Trimethylphosphine as a Reactive Solvent: Synthesis, Crystal Structures, and Reactions of $[Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)]$ and $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ † and Related Studies

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Reduction of WCl_6, $MoCl_5$, $TaCl_5$, $ReCl_5$, and $RuCl_3$ using sodium sand in pure trimethylphosphine as a reactive solvent gives the compounds $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$, $[Mo(PMe_3)_5H_2]$, $[Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)]$, $[Re(PMe_3)_5H]$, $[Ru(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$, and $[(PMe_3)_3HRu(\mu\text{-}CH_2PMe_2)_2RuH(PMe_3)_3]$, respectively. The crystal structures of the tungsten and tantalum compounds have been determined. The previously unknown ligand $\eta^2\text{-}CHPMe_2$ is shown to be present in the tantalum compound. The reduction of WCl_6 in PMe_3 by magnesium is shown to proceed in the sequence $[W(PMe_3)_3Cl_4]$, $[\{W(PMe_3)_3Cl_2\}_2]$, $[W(PMe_3)_4Cl_2]$. Reduction of $[W(PMe_3)_3Cl_4]$ with sodium sand under hydrogen gives $[W(PMe_3)_4Cl_2H_2]$. The compound $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ reacts with butadiene giving *cis*-$[W(PMe_3)_2(\eta\text{-}C_4H_6)_2]$ and with cyclopentadiene forming $[W(\eta\text{-}C_5H_5)(PMe_3)_3H]$ and $[W(\eta\text{-}C_5H_5)_2H_2]$. Variable-temperature n.m.r. studies on $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ show it to be fluxional. Reduction of $RuCl_3$ in trimethylphosphine–cyclopentene gives $[Ru(PMe_3)_4(\sigma\text{-}\overline{C{=}CHCH_2CH_2C}H_2)H]$. The compound $[W(PMe_3)_3H_6]$ with spiro[2.4]hepta-4,6-diene gives $[W(\eta\text{-}C_5H_4Et)(PMe_3)_3H]$.

The compound $[Mo(PMe_3)_6]$ may be prepared by co-condensation of molybdenum atoms with PMe_3.[1,2] In benzene solution there is an equilibrium between $[Mo(PMe_3)_6]$ and $[Mo(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ and dissociated PMe_3. Furthermore, treatment of $[Mo(PMe_3)_6]$ with dinitrogen gives $[Mo(PMe_3)_5(N_2)]$ whilst with an excess of ethylene or dihydrogen two PMe_3 groups are displaced giving $[Mo(PMe_3)_4(\eta\text{-}C_2H_4)_2]$ and $[Mo(PMe_3)_4H_4]$ respectively.[2] These reactions exemplify the highly electron-rich nature of the molybdenum centre of $[Mo(PMe_3)_6]$ which prefers to substitute weak donor ligands such as N_2 and ethylene for the more basic PMe_3 or to undergo a four-electron formal oxidative displacement of PMe_3 ligands by two molecules of dihydrogen.

We wished to explore further the chemistry of highly electron-rich systems of the general class $[M(PMe_3)_n]$, where M is an early transition metal, and as a first step we set out to prepare $[W(PMe_3)_6]$. Co-condensation of tungsten atoms with PMe_3 gave the compound $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ (**1**) in modest yield (*ca.* 20%).[3] In a search for alternative routes it was decided to explore the reduction of WCl_6 with alkali metals in pure PMe_3 as a reactive solvent. It was considered that during the course of the required six-electron reduction of WCl_6 many intermediates would be formed and with each reduction step the metal *d* electrons would become higher in energy. In these circumstances there would be an increased probability that the metal centre would react with normally inert systems such as the C–H bonds of hydrocarbons used as solvents. Therefore, it was decided to use pure trimethylphosphine as both the solvent and ligand. The potentially reactive centres of PMe_3 are the donor electron pair on the phosphorus and, less commonly, the methyl C–H bond. In the latter case the resulting $M(\eta^2\text{-}CH_2PMe_2)H$ system could be envisaged to be able to rearrange to the $M\text{–}PMe_3$ system. The only other possible reaction would be between the metal centre and the P–C bond but there are few precedents for this. The simplicity of the molecule PMe_3 means that there are fewer potential reactive centres than for all other tertiary alkyl- or aryl-phosphines. Furthermore, PMe_3 is readily prepared and, typically, we obtained 300 cm^3 in a 'one-pot' reaction. It is highly volatile (b.p. 38 °C) enabling excess unreacted PMe_3 to be removed readily by distillation under vacuum.

We have found that reduction of WCl_6 with sodium metal in pure trimethylphosphine leads to the synthesis of (**1**). Here we describe the chemistry of (**1**) and of other compounds such as $[Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)]$ which have been prepared in a similar manner; part of this work has been briefly communicated.[4,5]

Results and Discussion

The reduction of tungsten hexachloride with sodium sand in excess trimethylphosphine under an atmosphere of dinitrogen proceeded smoothly to afford a volatile air-sensitive yellow solid. Recrystallisation from cold light petroleum gave large, yellow crystals of the compound $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ (**1**). The mass spectrum gave a parent ion peak at M/e 564 (^{184}W) and fragments at $M/e = 488$ and $M/e = 412$ corresponding to loss of one and two PMe_3 ligands respectively. The i.r. spectrum showed a strong band at 1 925 cm^{-1} attributable to a metal hydride as well as a band at 920 cm^{-1} assignable to a ν(P–C) vibration of the PMe_3 ligands. The crystal structure of (**1**) has been determined and the molecular structure is shown in Figure 1 together with a diagram in which some of the C atoms are omitted for clarity (see ref. 6). Selected bond lengths and angles are given in Table 1.

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† [η^2-(Dimethylphosphino)methyl][η^2-(dimethylphosphino)methylene]tris(trimethylphosphine)tantalum(III) and [η^2-(dimethylphosphino)methyl]hydridotetrakis(trimethylphosphine)tungsten(II) respectively.

Supplementary data available (No. SUP 56249, 9 pp.): thermal parameters, least-squares planes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: atm = 101 325 Pa, Torr = 133 Pa.

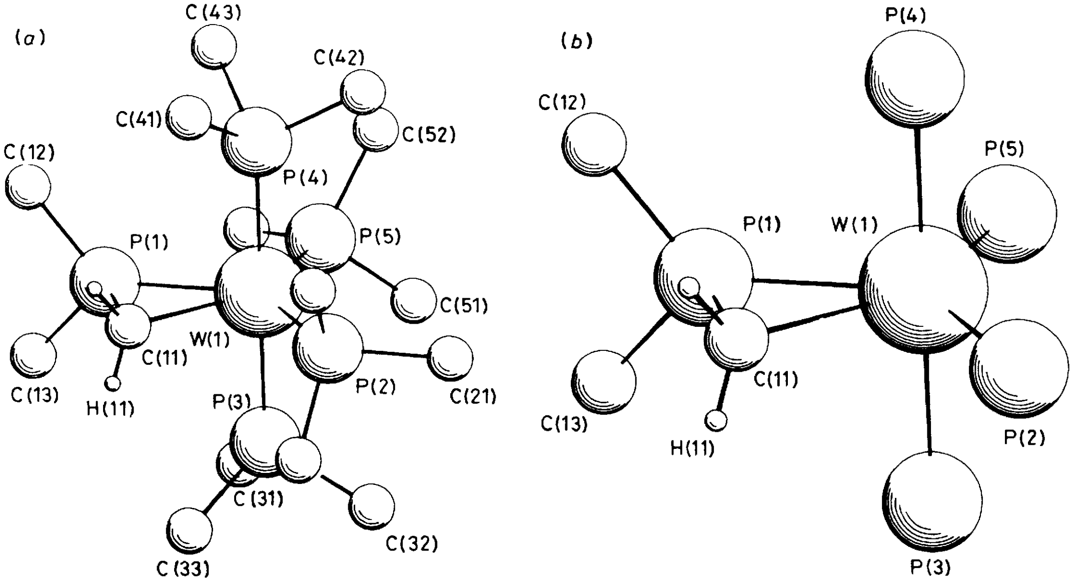


Figure 1. (*a*) Crystal structure of (**1**). (*b*) Diagram in which the carbon atoms bonded to P(2), P(3), P(4), and P(5) have been omitted for clarity (see ref. 6)

The ^{1}H n.m.r. spectrum of (**1**) shows a marked temperature dependence. At the low-temperature limit, -60 °C, the spectrum was consistent with the crystal structure (all n.m.r. data are given in Table 2). Thus the high-field resonance at δ -3.75 is assigned to a W–H proton, coupling to two magnetically equivalent nuclei, P_B [$J(^{31}P-^1H) = 9.5$ Hz], and two inequivalent nuclei P_C and P_D [$J(^{31}P-^1H) = 54$, 78 Hz]. Interestingly, coupling between the W-hydrogen and P_A was too small to be resolved. There are four distinct signals in the region (*ca.* δ 1.0—2.0) associated with the hydrogens of co-ordinated PMe_3 ligands; a broad complex band is assigned to the equivalent *trans* PMe_3 ligands (P_B) and the sharp doublet at δ 1.42 is assigned to the methyl protons of the η^2-CH_2PMe_2 moiety. There is a sharp doublet assignable to the methyl protons of P_C or P_D. Apart from these features there are bands at δ 1.23 and 1.71 which remain unassigned. The broad band at δ 0.43 is consistent with methylene hydrogens bound to the tungsten. At -20 °C, the high-field W–H band changed to a symmetrical pattern with two sharp outer lines, characteristic of virtual coupling effects. Also, the bands assigned to co-ordinated PMe_3 partially coalesce to a broad and virtually featureless band. At room temperature (r.t.) the spectrum is consistent with rapid fluxional behaviour. A broad signal at δ 1.47 of relative intensity 36 may be assigned to the methyl hydrogens of four rapidly equilibrating PMe_3 groups, while a sharp doublet at δ 1.41 of relative intensity 6, along with a multiplet at δ 0.43 of relative intensity 2 are attributable to the η^2-CH_2PMe_2 moiety. The metal–hydride resonance changed to a binomial quintet, due to coupling to four equivalent PMe_3 ligands. Once again, the W–H proton does not couple to P_A. Mass spectral data of (**1**) and the ^{1}H n.m.r. spectrum of (**1**) in the presence of excess trimethylphosphine provide no evidence for the formation of $[W(PMe_3)_6]$.

