Trimethylphosphine Polyhydrides of Tungsten and Rhenium†

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The new compounds $WH_6(PMe_3)_3$, $ReH_7(PMe_3)_2$, $ReH_7(PMe_3)_2{\cdot}PhNH_2$, and $Re_2H_8(PMe_3)_4$ have been synthesised. Improved syntheses of $MH_4(PMe_3)_4$ (M = Mo or W) are also described. The complex $WH_6(PMe_3)_3$ reacts with carbon dioxide under pressure to yield the fluxional molecule $WH_2(OCHO)(O_2CH)(PMe_3)_3$ with uni- and bi-dentate formate groups. The compounds have been characterised by infrared and nuclear magnetic resonance (^1H and ^{31}P) spectroscopy.

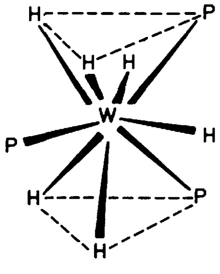
There has been much recent interest[1] in transition-metal polyhydrido-complexes in high oxidation states, especially those of rhenium which react with alkanes. We now report the synthesis of hexahydridotris(trimethylphosphine)tungsten(VI), and its reaction with carbon dioxide to give the insertion product, (formato-*O*)(formato-*O,O'*)dihydridotris(trimethylphosphine)tungsten(IV). We also report the synthesis of heptahydridobis(trimethylphosphine)rhenium(VII) and octahydridotetrakis(trimethylphosphine)dirhenium(IV) and also new, more convenient syntheses of tetrahydridotetrakis(trimethylphosphine)-tungsten(IV)[2] and -molybdenum(IV).[3] A preliminary account of some of this work has appeared.[4]

Results

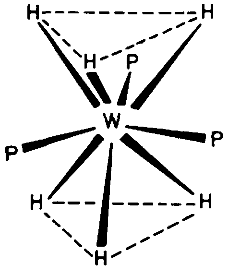
N.m.r. data for the new compounds are collected in the Table.

Hexahydridotris(trimethylphosphine)tungsten(VI).—The interaction of $WCl_4(PMe_3)_3$[5] with $LiAlH_4$ in diethyl ether followed by methanol at −78 °C and crystallisation from hexane affords moderate yields of the colourless $WH_6(PMe_3)_3$, which is a new member of the well known series of compounds $WH_6(PR_3)_3$.[6]

The ^1H and ^{31}P n.m.r. spectra of $WH_6(PMe_3)_3$ indicate that the molecule is fluxional in solution from *ca.* 295 to 183 K. The coupling constants and chemical shifts are similar to those found in other analogues.[6] The crystal structure of the related compound $WH_6(PPhPr^i{}_2)_3$ has been reported.[6b] As no crystals of $WH_6(PMe_3)_3$ suitable for *X*-ray study were obtained and as it is non-rigid in solution it is not possible to define the geometry with certainty. However, it is likely that $WH_6(PMe_3)_3$ adopts either the geometry found for $WH_6(PPhPr^i{}_2)_3$, (**1a**), or alternatively the geometry (**1b**) originally predicted for molecules of this type.[7]



(**1a**)



(**1b**)

(*Formato*-O)(*formato*-O,O'*)dihydrotris(trimethylphosphine)-tungsten*(IV).—The interaction of $WH_6(PMe_3)_3$ with CO_2 (7 atm) in toluene affords good yields of the orange, 18-electron compound $WH_2(OCHO)(O_2CH)(PMe_3)_3$ formed on insertion of CO_2 into the metal–hydrogen bond.[8] The reaction of CO_2 with $MoH_2(PMe_3)_4$ has been studied previously.[9]

The i.r. spectrum of the complex has a broad band at 2 700 cm^{-1}, due to formate hydrogen,[10a] bands at 1 900 and 1 750 cm^{-1} due to tungsten hydrides, and bands at 1 630, 1 620, 1 580, and 1 500 cm^{-1} due to CO_2 stretches of the carboxylate groups.[10b]

