis. The structure was solved using Patterson and electron-density synthesis and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. With the exception of the five tungsten-bound hydrides, hydrogen atoms were included in calculated positions (C–H 1.0 Å) which were modified between successive cycles of refinement. The five tungsten-bound hydrides were located and refined. Refinement converged to residues of R 0.023 and R' 0.025.

$[K(18\text{-crown-}6)][Mo(\eta\text{-}C_5H_5)_2H]$ **18**. A crystal recrystallised from tetrahydrofuran was found to be monoclinic $I2/c$. The body-centred setting was chosen because the face-centred cell preferred by convention has a monoclinic angle of 149.9°. The structure was solved from Patterson function and subsequent electron-density syntheses. The 18-crown-6 showed indications of disorder during the refinement but it proved impossible to obtain a convincing disordered model. The tendency to disorder is reflected in the preponderance of short C–C and C–O bond lengths in the refined structure of the crown ring. All atoms except hydrogen were refined with anisotropic thermal parameters. The third largest peak in the final difference electron-density map corresponds to a hydrogen atom attached to the molybdenum atom forming a bent Mo–H–K bridge.

$[K(18\text{-crown-}6)][cis\text{-}Re(PMe_3)_4H_2]$ **12**. A crystal recrystallised from tetrahydrofuran was used for the analysis. The crystal was a poor diffractor and Cu-Kα radiation was used in spite of the relatively high absorption coefficient. The intensity standards indicated some decomposition during the data collection. The location of the ReP_4 group was obtained from the Patterson function and subsequent electron-density difference syntheses revealed the location of all non-hydrogen atoms. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all non-carbon atoms. The hydrogen atoms were placed geometrically and refined by the riding method. The refinement proceeded smoothly but the final structure had very large thermal parameters for all atoms. This is contrary to expectation if high absorption was a significant problem with the data.

$[\{(Ph_3P)Au\}_3W(PMe_3)_3H_4]Cl\cdot xCH_2Cl_2$ **17**. A crystal recrystallised from dichloromethane was used for the analysis. The long cell dimensions coupled with broad reflections gave some problems with overlapping peaks in the data collection. The structure was solved by direct methods (MULTAN) to give the heavy-atom positions and electron-density syntheses which revealed the remaining non-hydrogen atoms. Hydrogen atoms, with the exception of the tungsten-bound hydride ligands, were included in calculated positions which were refined with a riding model. A total of 6088 independent reflections were measured and refinement converged to a conventional R value of 0.032 (R' 0.042). During the refinement all phenyl rings were restrained to be planar with C–C bond distances and angles of 1.359 Å and 120° and estimated standard deviations of 0.020 Å and 3.0° respectively.

The geometry of the molecule of CH_2Cl_2 found in the structure was restrained to have C–Cl bond lengths of 1.77(2) Å and an angle of 112(3)° for Cl(2)–C–Cl(3). The observed site occupancy was 0.7529.

Additional material for each structure available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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