The ^{31}P n.m.r. data show $J(^{183}W-^{31}P_A) = 166$ Hz at all temperatures. At the low-temperature limit, there are four multiplets which are centred at δ -70.01, δ -42.04, δ -25.52, and δ -23.99. The resonance at δ -42.04 integrates for two PMe_3 ligands and thus has been assigned to P_B. The multiplet at δ -70.01, shielded relative to the other PMe_3 ligands, is typical for the $M(\eta^2-CH_2PMe_2)$ metallacycle.[7–9] A large coupling of 63.5 Hz between P_A and the *trans* PMe_3 ligand, P_D, allowed the assignment of the doublet of quartets at δ -23.99 to P_D. The remaining signal at δ -25.52 was thus assigned to P_C.

The variable-temperature ^{31}P n.m.r. spectra show that the signals due to P_C and P_D coalesce to give a broad band. This is accompanied by broadening of the P_B multiplet, resulting in two broad bands of equal intensity. At r.t. the two bands further coalesce to afford a single broad band at δ -34.6. In addition, the signal due to P_A becomes a binomial quintet. Clearly, at r.t., the PMe_3 ligands are undergoing rapid intramolecular exchange resulting in the equilibration of four PMe_3 ligands. The appearance of two broad bands on cooling corresponds to an equilibration of the two P_B groups and, separately, the two groups P_C and P_D (Figure 3).

The $^{13}C-\{^1H\}$ n.m.r. spectrum at r.t. has two sharp bands due to the η^2-CH_2PMe_2 group. Irradiation of P_A collapses the doublet couplings of C_A and C_S to singlets. The only other signal present at r.t. is a broad band at δ 29.01 which, on cooling, resolves into three bands which may be assigned by decoupling experiments.

We propose that the variable-temperature n.m.r. spectra are most consistent with a mechanism involving a concerted pseudo-rotation whereby the two P_B groups interchange with P_C and P_D. In a concerted movement the ligands P_C and P_D (equatorial) bend towards the P_A–CH_2 moiety while the two ligands P_B (axial) bend away. The former will increase the interaction between the equatorial ligands and the P–CH_2 moiety which may cause the latter to rotate (through 90°). The net result is an exchange of the equatorial and axial phosphine ligand sites in this quasi-pentagonal-bipyramidal complex. Such a concerted process would be expected to give two broad symmetrical bands at intermediate temperatures corresponding to the axial and equatorial sites, as observed. A similar interchange of ligands has been proposed to occur in pentagonal-bipyramidal compounds such as IF_7.[10]

We studied the reduction of WCl_6 in pure trimethylphosphine with magnesium turnings. The reaction mixture undergoes a distinct sequence of colour changes. The initial red solution deposits a pink precipitate which redissolves to a mauve solution. This turns green and finally brown-orange. The pink precipitate was shown to be $[W(PMe_3)_3Cl_4]$ (**2**) by comparison of the data with those of an authentic sample.[11]

Mauve-pink diamagnetic crystals could be isolated from the mauve solution. The data in Table 2 are consistent with the binuclear compound $[\{W(PMe_3)_3Cl(\mu-Cl)\}_2]$ (**3**). The virtually coupled triplet at δ 1.65 in the ^{1}H n.m.r. spectrum suggests the

Table 1. Selected bond lengths (Å) and angles (°)

		For compound (**1**)	
W(1)–P(1)	2.375(1)	P(1)–W(1)–P(2)	127.08(5)
W(1)–P(2)	2.448(1)	P(1)–W(1)–P(3)	90.51(5)
W(1)–P(3)	2.418(1)	P(1)–W(1)–P(4)	89.93(5)
W(1)–P(4)	2.427(1)	P(1)–W(1)–P(5)	98.90(5)
W(1)–P(5)	2.423(1)	P(1)–W(1)–C(11)	44.14(15)
W(1)–C(11)	2.307(5)	P(2)–W(1)–P(3)	88.62(5)
		P(2)–W(1)–P(4)	90.68(4)
		P(2)–W(1)–P(5)	133.94(5)
		P(2)–W(1)–C(11)	82.93(15)
		P(3)–W(1)–P(4)	179.30(5)
		P(3)–W(1)–P(5)	88.43(5)
		P(3)–W(1)–C(11)	89.50(16)
		P(4)–W(1)–P(5)	92.04(5)
		P(4)–W(1)–C(11)	90.42(16)
		P(5)–W(1)–C(11)	142.97(15)
P(1)–C(11)	1.760(6)	C(11)–P(1)–C(12)	110.9(3)
P(1)–C(12)	1.835(7)	C(11)–P(1)–C(13)	112.8(3)
P(1)–C(13)	1.848(7)	C(12)–P(1)–C(13)	98.2(3)
		W(1)–P(1)–C(11)	65.9(2)
		W(1)–P(2)–C(12)	130.2(2)
		W(1)–P(1)–C(13)	129.9(2)
C(11)–H(11)	0.91(6)	W(1)–C(11)–P(1)	70.0(2)
C(11)–H(12)	1.11(7)	H(11)–C(11)–H(12)	103(5)
P(2)–C(21)	1.827(6)	C(21)–P(2)–C(22)	98.4(3)
P(2)–C(22)	1.839(6)	C(21)–P(2)–C(23)	99.3(4)
P(2)–C(23)	1.835(6)	C(22)–P(2)–C(23)	95.7(3)
		W(1)–P(2)–C(21)	116.6(2)
		W(1)–P(2)–C(22)	121.6(2)
		W(1)–P(2)–C(23)	120.4(2)
P(3)–C(31)	1.860(7)	C(31)–P(3)–C(32)	96.8(4)
P(3)–C(32)	1.849(7)	C(31)–P(3)–C(33)	96.0(3)
P(3)–C(33)	1.865(7)	C(32)–P(3)–C(33)	98.0(4)
		W(1)–P(3)–C(31)	120.8(3)
		W(1)–P(3)–C(32)	119.7(3)
		W(1)–P(3)–C(33)	120.1(2)
P(4)–C(41)	1.857(7)	C(41)–P(4)–C(42)	98.6(3)
P(4)–C(42)	1.848(6)	C(41)–P(4)–C(43)	96.1(3)
P(4)–C(43)	1.859(7)	C(42)–P(4)–C(43)	98.0(3)
		W(1)–P(4)–C(41)	120.4(2)
		W(1)–P(4)–C(42)	117.8(2)
		W(1)–P(4)–C(43)	121.0(2)
P(5)–C(51)	1.829(7)	C(51)–P(5)–C(52)	94.4(4)
P(5)–C(52)	1.848(8)	C(51)–P(5)–C(53)	99.9(4)
P(5)–C(53)	1.824(7)	C(52)–P(5)–C(53)	98.0(4)
		W(1)–P(5)–C(51)	118.2(3)
		W(1)–P(5)–C(52)	122.1(3)
		W(1)–P(5)–C(53)	119.1(3)

		For compound (**11**)	
Ta(1)–P(1)	2.516(1)	P(1)–Ta(1)–P(2)	138.39(4)
Ta(1)–P(2)	2.435(1)	P(1)–Ta(1)–P(3)	93.39(5)
Ta(1)–P(3)	2.551(1)	P(1)–Ta(1)–P(4)	92.07(5)
Ta(1)–P(4)	2.553(1)	P(1)–Ta(1)–P(5)	91.36(4)
Ta(1)–P(5)	2.596(1)	P(1)–Ta(1)–C(11)	42.75(13)
Ta(1)–C(11)	2.015(4)	P(1)–Ta(1)–C(21)	177.76(11)
Ta(1)–C(21)	2.324(4)	P(2)–Ta(1)–P(3)	88.21(4)
		P(2)–Ta(1)–P(4)	88.83(4)
		P(2)–Ta(1)–P(5)	130.23(4)
		P(2)–Ta(1)–C(11)	95.70(13)
		P(2)–Ta(1)–C(21)	43.74(11)
		P(3)–Ta(1)–P(4)	170.30(4)
		P(3)–Ta(1)–P(5)	90.22(4)
		P(3)–Ta(1)–C(11)	90.58(14)
		P(3)–Ta(1)–C(21)	87.29(13)
		P(4)–Ta(1)–P(5)	87.98(4)
		P(4)–Ta(1)–C(11)	94.55(14)
		P(4)–Ta(1)–C(21)	87.20(13)
		P(5)–Ta(1)–C(11)	134.06(13)
		P(5)–Ta(1)–C(21)	86.50(11)
		C(11)–Ta(1)–C(21)	139.41(17)
P(1)–C(11)	1.716(5)	C(11)–P(1)–C(12)	114.1(3)
P(1)–C(12)	1.840(6)	C(11)–P(1)–C(13)	113.5(3)
P(1)–C(13)	1.849(6)	C(12)–P(1)–C(13)	97.2(4)
		Ta(1)–P(1)–C(11)	52.9(1)
		Ta(1)–P(1)–C(12)	131.0(3)
		Ta(1)–P(1)–C(13)	131.8(3)
C(11)–H(11)	0.87(4)	P(1)–C(11)–H(11)	130(3)
		P(1)–C(11)–Ta(1)	84.4(2)
		Ta(1)–C(11)–H(11)	145(3)
P(2)–C(21)	1.776(5)	C(21)–P(2)–C(22)	112.1(3)
P(2)–C(22)	1.840(5)	C(21)–P(2)–C(23)	111.5(2)
P(2)–C(23)	1.846(5)	C(22)–P(2)–C(23)	96.2(3)
		Ta(1)–P(2)–C(21)	64.8(1)
		Ta(1)–P(2)–C(22)	130.4(2)
		Ta(1)–P(2)–C(23)	132.3(2)
C(21)–H(21)	0.92(4)	P(2)–C(21)–H(21)	117(3)
C(21)–H(22)	1.01(4)	P(2)–C(21)–Ta(1)	71.5(2)
		P(2)–C(21)–H(22)	113(3)
		Ta(1)–C(21)–H(21)	115(3)
		Ta(1)–C(21)–H(22)	113(3)
P(3)–C(31)	1.830(5)	C(31)–P(3)–C(32)	101.3(3)
P(3)–C(32)	1.842(6)	C(31)–P(3)–C(33)	98.2(3)
P(3)–C(33)	1.849(5)	C(32)–P(3)–C(33)	97.5(3)
		Ta(1)–P(3)–C(31)	113.4(2)
		Ta(1)–P(3)–C(32)	121.3(2)
		Ta(1)–P(3)–C(33)	121.1(2)
P(4)–C(41)	1.831(6)	C(41)–P(4)–C(42)	98.1(3)
P(4)–C(42)	1.857(5)	C(41)–P(4)–C(43)	101.3(3)
P(4)–C(43)	1.840(6)	C(42)–P(4)–C(43)	97.5(3)
		Ta(1)–P(4)–C(41)	114.5(2)
		Ta(1)–P(4)–C(42)	120.2(2)
		Ta(1)–P(4)–C(43)	121.1(2)
P(5)–C(51)	1.808(5)	C(51)–P(5)–C(52)	101.5(3)
P(5)–C(52)	1.810(6)	C(51)–P(5)–C(53)	101.1(4)
P(5)–C(53)	1.828(6)	C(52)–P(5)–C(53)	96.2(3)
		Ta(1)–P(5)–C(51)	117.6(2)
		Ta(1)–P(5)–C(52)	118.4(2)
		Ta(1)–P(5)–C(53)	118.4(2)