At room temperature the molecule is non-rigid in solution. The ^1H n.m.r. spectrum has a binomial quartet due to the hydrides [δ −0.45, *J*(PH) = 52.6 Hz], and a broad singlet (δ 9.05) due to the formate hydrogens. On cooling to −50 °C the singlet at δ 9.05 splits into two lines of equal intensity separated by 11 Hz; this pattern collapses between −55 and −60 °C to a very broad singlet which, between −60 and −70 °C, splits into three lines (δ 9.37, 9.12, 8.77, approximate ratio of intensities 2:1:1). The ^{31}P-{^1H} spectrum is a singlet showing ^{183}W satellites [δ 0.96, *J*(PW) = 246 Hz], which splits into a triplet [*J*(PH) = 52.6 Hz] when the phosphine methyls are selectively decoupled. These observations suggest that the fluxional process involves not only exchange between phosphine and hydride ligands but also exchange between uni- and bi-dentate carboxylate groups. The latter process has previously been observed for $Ru(O_2CMe)_2(CO)(PPh_3)_2$[11a] and the related compounds $M(O_2CR)_2(CO)(PPh_3)_2$ (M = Ru; R = Me, CF_3, C_2F_5, or C_6F_5 and M = Os; R = Me or CF_3).[11b]

Heptahydridobis(trimethylphosphine)rhenium(VII)*–Aniline* (1/1), *Heptahydridobis(trimethylphosphine)rhenium*(VII), *and Octahydridotetrakis(trimethylphosphine)dirhenium*(IV).—The interaction of $Re(NPh)Cl_3(PMe_3)_2$[12] with $LiAlH_4$ in diethyl ether, followed by methanol at −78 °C, afforded moderate yields of $ReH_7(PMe_3)_2{\cdot}PhNH_2$, originally believed[4] to be $ReH_6(PhNH)(PMe_3)_2$, together with small quantities of $Re_2H_8(PMe_3)_4$; these compounds can be separated by fractional crystallisation. $Re_2H_8(PMe_3)_4$ can also be synthesised by the interaction of $ReCl_5$, in the presence of excess PMe_3, in diethyl ether with $LiAlH_4$ followed by treatment with methanol

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† *Non-S.I. unit employed*: atm = 101 325 N m^{-2}.

Table. Proton and ^{31}P nuclear magnetic resonance data

Compound	$\delta(^1H)^a$/p.p.m.	Multiplicity and coupling constants[b]	Assignment	$\delta(^{31}P)^c$/ p.p.m.	Multiplicity and coupling constants[b]	
					^1H broad-band decoupled	^1H of P–CH_3 selectively decoupled
$WH_6(PMe_3)_3$	1.57	't', $\lvert ^2J(PH) + ^4J(PH)\rvert = 8.2$	P–CH_3	−18.55	s, with ^{183}W satellites, $J(PW) = 73.1$	septet, $J(PH) = 37.6$
	−2.61	q, $J(PH) = 37.6$, with ^{183}W satellites, $J(WH) = 27.0$	W–H			
$WH_2(OCHO)_2(O_2CH)(PMe_3)_3$	9.05	s	H–CO_2			
	1.30	't', $\lvert ^2J(PH) + ^4J(PH)\rvert = 7.8$	P–CH_3	−0.96	s, with ^{183}W satellites, $J(PW) = 246.1$	t, $J(PH) = 52.6$
	−0.45	q, $J(PH) = 52.6$	W–H			
$ReH_7(PMe_3)_2\cdot PhNH_2$	6.92	s	Ph			
	2.73	br s	–NH_2			
	1.39	't', $\lvert ^2J(PH) + ^4J(PH)\rvert = 8.9$	P–CH_3	−30.90	s	octet, $J(PH) = 21.0$
	−5.73	t, $J(PH) = 21.0$	Re–H			
$ReH_7(PMe_3)_2$	1.39	't', $\lvert ^2J(PH) + ^4J(PH)\rvert = 8.9$	P–CH_3	−30.90	s	octet, $J(PH) = 21.0$
	−5.73	t, $J(PH) = 21.0$	Re–H			
$Re_2H_8(PMe_3)_4$	1.63	't', $\lvert ^2J(PH) + ^4J(PH)\rvert = 9.6$	P–CH_3	−27.22	s	nonet, $J(PH) = 10.0$
	−6.87	quin, $J(PH) = 10.0$	Re–H			
$WH_4(PMe_3)_4{}^d$	1.62	s	P–CH_3	−27.34	s, with ^{183}W satellites $J(PW) = 170.0$	quin, $J(PH) = 32.9$
	−3.60	quin, $J(PH) = 32.9$ with ^{183}W satellites, $J(WH) = 27.0$	W–H			
$MoH_4(PMe_3)_4{}^d$	1.37	s	P–CH_3	9.30	s	quin, $J(PH) = 35.0$
	−3.96	quin, $J(PH) = 35.0$	Mo–H			