presence of *trans* PMe_3 groups but the data do not permit distinction between the two isomers given for (**3**) in Scheme 1. The crystals isolated from the green solution in the reduction sequence were shown by comparison with published data to be the recently described compound $[W(PMe_3)_4Cl_2]$ (**4**).[12]

We conclude that the reduction of WCl_6 by magnesium turnings in pure PMe_3 proceeds in the sequence given above.

$$WCl_6 \longrightarrow [W(PMe_3)_3Cl_4] \longrightarrow [\{W(PMe_3)_3Cl(\mu\text{-}Cl)\}_2] \longrightarrow [W(PMe_3)_4Cl_2]$$

The reaction may be stopped at each stage giving, in each case, high yields of the tertiary phosphine chloride derivatives, as described in the Experimental section.

Reduction of (**2**) in thf with sodium sand under dihydrogen

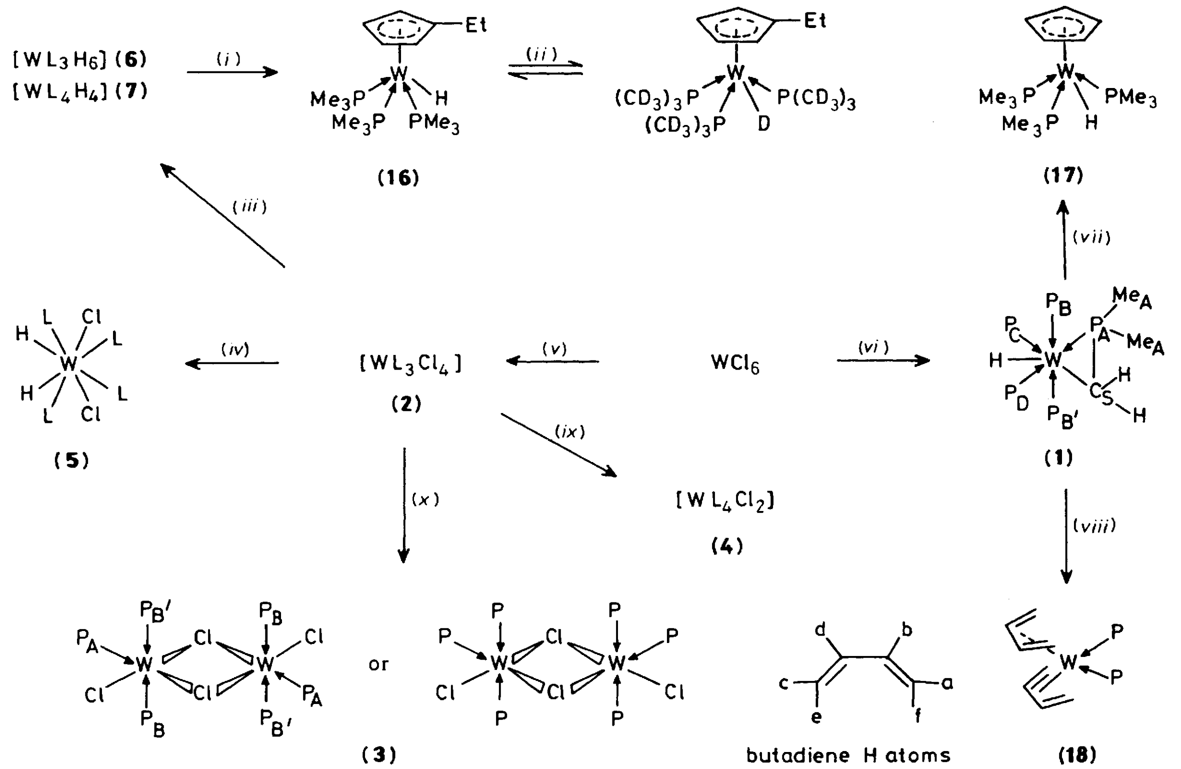
Table 2. Analytical and spectroscopic data