[a] Referenced to $SiMe_4$ at δ 0.00 p.p.m., in C_6D_6; positive shifts downfield of $SiMe_4$. [b] Coupling constants in Hz; s = singlet, d = doublet, t = triplet, 't' = pseudo–triplet, q = quartet, quin = quintet, br = broad. [c] Referenced to external 85% H_3PO_4 at δ 0.00 p.p.m., in C_6D_6; positive shifts downfield of reference. [d] at 70 °C.

at −78 °C. Sublimation of $ReH_7(PMe_3)_2\cdot PhNH_2$ under a dynamic vacuum affords a good yield of $ReH_7(PMe_3)_2$.

Similar rhenium hydrido-compounds with other phosphine ligands are known[13] and recently their reactivity towards alkanes has attracted interest.[1] The compound $ReH_7(PMe_3)_2$ is non-rigid in solution and the ^1H and ^{31}P-$\{^1H\}$ n.m.r. spectra are unchanged down to 183 K. When the phosphine methyls are selectively decoupled the singlet ^{31}P resonance splits into a binomial octet, confirming the presence of seven equivalent hydrides bound to the metal.

A preliminary *X*-ray crystal structure[14] of $ReH_7(PMe_3)_2$ indicates a P–Re–P angle of 142°. This is smaller than the angle observed in $ReH_7(PMe_2Ph)_2$ of 146.8°.[7b] This difference is consistent with the cone angles for PMe_3 (118°) and PMe_2Ph (122°)[15] and implies that the two compounds are isostructural.

The aniline adduct $ReH_7(PMe_3)_2\cdot PhNH_2$ evidently arises from reduction of the phenylimido-group of the starting material. The weak binding of aniline is indicated by the fact that in solution the ^1H and ^{31}P n.m.r. spectra are merely those of $ReH_7(PMe_3)_2$ and aniline with the same chemical shifts and patterns, indicating complete dissociation.

For the dimer $Re_2H_8(PMe_3)_4$, a preliminary structural determination[14] confirmed that the molecule is essentially isostructural with $Re_2H_8(PEt_2Ph)_4$.[7b] It has a planar $Re_2(PMe_3)_4$ unit with an Re–Re distance of 2.53 Å and a P–Re–P angle of 105.4°.

At room temperature in solution $Re_2H_8(PMe_3)_4$ is non-rigid; in the ^1H spectrum the hydride resonance is a binomial quintet [δ −6.87, $J(PH) = 10.0$ Hz]. On cooling this signal begins to broaden, indicating that the rapid exchange between terminal and bridging hydrides is beginning to slow down and by 183 K the signal is a broad singlet, half-width 45 Hz. This observation is consistent with, but does not prove that exchange between non-equivalent sites is occurring.

New Syntheses of $MH_4(PMe_3)_4$ (M = Mo *or* W).—The original synthesis[2] of $WH_4(PMe_3)_4$ required WMe_6 as precursor, while that of $MoH_4(PMe_3)_4$ required $Mo(PMe_3)_6$.[3]

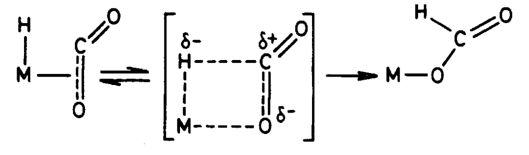
The interaction of $WCl_4(PMe_3)_3{}^5$ in tetrahydrofuran (thf) with hydrogen (*ca.* 7 atm) in the presence of an excess of sodium amalgam gives good yields of the hydride $WH_4(PMe_3)_4$. Similarly, interaction of $MoCl_4(thf)_2{}^{16}$ in thf containing four equivalents of PMe_3 and magnesium under hydrogen (*ca.* 7 atm) gave high yields of $MoH_4(PMe_3)_4$.