Compd.	Colour	Analysis[a] (%) C	Analysis[a] (%) H	N.m.r. data[b]
(1)[c]	Yellow	31.3 (31.9)	8.0 (8.0)	^{1}H N.m.r. at 20 °C: 1.47 (36 H, s br, 4 PMe$_3$), 1.41 [6 H, d, *J*(P–H) 7.99, P$_A$Me$_2$], 0.43 (2 H, m, CH$_2$), −3.75 [1 H, quintet, *J*(P–H) 39, *J*(^{183}W–H) 26, W–H][d] At −60 °C: 1.56 (d, P$_C$Me$_3$ or P$_D$ Me$_3$), 1.47 (br c, 2 P$_B$Me$_3$), 1.42 (d, P$_A$Me$_2$), 0.43(2 H, v br, CH$_2$), −3.75 [1 H, ddt, *J*(P–H) 78, 54, 9.5, W–H]; also there are bands at 1.71 and 1.23 (see text)[d] ^{31}P N.m.r. at 25 °C: −80.30 [1 P, quintet, *J*(P$_A$–P$_{BCD}$) 21.5, *J*(^{183}W–P$_A$) 166, P$_A$], −34.6 (4 P, c br, P$_{BCD}$) At −60 °C (partial): −70.01 [1 P, dt, *J*(P$_A$–P$_D$) 63.5, *J*(P$_B$–P$_A$) 10, *J*(P$_A$–P$_C$) 0, *J*(^{183}W–P$_A$) 166, P$_A$], −42.04 [2 P, dt, *J*(P$_B$–P$_A$) 10, *J*(P$_B$–P$_D$) 10, *J*(P$_B$–P$_C$) 14, *J*(^{183}W–P$_B$) 300, P$_B$], −25.52 [1 P, q, *J*(P$_C$–P$_B$) 14, *J*(P$_C$–P$_D$) 10 *J*(P$_C$–P$_A$) 0, *J*(^{183}W–P$_C$) 232, P$_C$], −23.99 [1 P, dq, *J*(P$_D$–P$_A$) 63.5, *J*(P$_D$–P$_B$) 10, *J*(P$_D$–P$_C$) 10, *J*(^{183}W–P$_D$) 214, P$_D$][d] ^{13}C N.m.r. at 25 °C: 29.01 (c, C$_B$, C$_C$, C$_D$), 19.02 [d, *J*(C$_A$–P$_A$) 10.7, C$_A$[e]], −11.7 [d, *J*(C$_S$–P$_A$) 29.3, C$_S$[e]][d] At −65 °C: 30.78 (t, C$_B$[f]), 30.33 (d, C$_D$), 27.52 [d, *J*(C$_C$–P$_C$) 24.1, C$_C$[g]], 18.96 (c, C$_A$[e]), −12.96 (t, C$_S$[e])
(2)[i]	Red	19.4 (19.5)	5.1 (4.9)	^{1}H N.m.r.: −8.5 (s br, PMe$_3$)[h]
(3)[j]	Mauve-pink	21.6 (22.3)	5.8 (5.6)	^{1}H N.m.r.: 1.78 [9 H, d, *J*(P–H) 9, 3 Me], 1.65 (18 H, apparent triplet, 6 Me)[d] ^{31}P-{^{1}H} N.m.r.: −27.83 [*J*(P–P) 4.5, *J*(^{183}W–P) 341, 2 P$_B$], −32.57 [t, *J*(P–P) 4.4, *J*(^{183}W–P) 447, P$_A$][d]
(4)[k]	Orange	25.3 (25.8)	6.3 (6.4)	^{1}H N.m.r.: 4.0 (s, br)[l]
(5)[m]	Yellow	24.9 (25.7)	6.7 (6.8)	^{1}H N.m.r.: 1.39 (36 H, virtually coupled triplet, 4 PMe$_3$), −3.45 [2 H, tdd, *J*(P–H) 61, 42.6, 37.4, 2 W–H][l] ^{31}P N.m.r.: −24.32 [t, *J*(P–P) 16.1, *J*(^{183}W–P) 174.1, 2 PMe$_3$], −30.80 [t, *J*(P–P) 16.1, *J*(^{183}W–P) 194.2, 2 PMe$_3$] Selective decoupling of PMe$_3$ hydrogens: −24.32 [tt, *J*(P–P) 16.1, *J*(P–H) 61, 2 PMe$_3$], −30.80 [tdd, *J*(P–P) 42.6, 37.4, 2 PMe$_3$][l]
(6)	White	26.0 (25.8)	7.6 (7.9)	^{1}H N.m.r.: 1.57 (27 H, virtually coupled triplet, 3 PMe$_3$). −2.62 [6 H, q, *J*(P–H) 37.6, *J*(^{183}W–P) 26.5, 6 W–H][l] ^{31}P N.m.r.: −20.74 [s, *J*(^{183}W–P) 71][l] Selective decoupling of the PMe$_3$ hydrogens: −20.74 [septet, *J*(P–H) 37.6][l]
(9)[n]	Yellow			^{1}H N.m.r.: −5.23 [2 H, sextet, *J*(P–H) 40.41, 2 Mo–H], 1.43 (45 H, s, 5 PMe$_3$)[l] ^{31}P-{^{1}H} N.m.r.: −0.65 (s)[l]
(11)[o]	Dark green			^{1}H N.m.r.: 9.46 [1 H, dddt, *J*(P^1–H) 21.5, *J*(P^2–H) 6.5, *J*(P^{3,4}–H) 3.3, Ta=CH], 1.65 [9 H, d, *J*(P–H) 6.09, P^{5}Me$_3$], 1.49 [6 H, dd, *J*(P–H) 5.55, 1.01, PMe$_2$], 1.35 [6 H, dd, *J*(P–H) 5.08, 1.03, PMe$_2$], 1.24 [18 H, t (second-order, virtually-coupled triplet), P^{3}Me$_3$, P^{4}Me$_3$], −0.87 [2 H, apparent ddt[b], *J*(P^{3,4}–H) 13.8, *J*(P^2–H) 2.3, *J*(P^1–H) 4.9, Ta–CH$_2$] ^{31}P N.m.r.: −17.04 [1 P, ddt, *J*(P^5–P^2) 30.50, *J*(P^5–P^1) 14.5, *J*(P^5–P^{3,4}) 4.4, P^5], −25.97 [2 P, m, *J*(P^{3,4}–P^5) 4.4, P^3,P^4], −77.52 [1 P, m, *J*(P^1–P^5) 14.5, *J*(P^1–P^2) 6.0, *J*(P^1–P^{3,4}) 2.5—3.0, P^1], −135.31 [1 P, dd, *J*(P^2–P^5) 30.5, *J*(P^2–P^1) 6.0, P^2][l] ^{13}C N.m.r.: 193.51 [ddt, *J*(C–P^1) 78, *J*(C–P^2) 19.6, *J*(C–P^{3,4}) 8.8, C$_S$], 26.9 (t, C^3, C^4), 25.6 (m, C^5), 24.26 (c, C^1 or C^2), 22.16 (d, C^2 or C^1), 3.6 [m, *J*(C–P^2) 41, C$_T$][p]
(12)[q]	White			^{1}H N.m.r.: −8.84 [1 H, doublet of quintets, *J*(P–H) 23.53, *J*(P–H) 13.24, Re–H], 1.52 (36 H, s, 4 PMe$_3$), 1.39 (9 H, d, PMe$_3$) ^{31}P-{^{1}H} N.m.r.: broad signals at −44.5 and 52.0[d]
(14)[r]		34.6 (35.0)	8.7 (8.8)	^{1}H N.m.r.: 2.83, 2.59 [4 H, complex AB system, 2–CH$_2$–], 1.24 [9 H, d, *J*(P–H) 6.43, P–Me$_3$ (b or c or d)], 1.21 [3 H, d, *J*(P–H) 7.71, P–Me$_2$ (d or e)], 1.03 [9 H, d, *J*(P–H) 5.77, P–Me$_3$ (b or c or d)], 0.94 [3 H, d, *J*(P–H) 5.66, P–Me$_2$ (d or e)], 0.86 [9 H, d, *J*(P–H) 7.84, P–Me$_3$ (b or c or d)], −8.18 [1 H, dq, *J*(H$_c$–P$_{a,b,c}$) (*cis*) 27.20, *J*(H$_c$–P$_d$) (*trans*) 96.90, Ru–H$_c$][l] ^{31}P N.m.r.: 17.9 [1 P, dt, *J*(P$_a$–P$_d$) 23.20, *J*(P$_a$–P$_{b,c}$) 33.3, P$_a$], −0.42, −3.79 [2 P, dddd, AB system, *J*(P$_b$–P$_c$) 258.59, *J*(P$_c$–P$_d$) = *J*(P$_b$–P$_d$) = *J*(P$_a$–P$_d$) 23.30, *J*(P$_{b,c}$–P$_a$) 33.3, $\Delta\nu$ = 341.02, P$_c$,P$_b$], −14.06 [1 P, ^{2}*J*(P$_d$–P$_a$) = ^{2}*J*(P$_d$–P$_{b,c}$) 23.20, P$_d$][l]
(15)[s]	White	42.3 (42.5)	9.2 (9.2)	^{1}H N.m.r.: 5.7 (1 H, vbr s, H$_f$), 2.63 (4 H, br s, H$_{g,g',i,i'}$), 2.01 [2 H, quintet, *J*(H$_{h,h'}$–H$_{g,g',i,i'}$) 7.23, H$_{h,h'}$], 1.24 [18 H, virtually-coupled triplet, *J*′(P–H) 5.1, 2 PMe$_3$], 1.16 [18 H, virtually-coupled triplet, *J*′(P–H) 11.4, 2 PMe$_3$], −9.39 [1 H, doublet of quartets, *J*(H$_e$–P$_{b,c,d}$) 26.15, *J*(H$_e$–P$_a$) (*trans*) 94.06, H$_e$] ^{31}P N.m.r.: −5.4 (2 P, br[t], P$_b$, P$_d$), −15.3 (1 P, br[t], P$_c$ or P$_a$), −20.6 (1 P, br[t], P$_a$ or P$_c$)[l]
(16)[u]	Orange	38.7 (38.0)	7.1 (7.3)	^{1}H N.m.r.: 4.53 (2 H, s, 2 H of η-C$_5$H$_4$), 4.21 (2 H, s, 2 H of η-C$_5$H$_4$), 2.22 [2 H, q, *J*(H–H) 8, CH$_2$], 1.46 (27 H, virtually-coupled triplet, 3 PMe$_3$), 1.17 [3 H, t, *J*(H–H) 8, Me], −10.19 [1 H, q (with satellites), *J*(P–H) 48.3, *J*(^{183}W–H) 47.6, W–H][d] ^{31}P-{^{1}H} N.m.r.: −36.4 [s, *J*(^{183}W–P) 407][d]

Table 2 (*continued*)

Compd.	Colour	Analysis[a] (%) C	Analysis[a] (%) H	N.m.r. data[b]
(17)	Yellow			^{1}H N.m.r.: 4.46 (5 H, s, C_5H_5), 1.45 (27 H, s, 3 PMe_3), −10.56 [1 H, q, J(P–H) 48.0, J(^{183}W–H) 49, W–H][d]
(18)	Yellow	37.7 (37.9)	6.75 (6.7)	^{1}H-{^{31}P} N.m.r.: 3.83 [1 H, ddt, $J(H_a–H_b)$ 6, $J(H_a–H_c) = J(H_a–H_e)$ 6, $J(H_a–H_f) = J(H_a–H_d)$ 1, H_a], 2.95 [1 H, dtt, $J(H_b–H_a)$ 6, $J(H_b–H_f) = J(H_b–H_d)$ 6, $J(H_b–H_c) = J(H_b–H_e)$ 1.5, H_b], 1.42 (18 H, s, 2 PMe_3), 0.88 [1 H, ddd, $J(H_c–H_a)$ 7, $J(H_c–H_e)$ 4, $J(H_c–H_b)$ 2, H_c], 0.33 [1 H, ddd, $J(H_d–H_b)$ 7, $J(H_d–H_f)$ 3, $J(H_d–H_a)$ 1.5, H_d], −1.08 (1 H, m, H_e), −1.15 (1 H, m, H_f)[v] ^{13}C N.m.r.: 20.8 (PMe_3), 30.3 (=CH_2), 38.3 (=CH_2), 64.0 (–CH=), 74.8 (–CH=)[v]

[a] Calculated values are given in parentheses. [b] Data given as: chemical shift (δ), relative intensity, multiplicity, J in Hz, assignment; for labelling, see Schemes 1 and 2; c = complex, br = broad, q = quartet, s = singlet, d = doublet, t = triplet. [c] Mass spectrum: (M/e, ^{184}W) 564 (M^+). I.r. (Nujol mull): 1 655s, 1 710s, 1 925s cm^{-1}. [d] In [$^2H_8$]toluene. [e] Shown by irradiation at P_A. [f] Shown by irradiation at P_B. [g] Shown by irradiation at P_C. [h] In CD_2Cl_2, 300 MHz. [i] Cl: 24.5 (25.6%). [j] Cl: 15.0 (14.7%). [k] Cl: 12.8 (12.7%). [l] In C_6D_6, 300 MHz. [m] Cl: 12.8 (12.7%). [n] ν(Mo–H) = 1 960s cm^{-1}. [o] Mass spectrum: M/e 486 [P^+]. [p] C^n refers to carbons attached to P^n. [q] Mass spectrum: (M/e, ^{187}Re) 567 (M^+ − H), 490 (M^+ − PMe_3). [r] ν(Ru–H) (Nujol mull) = 1 850s cm^{-1}. [s] ν(Ru–H) (Nujol mull) = 1 795s cm^{-1}. [t] Showed partially resolved structure. [u] Mass spectrum: (M/e, ^{184}W) 506. I.r (Nujol mull): ν(W–H) = 1 830m(br) cm^{-1}. [v] In [$^2H_4$]methanol.



Scheme 1. L = PMe_3. (*i*) Spiro[2.4]hepta-4,6-diene in light petroleum (b.p. 100—120 °C) at 80 °C for 5 d, 46%; (*ii*) photolysis in $C_6D_5CD_3$ using a medium-pressure Hg lamp in Pyrex glass; (*iii*) sodium sand, a trace of PMe_3 in thf with H_2 (40 atm) for 36 h, 50%; (*iv*) sodium sand in thf and H_2 (40 atm) for 12 h, 40%; (*v*) activated magnesium in pure PMe_3, *ca.* 3 h at r.t., 85%; (*vi*) sodium sand in PMe_3 at r.t. for 2 d, 40%; (*vii*) excess of cyclopentadiene in light petroleum (b.p. 100—120 °C) at 80 °C for 5 d, 25%; (*viii*) excess butadiene in light petroleum (b.p. 60—80 °C) at 50 °C for 12 h, *ca.* 40%; (*ix*) activated magnesium in liquid PMe_3 for 2 d, 60%; (*x*) magnesium turnings in PMe_3 at r.t. for *ca.* 24 h, *ca.* 80%

gave air-sensitive, yellow crystals of [$W(PMe_3)_4Cl_2H_2$] (**5**).[13] The ^{1}H n.m.r. spectrum strongly supports the proposed formulation and shows there to be a high-field band at δ −3.45 which is a triplet of doublets of doublets. The ^{31}P n.m.r. spectrum is consistent with the dodecahedral geometry in which the PMe_3 ligands occupy the A sites of two intersecting tetrahedra and with the chloride and hydride groups occupying *cis* positions. The structure is shown in Scheme 1. The crystal structure of the closely related derivative [$W(PMe_2Ph)_4Cl_2H_2$] has been described recently.[13]

Reduction of (**2**) with sodium sand in the presence of a small excess of PMe_3 gave, in low yields, the previously described[14] white crystalline hexahydride [$W(PMe_3)_3H_6$] (**6**).

When the reduction of (**2**) with sodium sand in thf was carried out in the presence of dihydrogen and one equivalent of PMe_3, the hexahydride (**6**) was formed together with a small amount of a yellow compound which the data showed to be the tetrahydride [$W(PMe_3)_4H_4$] (**7**).[14,15] It was not possible to separate the two compounds by crystallisation or sublimation.

Tungsten hexachloride in excess trimethylphosphine was reduced in the presence of dihydrogen (2 atm) giving a yellow solid. The ^{1}H n.m.r. spectrum showed the product to be a 3:1

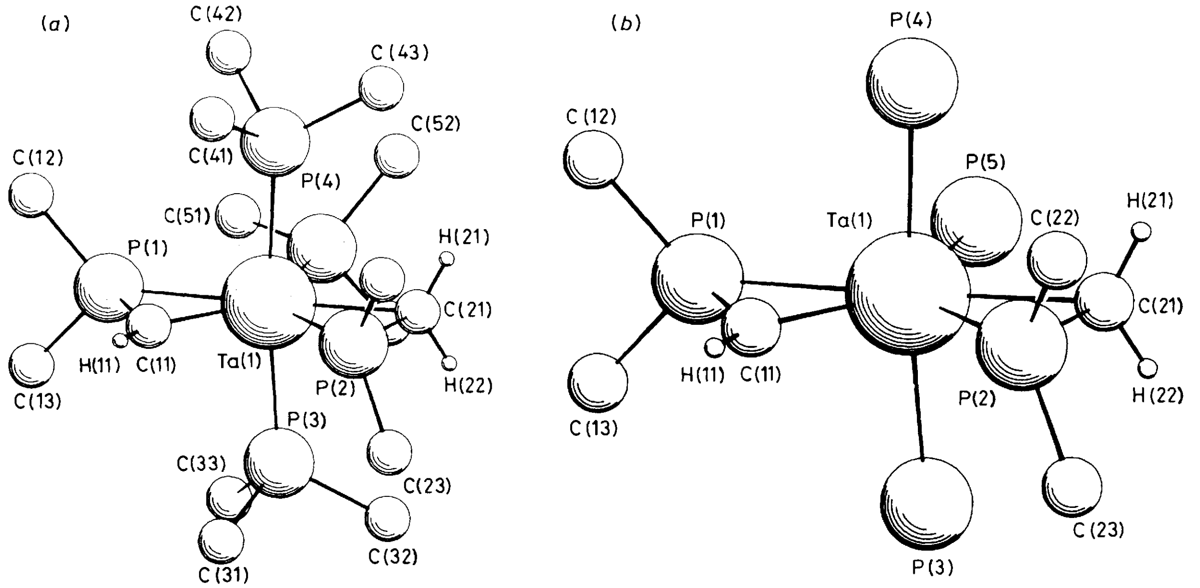


Figure 2. (*a*) Crystal structure of (**11**). (*b*) Diagram in which the carbon atoms bonded to P(3), P(4), and P(5) have been omitted for clarity (see ref. 6)

mixture of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H)]$ and $[W(PMe_3)_5H_2]$ (**8**). The latter was characterised by comparison with ^1H n.m.r. data of an authentic sample.[14] Notably, the product ratio of 3 : 1 was reproduced in three separate experiments and longer reaction times did not serve to increase the proportion of $[W(PMe_3)_5H_2]$.*

These observations support a mechanism in which dihydrogen reacts not with $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ but with a prior intermediate. To test this hypothesis, $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ was treated with dihydrogen (2 atm) for 2 d. The ^1H n.m.r. spectrum revealed unreacted $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ exclusively.

Reduction of $MoCl_5$ with sodium sand in pure PMe_3 under argon proceeded smoothly giving pale yellow crystals of the previously described[16] $[Mo(PMe_3)_5H_2]$ (**9**). Treatment of (**9**) with dihydrogen gives $[Mo(PMe_3)_4H_4]$ (**10**).

Treatment of tantalum pentachloride in excess trimethylphosphine with sodium sand gave very air- and water-sensitive dark green crystals of $[Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)]$ (**11**). The crystal structure of (**11**) has been determined: the molecular structure is shown in Figure 2 and selected bond lengths and angles are given in Table 1.

The n.m.r. data for (**11**) are fully consistent with maintenance of the same structure in solution. In particular H(11) shows a characteristic low-field shift at δ 9.46 while H(21) occurs at δ −0.87. Selective ^{31}P decoupling experiments have identified most of the $^{31}P\text{-}^1H$ coupling constants (Table 2).

The reduction of $ReCl_5$ in excess of pure PMe_3 with sodium gave, after sublimation, white crystals of the previously described[17] $[Re(PMe_3)_5H]$ (**12**), in 18% yield.

Reduction of anhydrous ruthenium trichloride with sodium sand in pure trimethylphosphine gives a mixture of products. The n.m.r. spectrum of the impure solids obtained by extraction with light petroleum of initial reaction products showed the presence of the three compounds $[Ru(PMe_3)_4H_2]$, $[Ru(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$ (**13**) and the binuclear $[(PMe_3)_3HRu(\mu\text{-}CH_2PMe_2)_2RuH(PMe_3)_3]$ (**14**). The first two mononuclear compounds have been described previously.[18,19] Pure (**14**) was obtained by crystallisation of the initial reaction solids from pentane at r.t. as air-sensitive, colourless crystals, in 36% yield. Microanalysis and detailed n.m.r. studies show (**14**) to have one of two binuclear structures (Scheme 2) but do not permit distinction between them. The closely related compounds $[(PMe_3)_2Rh(\mu\text{-}CH_2PMe_2)_2Rh(PMe_3)_2]$ and $[(PMe_3)_2HPt(\mu\text{-}CH_2PMe_2)_2PtH(PMe_3)_2]$ have been described recently.[20,21]

Reduction of $RuCl_3$ with sodium sand in a trimethylphosphine–cyclopentene (1 : 1) mixture gives a dark solid and air-sensitive white crystals which separate from the pentane extract at room temperature. The pure compound $[Ru(PMe_3)_4(\sigma\text{-}\overline{C{=}CHCH_2CH_2CH_2})H]$ (**15**), is only slightly soluble in pentane. The structure was determined by detailed n.m.r. studies (Table 2). For example, double-resonance experiments showed the connectivity of the resonances assigned to the C_5-ring hydrogens f,g,g′,h,h′,i, and i′.

The insertion of ruthenium into the olefinic C–H bond of cyclopentene is unusual: we presume that the reaction proceeds *via* an intermediate η^2-cyclopentene compound in a manner somewhat analogous to the formation of $[Rh(\eta\text{-}C_5Me_5)(PMe_3)(Ph)H]$ from the intermediate $[Rh(\eta\text{-}C_5Me_5)(PMe_3)(\eta^2\text{-}C_6H_6)]$.[22]

Some reactions of the compounds described above have been investigated. We were interested to find compounds which would activate C–H bonds and towards this end we sought analogues of the compound $[Mo(\eta\text{-}C_5H_5)(dmpe)H_3]$ [dmpe = 1,2-bis(dimethylphosphino)ethane].[23]

Treatment of the hexahydride (**6**) with spiro[2.4]hepta-4,6-diene at 80 °C gave air-sensitive, orange crystals of the compound $[W(\eta\text{-}C_5H_4Et)(PMe_3)_3H]$ (**16**). The ^1H and ^{31}P n.m.r. data show the three PMe_3 groups to be equivalent, even at −60 °C.

Photolysis of (**16**) in $[^2H_8]$toluene using a 100-W medium-pressure mercury lamp was monitored by ^1H n.m.r. spectroscopy. The data showed that the hydrogens of the W–H and PMe_3 groups were readily exchanged with those of the deuteriums of the toluene but that there was no evidence for exchange of the hydrogens of the $\eta\text{-}C_5H_4Et$ group. The mass spectrum of the deuteriated tungsten products suggested that the most highly deuteriated species present was $[W(\eta\text{-}C_5H_4Et)(PCD_3)_3D]$.

The compound $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ (**1**) reacts with an excess of cyclopentadiene at 80 °C giving yellow, air-sensitive

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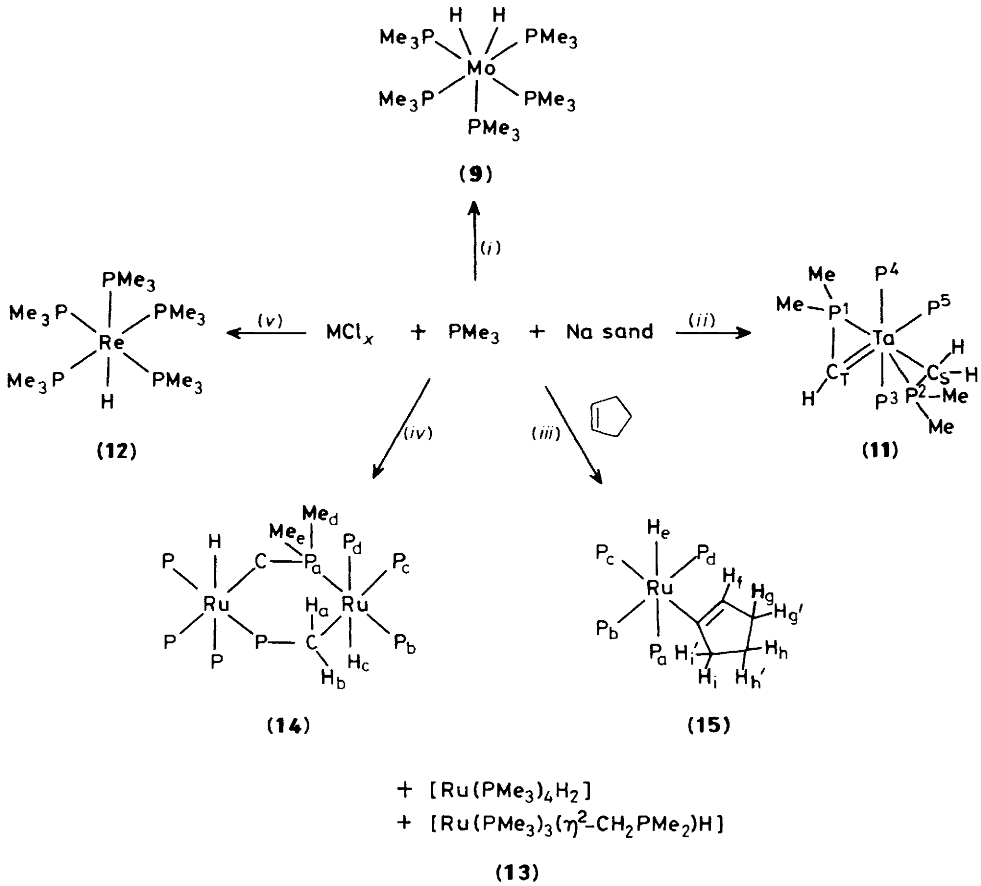
* *Note added in proof:* (**1**) reacts with H_2 (2 atm) at 65 °C giving $[W(PMe_3)_5H_2]$ and $[W(PMe_3)_4H_4]$.



Scheme 2. (*i*) MoCl$_5$ in liquid PMe$_3$ with sodium sand at r.t. for 48 h, 55%; (*ii*) TaCl$_5$ in liquid PMe$_3$ with sodium sand for 40 h, 11%; (*iii*) RuCl$_3$ in liquid trimethylphosphine–cyclopentene mixture (1 : 1) at r.t. for 3 d, 22%; (*iv*) RuCl$_3$ in liquid PMe$_3$ with sodium sand at r.t. for 48 h, 36%; (*v*) ReCl$_5$ in liquid PMe$_3$ with sodium sand for 12 h, 18%

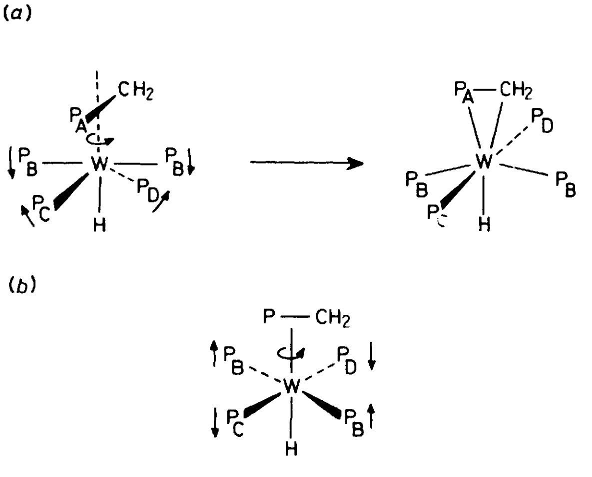


Figure 3. (*a*) Proposed equilibrium for exchange of 2P$_B$ with P$_D$ and P$_C$ in (**1**); (*b*) proposed rotation for the η^2-CH$_2$PMe$_2$ group in (**1**)

crystals. The n.m.r. spectra of the sublimed reaction mixture showed two high-field signals. The signal at δ −10.56 consisted of a binomial quartet and was assigned to a metal-bound hydrogen coupled to three equivalent ^{31}P nuclei [$J(^{31}P-^{1}H)$ = 48 Hz]. An accompanying singlet at δ 1.45 of relative intensity 27 was attributed to the protons of the three PMe$_3$ ligands, while a singlet at δ 4.46 of relative intensity 5 was assigned to an unsubstituted η^5-C$_5$H$_5$ ring. Thus, the data suggested the one hydride compound to be [W(η-C$_5$H$_5$)(PMe$_3$)$_3$H] (**17**). The second high-field band may be assigned to [W(η-C$_5$H$_5$)$_2$H$_2$]. The n.m.r. data indicated that the recrystallised sublimate was a *ca.* 1:1 mixture of [W(η-C$_5$H$_5$)$_2$H$_2$] and [W(η-C$_5$H$_5$)(PMe$_3$)$_3$H] (**17**). Attempts to separate the two products by crystallisation and sublimation proved unsuccessful though the proportion of (**17**) could be increased by careful sublimation (110 °C, 10^{-1} Torr).

The reaction between (**1**) and cyclopentadiene at 80 °C was monitored (n.m.r.). This showed that the rate of formation of (**17**) from (**1**) was comparable to the rate of formation of [W(η-C$_5$H$_5$)$_2$H$_2$] from (**17**).

Finally, treatment of (**1**) with an excess of butadiene at 50 °C gave yellow crystals of [W(PMe$_3$)$_2$(η^4-C$_4$H$_6$)$_2$] (**18**).

The ^{1}H n.m.r. spectrum of (**18**) may be assigned readily by comparison with that of the molybdenum analogue [Mo(η^4-C$_4$H$_6$)$_2$(PMe$_3$)$_2$].[2] Compound (**18**) has also been prepared independently by treatment of [W(η^4-C$_4$H$_6$)$_3$] with PMe$_3$ and the crystal structure has been determined.[24]

The reactions and structures proposed for the compounds (**1**)—(**18**) are shown in Schemes 1 and 2. Trimethylphosphine is an effective reactive solvent medium for the one-pot syntheses of low-valent PMe$_3$ derivatives. The formation of hydrido-derivatives and the η-CH$_n$PMe$_2$ (n = 1 or 2) ligand systems shows that the anticipated insertion of the metal centres into the C–H bonds of PMe$_3$ occurs readily during the reactions.

Carmona *et al.*[11] have isolated [W(PMe$_3$)$_5$(N$_2$)] from reduction of [W(PMe$_3$)$_3$Cl$_4$] with sodium sand in thf and excess PMe$_3$. The reaction of the dinitrogen compound with excess PMe$_3$ in the absence of thf has not been reported.

Molecules of (**1**) and (**11**) both possess pseudo-pentagonal-bipyramidal co-ordination geometry around the central metal atom, with an approximate equatorial mirror plane. The 'tucked-in' ligands occupy equatorial sites. The axial phosphine ligands are eclipsed, presumably reflecting steric interactions from equatorial ligands. There appears to be no systematic variation in metal phosphorus distances between axial and equatorial sites unlike $[Re(PMe_3)_4(\eta^2-CH_2PMe_2)]$ in which the axial Re–P distances are longer than the equatorial.[17] The hydride in (**1**) was not observed, but it may reasonably be placed in the equatorial plane between P(2) and P(5) [P(2)–W(1)–P(5) 133.94(5)°]. Both (**1**) and (**11**) contain the η^2-CH_2PMe_2 ligand, and this type of M–P–C metallacycle has been characterised by *X*-ray analysis previously.[17,25–28] We note that in both (**1**) and (**11**) the metal–phosphorus and P–C(11) distances are shorter than in the PMe_3 ligands, indicating the possibility of some multiple-bond character.[26] The metal–carbon distances are not exceptional for single bonds.[29,30] The carbons of the two methyls and the phosphorus of the η^2-CH_2PMe_2 ligand are approximately coplanar with the metal.

The η^2-$CHPMe_2$ ligand was found in (**11**) and this is the first example reported. H(11) was found to be coplanar with the Ta–C–P metallacycle and close to the external bisector of the Ta–C–P angle. Ta–C(11) is 0.31 Å shorter than Ta–C(21) and is reasonably described as a Ta–C double bond; the difference between Ta–C and Ta=C in $[Ta(\eta-C_5H_5)_2(CH_3)(CH_2)]$ is 0.22 Å.[29] C(11)–P(1) is 0.13 Å shorter than the mean P(1)–C(methyl) distance, suggesting some carbon–phosphorus multiple bonding. We note that one other carbene metallacycle has been characterised, $[W\{\eta^2-C(NEt_2)PMePh\}(CO)_4]$.[31]

Trimethylphosphine complexes of stoicheiometry corresponding to $M(PMe_3)_n$ were previously known for Co,[8,32,33] Ni,[32] Pd,[32] Fe,[8,33,34] Ru,[19] Os,[19] and Mo;[1,2] this chemistry combined with the new syntheses described above show that there is likely to be a very extensive chemistry where the dominant ligand environment is PMe_3.

Experimental

All preparations and reactions were carried out under an atmosphere of purified argon. Solvents were dried and purified by reflux over a suitable drying agent under dinitrogen, followed by distillation under dinitrogen. Benzene, tetrahydrofuran (thf), light petroleum (b.p. 60—80 °C), and cyclohexane were dried over potassium; toluene and light petroleum (b.p. 100—120 °C) were dried over sodium; light petroleum (b.p. 30—40 °C) and diethyl ether were dried over sodium–potassium alloy. Butadiene was purified by distillation over solid potassium hydroxide and then 4Å molecular sieves. All other reagents were used as supplied. Microanalyses were performed by the analytical department of this laboratory or by Alfred Bernhardt Ltd.

Infrared spectra were recorded on Pye-Unicam SP2000 and Perkin-Elmer 457 double-beam grating spectrophotometers.

Nuclear magnetic resonance spectra were recorded on JEOL PMX60 (^{1}H, 60 MHz), Bruker WH300 (^{1}H, 300 MHz; ^{13}C, 75.4 MHz), Bruker WH90 (^{1}H, 90 MHz; ^{31}P, 36.43 MHz), and Bruker WH400 spectrometers (^{1}H and ^{13}C). Solvent bands were used as internal standards. Mass spectra were recorded on an A.E.I. MS 902 spectrometer.

[η^2-*(Dimethylphosphino)methyl*]*hydridotetrakis*(*trimethylphosphine*)*tungsten*(II), (**1**).—Trimethylphosphine (25 cm^3) was condensed onto a mixture of tungsten hexachloride (2.0 g, 5 mmol) and sodium sand (1 g, 43.5 mmol) in a 250-cm^3 glass ampoule fitted with a poly(tetrafluoroethylene) (ptfe) tap. After allowing the mixture to warm up to *ca.* –20 °C, dinitrogen was admitted and vigorous stirring was commenced. Within 1 h a grey solid was deposited. Stirring for 2 d gave a yellow-orange trimethylphosphine solution.

Trimethylphosphine was removed under reduced pressure and recovered for future use. The remaining residue was extracted with light petroleum (b.p. 40—60 °C, 150 cm^3) to give a yellow-orange extract. After removal of the light petroleum under reduced pressure, the resulting waxy yellow residue was dried overnight *in vacuo*. Recrystallisation from a concentrated light petroleum (b.p. 40—60 °C) solution at –78 °C gave large yellow prisms of $[W(PMe_3)_4(\eta^2-CH_2PMe_2)H]$. Average yield *ca.* 40%.

Tetrachlorotris(*trimethylphosphine*)*tungsten*(IV), (**2**).—Trimethylphosphine (30 cm^3) was condensed at –196 °C onto a mixture of tungsten hexachloride (1.3 g, 3.3 mmol) and activated magnesium (4 g). The mixture was allowed to warm, initially to –78 °C, with stirring, during which time the PMe_3 solution developed a red colouration. After allowing to warm to r.t., argon was admitted, and stirring was continued. Within 3 h the red colour had been discharged leaving a mauve-pink solution and a copious pink precipitate (**A**). Removal of excess of PMe_3 *in vacuo* gave a pale residue which was washed with toluene (3 × 15 cm^3). The resulting salmon pink solid was extracted into dichloromethane (50 cm^3) to give a deep red solution. Filtration, followed by concentration and cooling to –20 °C gave red air-sensitive crystals of the product. Yield *ca.* 85%.

Bis[*dichlorotris*(*trimethylphosphine*)*tungsten*(II)], (**3**).—The pink precipitate (**A**) from the above reaction was stirred in pure trimethylphosphine at r.t. for 24 h giving a mauve-pink solution. The excess of trimethylphosphine was removed under reduced pressure and the residue was extracted with light petroleum (40—60 °C). Filtration of the resulting mauve-pink solution followed by slow removal of solvent under reduced pressure afforded mauve-pink crystals which were collected and dried *in vacuo*. Yield *ca.* 80%.

Dichlorotetrakis(*trimethylphosphine*)*tungsten*(II), (**4**).—The pink precipitate (**A**) (1.0 g) in liquid trimethylphosphine (15 cm^3) was stirred with activated magnesium for 2 d giving a green solution and a grey, amorphous residue. After removal of excess of trimethylphosphine under reduced pressure, the residue was extracted with light petroleum (b.p. 40—60 °C, 50 cm^3) giving a green solution. Concentration and cooling to –20 °C gave paramagnetic orange crystals. Yield *ca.* 60%. The reduction may take several more days if the magnesium is not well activated (the magnesium was activated by heating *in vacuo* in the presence of a trace of iodine).

Dichlorodihydridotetrakis(*trimethylphosphine*)*tungsten*(IV), (**5**).—The compound $[W(PMe_3)_3Cl_4]$ (2 g, 3.6 mmol) was stirred with sodium sand (1 g, 43.5 mmol) in thf (30 cm^3) under dihydrogen (40 atm). After 12 h, the extract from the autoclave had a brown colouration with a copious suspension of amorphous grey solid. The solvent was removed under reduced pressure and extracted with light petroleum (b.p. 40—60 °C, 80 cm^3) to give a lime-green solution. After filtration, the solution was concentrated and cooled to –78 °C. The resulting yellow crystals were collected and dried *in vacuo*. Yield *ca.* 40%.

Hexahydridotris(*trimethylphosphine*)*tungsten*(VI), (**6**).—The compound $[W(PMe_3)_3Cl_4]$ (0.5 g, 0.9 mmol), sodium sand (0.7 g, 30 mmol) and a trace of trimethylphosphine were stirred in thf (30 cm^3) under dihydrogen (40 atm) for 36 h. The extract from the autoclave had a black appearance due to a fine suspension of dark particles. The volatile components were removed under reduced pressure and the residue was extracted with light petroleum (b.p. 60—80 °C) to give an orange solution.

Filtration of the solution followed by concentration and cooling to −78 °C gave white crystals of the product. Yield 0.19 g, *ca.* 50%. I.r. spectrum (Nujol mull): ν(W–H) 1 820 (s, br), 1 870 cm^{-1} (m, br).

Dihydridopentakis(trimethylphosphine)molybdenum(II), (**9**).—Trimethylphosphine (30 cm^3) was condensed onto a mixture of molybdenum pentachloride (2.0 g, 7.3 mmol) and sodium sand (2.0 g, 87 mmol) in a 250-cm^3 glass ampoule fitted with a ptfe tap. After allowing the mixture to warm to r.t. argon was admitted and vigorous stirring was commenced. The trimethylphosphine solution developed a pale green colouration which darkened overnight to give a red-green dichroic solution. After 48 h, the solution was yellow-orange, and no further change was observed. Trimethylphosphine was removed from the reaction mixture under reduced pressure to leave a residue which was extracted with light petroleum (b.p. 40—60 °C, 150 cm^3). The resulting red solution was concentrated and cooled to −78 °C to afford a green solid which was recrystallised from cyclohexane (15 cm^3) at 8 °C. Yellow prisms separated and were collected and dried *in vacuo* to give the product. Yield 55%.

[η^2-*(Dimethylphosphino)methyl*][η^2-*(dimethylphosphino)methylene*]*tris(trimethylphosphine)tantalum*(III), (**11**).—Trimethylphosphine (30 cm^3) was condensed onto a mixture of tantalum pentachloride (2.0 g, 5.58 mmol) and sodium sand (2.0 g, 87 mmol). After allowing the mixture to warm to r.t., argon was admitted and it was stirred. The trimethylphosphine solution developed a yellow colouration which darkened to orange over a period of 2 h and a green precipitate was formed. After stirring at r.t. for 40 h, an intense green solution resulted, supporting a finely divided grey deposit. Trimethylphosphine was removed under reduced pressure and the residue was extracted with light petroleum (b.p. 40—60 °C, 150 cm^3) to give a dark green solution. Concentration of the solution and cooling to −20 °C afforded air-sensitive green crystals of $[Ta(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)(\eta^2\text{-}CHPMe_2)]$. Yield 0.35 g, 11.2%.

Hydridopentakis(trimethylphosphine)rhenium(I), (**12**).—Trimethylphosphine (30 cm^3) was condensed onto a mixture of rhenium pentachloride (0.9 g, 2.47 mmol) and sodium sand (1.0 g, 44 mmol). After allowing the mixture to warm to r.t., argon was admitted and stirring was commenced. The trimethylphosphine solution developed an orange colouration which intensified over a period of 12 h. No further change was observed. Trimethylphosphine was removed under reduced pressure and the residue was extracted with light petroleum (b.p. 40—60 °C, 150 cm^3). Concentration and cooling of the solution failed to give a precipitate. Therefore, the solvent was removed under reduced pressure and the residue was sublimed onto a liquid-nitrogen-cooled probe (120 °C, 10^{-3} Torr) to give an off-white sublimate. Recrystallisation from light petroleum (b.p. 40—60 °C) afforded white crystals of the product. Yield *ca.* 18%.

Bis{[μ-*(dimethylphosphino)methyl*]*hydridotris(trimethylphosphine)ruthenium*(II)}, (**14**).—Anhydrous ruthenium trichloride (2.0 g, 9.4 mmol) and sodium sand (*ca.* 2.0 g) in trimethylphosphine (50 cm^3) were stirred at r.t. for 2 d. The solution developed a deep red colour. The trimethylphosphine was removed under reduced pressure giving a black oily residue. This was extracted with pentane (100 cm^3). The extract was filtered and concentrated. On standing for 2 d, colourless crystals separated. These were collected, washed with cold pentane and dried *in vacuo* yield 0.3 g, 36%. Sublimation of the crude reaction solids at 50 °C and 0.01 Torr gave a whitish solid which the ^1H n.m.r. spectrum showed to contain $[Ru(PMe_3)_4H_2]$, a trace of $[Ru(PMe_3)_3(\eta^2\text{-}CH_2PMe_2)H]$, and the title compound.

(σ-*Cyclopenten*-1-*yl*)*hydridotetrakis(trimethylphosphine)ruthenium*(II), (**15**).—Anhydrous ruthenium trichloride (2.0 g, 9.4 mmol) and sodium sand (2.9 g) in a cyclopentene–trimethylphosphine mixture (60 cm^3, 1:1) was stirred at r.t. for 3 d. The solvent was removed from the resulting deep red reaction mixture under reduced pressure. The residue was extracted with light petroleum (2 × 100 cm^3) and the extract was filtered through Celite. The solvent was removed from the filtrate under reduced pressure and the residue was extracted with pentane. After filtration the filtrate was concentrated and allowed to stand at r.t. White crystals separated which were collected, washed with cold pentane and dried *in vacuo*. Yield 1.0 g, 22%.

(η-*Ethylcyclopentadienyl*)*hydridotris(trimethylphosphine)tungsten*(II), (**16**).—The compound $[W(PMe_3)_3H_6]$ (0.7 g, 1.67 mmol) and freshly distilled spiro[2.4]hepta-4,6-diene (5 cm^3) in light petroleum (b.p. 100—120 °C, 80 cm^3) were heated at 80 °C for 5 d. The more volatile components were removed under reduced pressure to give a yellow oil. The residue, which contained dimerised spiro[2.4]hepta-4,6-diene was sublimed onto a liquid-nitrogen-cooled probe at r.t. (5 × 10^{-3} Torr) to remove the more volatile impurities. The residual orange solid was extracted with light petroleum (b.p. 40—60 °C, 50 cm^3) and crystallised from a concentrated solution at −78 °C. The orange crystals were collected and dried *in vacuo*. Yield 0.4 g, 46%.

(η-*Cyclopentadienyl*)*hydridotris(trimethylphosphine)tungsten*(II), (**17**).—The compound $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ (0.5 g, 0.9 mmol) in light petroleum (b.p. 100—120 °C, 20 cm^3) was treated with freshly distilled cyclopentadiene (20 cm^3). The mixture was stirred at 80 °C over a period of 5 d by which time a considerable amount of off-white amorphous solid was in evidence. The yellow supernatant solution was separated by filtration and the volatile components were removed under reduced pressure to give *ca.* 10 cm^3 of fairly involatile oil. The less volatile components were removed by sublimation onto a liquid nitrogen-cooled probe at r.t. (10^{-4} Torr). Light petroleum (b.p. 40—60 °C, 5 cm^3) was added to the resulting waxy residue to precipitate a pale yellow solid which was collected and dried *in vacuo*. The solid was recrystallised from a concentrated solution in light petroleum (b.p. 40—60 °C, 10 cm^3) at −20 °C to afford a mixture of $[W(\eta\text{-}C_5H_5)(PMe_3)_3H]$ and $[W(\eta\text{-}C_5H_5)_2H_2]$.

Bis[(η-*buta*-1,3-*diene*)*bis(trimethylphosphine)*]*tungsten*, (**18**).—$[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ (0.5 g, 0.9 mmol) was treated with butadiene (10 cm^3) in light petroleum (b.p. 60—80 °C, 30 cm^3) and the mixture was left to stand overnight giving a small amount of pale residue in a yellow solution. Solvent was removed under reduced pressure and the residue was dried overnight *in vacuo*. Sublimation at 70 °C (10^3 Torr) gave a yellow sublimate which was dissolved in methanol and recrystallised from a concentrated solution at −20 °C. Yield *ca.* 40%.

Preparation of Trimethylphosphine.—This preparation is essentially the same as previously described by Wolfsberger and Schmidbaur[35] and modified by Sharp,[36] but we provide the details of our preparation since the scale is substantially larger. A 10-l, three-necked, round-bottomed flask was fitted with a solid CO_2–acetone condenser, a pressure-equalising dropping funnel (500 cm^3) and a high-torque stirrer. Dried magnesium turnings (360 g, 15.0 mol) and dried di-n-butyl ether (4 l) were placed in the apparatus, which was flushed with dinitrogen. An inert atmosphere was maintained throughout the experiment.

Table 3. Fractional atomic co-ordinates for (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W(1)	−0.011 38(1)	0.197 39(2)	0.235 10(1)	C(31)	0.082 4(5)	−0.152 1(7)	0.308 3(5)
P(1)	−0.134 51(9)	0.049 9(1)	0.166 79(8)	C(32)	0.143 4(5)	0.056 4(8)	0.417 2(4)
P(2)	−0.013 44(9)	0.363 0(1)	0.337 39(7)	C(33)	−0.037 3(5)	−0.049 4(7)	0.386 0(4)
P(3)	0.042 4(1)	0.020 4(1)	0.332 92(8)	C(41)	−0.180 3(5)	0.460 6(7)	0.124 7(4)
P(4)	−0.065 3(1)	0.377 0(1)	0.138 16(8)	C(42)	0.005 8(5)	0.536 3(7)	0.146 1(4)
P(5)	0.107 0(1)	0.121 2(2)	0.177 34(9)	C(43)	−0.081 2(6)	0.340 0(8)	0.034 4(4)
C(11)	−0.162 0(4)	0.155 6(6)	0.236 6(3)	C(51)	0.223 5(5)	0.086 5(10)	0.241 0(5)
C(12)	−0.219 8(5)	0.072 6(8)	0.072 0(4)	C(52)	0.148 1(6)	0.233 1(10)	0.110 9(5)
C(13)	−0.154 3(5)	−0.137 3(7)	0.180 1(5)	C(53)	0.087 9(6)	−0.037 7(9)	0.119 6(5)
C(21)	0.096 5(4)	0.448 4(7)	0.385 9(4)	H(11)	−0.173 9(42)	0.114 3(68)	0.277 9(37)
C(22)	−0.088 2(5)	0.518 3(7)	0.318 3(4)	H(12)	−0.224 3(46)	0.220 6(68)	0.212 3(39)
C(23)	−0.047 1(6)	0.305 8(8)	0.422 2(4)				

Table 4. Fractional atomic co-ordinates for (**11**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Ta(1)	0.391 35(1)	0.437 602(8)	0.262 45(1)	C(31)	0.683 5(6)	0.373 6(4)	0.417 5(4)
P(1)	0.259 3(1)	0.369 61(7)	0.386 9(1)	C(32)	0.729 9(5)	0.360 0(4)	0.205 8(5)
P(2)	0.539 3(1)	0.539 80(6)	0.263 82(8)	C(33)	0.577 8(7)	0.260 3(3)	0.302 0(6)
P(3)	0.594 1(1)	0.358 20(7)	0.293 1(1)	C(41)	0.160 2(7)	0.583 7(4)	0.317 3(5)
P(4)	0.198 5(1)	0.521 30(7)	0.215 5(1)	C(42)	0.029 8(5)	0.484 9(4)	0.187 8(6)
P(5)	0.305 5(1)	0.356 28(6)	0.111 63(9)	C(43)	0.201 2(7)	0.581 3(3)	0.104 1(5)
C(11)	0.365 1(4)	0.439 3(3)	0.414 3(3)	C(51)	0.185 8(8)	0.288 5(3)	0.138 7(5)
C(12)	0.091 2(6)	0.383 8(5)	0.428 2(6)	C(52)	0.227 8(7)	0.397 8(3)	−0.002 0(4)
C(13)	0.298 1(9)	0.289 3(3)	0.465 2(5)	C(53)	0.425 7(7)	0.304 1(4)	0.044 6(5)
C(21)	0.508 2(5)	0.498 5(2)	0.142 2(3)	H(11)	0.382(4)	0.462(2)	0.471(3)
C(22)	0.502 5(7)	0.635 8(3)	0.259 4(5)	H(21)	0.457(4)	0.523(3)	0.094(3)
C(23)	0.718 1(5)	0.549 1(3)	0.296 9(4)	H(22)	0.587(4)	0.471(3)	0.119(3)

Methyl iodide (2 kg, 14.1 mol) was added dropwise, with stirring, to the magnesium suspension over 5 h (an ice–water bath was used to prevent overheating). After addition of the methyl iodide, the reaction mixture was warmed to r.t. and stirred for a further 12 h. Subsequently, a degassed solution of triphenyl phosphite[35] (1 320 g, 4.25 mol) in an equal volume of di-n-butyl ether was added dropwise, with cooling in ice and stirring over 6 h. A further quantity of diethyl ether was added to the viscous reaction mixture to maintain effective stirring at r.t. for 18 h. The solution became extremely viscous. The dropping funnel was replaced with a short Vigreux column and condenser, leading to a three-necked, round-bottomed flask (500 cm^3), fitted with a solid CO_2–acetone condenser. The reaction mixture was placed in a 10-l heating mantle and steadily warmed to *ca.* 120 °C. The materials boiling in the range 40—50 °C were collected. The distillate was finally redistilled using an efficient distillation column and the fraction boiling at 38—39 °C was collected. Yield 312 cm^3, 70%.

Crystal Structure Determinations.—Crystal data for (**1**). $C_{15}H_{45}P_5W$, $M = 564.25$, monoclinic, $a = 15.039(1)$, $b = 9.595(2)$, $c = 18.113(2)$ Å, $\beta = 106.782(9)°$, $U = 2\,502.48$ Å^3, space group $P2_1/n$,[37] $Z = 4$, $D_c = 1.50$ Mg m^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 51.93$ cm^{-1}, $F(000) = 1\,136$, crystal dimensions 0.55 × 0.40 × 0.15 mm.

Crystal data for (**11**). $C_{15}H_{42}P_5Ta$, $M = 558.32$, monoclinic, $a = 10.143(3)$, $b = 18.769(3)$, $c = 13.040(2)$ Å, $\beta = 93.61(2)°$, $U = 2\,478.33$ Å^3, space group $P2_1/n$,[37] $Z = 4$, $D_c = 1.50$ Mg m^{-3}, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 49.9$ cm^{-1}, $F(000) = 1\,120$, crystal dimensions 1.0 × 1.0 × 0.9 mm.

Data collection and processing. Crystals sealed under nitrogen in Lindemann glass capillaries mounted on an Enraf-Nonius CAD4 diffractometer, cell dimensions obtained by least-squares methods from the positions of 25 carefully centred reflections. (**1**): scan mode ω–2θ with ω scan width $(1.0 + 0.35\tan\theta)°$ and ω scan-speed range 0.97—5.49° min^{-1}. Some overlapping reflections were remeasured with the scan angle reduced to $(0.8 + 0.35\tan\theta)°$. 8 003 Reflections measured $(1.0 < \theta < 27.0°)$, 5 449 unique [merging $R = 0.023$ after absorption correction[38] (max.,min. correction 2.36,1.00)] giving 4 278 observed $[I > 3\sigma(I)]$. Approx. 9% decay in intensity corrected during data collection. (**11**): scan mode ω–2θ with ω scan width $(0.7 + 0.35\tan\theta)°$ and ω scan-speed range 0.66—5.49° min^{-1}. 4 916 Reflections were measured $(1.0 < \theta < 26.0°)$, 3 608 unique [merging $R = 0.019$ after absorption correction (max.,min. correction 1.41,1.0)] giving 3 132 observed $[I > 3\sigma(I)]$.

Structure analysis and refinement. Solution by heavy-atom method. Refinement by the large-block approximation to the normal matrix with all non-hydrogen atoms anisotropic. For (**1**), hydrogen atoms were in calculated positions ($U_{\text{iso.}} = 0.06$ Å^3) except those on C(1) which were refined isotropically. For (**11**), hydrogen atoms were refined isotropically subject to soft constraints.[39] Corrections were made for anomalous dispersion[40] and isotropic extinction.[41] Chebyshev weighting schemes[42] were applied where $w = 1/\Sigma_{r=1}^{n} A_r T_r(X)$ and $X = F_o/|F_o|_{\text{max.}}$; T_r is the polynomial function with coefficients, A_r, for (**1**) of 482, 800, 543, 267, and 100, for (**11**) of 31, 29, and 20, to give satisfactory agreement analyses. Final R $(= \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ and R' $\{= [w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ values were 0.029 and 0.034 for (**1**) and 0.019 and 0.022 for (**11**) respectively. Solution and refinement used the Oxford CRYSTALS package[43] on the VAX 11/750 computer of the Chemical Crystallography Laboratory, Oxford University. Scattering factors were taken from International Tables for *X*-Ray Crystallography.[44]

Fractional atomic co-ordinates for (**1**) and (**11**) are given in Tables 3 and 4 respectively.

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