Discussion

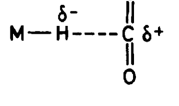
The stability of metal hydrides in high oxidation states is obviously influenced by the nature of the additional ligands, in most cases tertiary phosphines. The two most important factors are the steric requirement and the electronic nature of the phosphine. It has been suggested[6c] that steric bulk of a phosphine is more important than high basicity.

Trimethylphosphine is very basic but is sterically undemanding[15] (cone angle = 118°); however, both $WH_6(PMe_3)_3$ and $ReH_7(PMe_3)_2$ are quite stable thermally, and the latter is far more thermally stable than other phosphine analogues.[13a] This implies that high basicity is at least as important as steric bulk if not more so.

Regarding the CO_2 reaction with $WH_6(PMe_3)_3$, it has been suggested[8c] that CO_2 insertion into metal–hydride bonds can proceed (*a*) in a way similar to olefin insertion which requires prior co-ordination of CO_2 to the metal centre, see below, or (*b*)



by an acid–base interaction between CO_2 and the hydride prior to the formation of the transition state shown below.



$$\mathrm{M{-}\overset{\delta-}{H}{-}{-}{-}{-}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{C}}\;\delta+}$$

In the present case if mechanism (*a*) were involved phosphine or dihydrogen dissociation would be required to provide a vacant site. However $WH_6(PMe_3)_3$ does not exchange with other phosphines, it does not isomerise alk-1-ene at room temperature nor does it undergo exchange with D_2 (1 atm, 25 °C). It thus seems more likely that interaction as in (*b*) occurs leading to the initial insertion, loss of dihydrogen, and second insertion to give the observed tungsten(IV) species.

Experimental

Microanalyses were by Pascher, Bonn. Spectrometers: i.r., Perkin-Elmer 683 using Nujol mulls; n.m.r., Bruker WM-250 and JEOL FX90Q, δ in p.p.m. relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (^{31}P).

All operations were carried out under oxygen-free argon. Solvents, except methanol, were dried over sodium and distilled from sodium benzophenone under nitrogen immediately before use. Methanol was dried over and distilled from magnesium turnings under nitrogen. Melting points were determined in sealed tubes under argon and are uncorrected.

Hexahydridotris(trimethylphosphine)tungsten(VI).—To a stirred suspension of tetrachlorotris(trimethylphosphine)tungsten(IV)[5] (10 g, 18.06 mmol) in diethyl ether (400 cm^3) was added lithium aluminium hydride (7 g, 184 mmol). The colour of the mixture quickly changed from red to yellow-green and hydrogen was evolved. After stirring for 1 h the mixture was cooled to −78 °C and methanol (30 cm^3 of a 1:1 solution in diethyl ether) was added dropwise over 30 min; the mixture was then stirred for another hour at −78 °C and then allowed to warm to room temperature. On warming there is further gas evolution and the colour changes to brown. After stirring for a further hour at room temperature the mixture was centrifuged, the ether was removed, and the residue extracted with hexane (4 × 100 cm^3). The extracts were reduced to *ca.* 50 cm^3 and cooled to −20 °C affording several crops of white crystals. Yield 3.5 g, 46%; m.p. 115 °C (decomp.) (Found: C, 25.9; H, 7.8; P, 20.9. $C_9H_{33}P_3W$ requires C, 25.9; H, 8.0; P, 22.2%). I.r., 1 745s, 1 420s, 1 305m, 1 300s, 1 280s, 950s, 860m, 770w, 725s, and 680s cm^{-1}.

(*Formato*-O)(*formato*-O,O′)*dihydridotris(trimethylphosphine)tungsten*(IV).—Hexahydridotris(trimethylphosphine)tungsten(VI) (0.35 g, 0.84 mmol) in toluene (20 cm^3) was transferred to a pressure bottle, cooled to −78 °C, and pressurised with CO_2 (7 atm). On warming to room temperature, the colour of the mixture slowly changed to yellow, and after 2 h, orange. After stirring for 24 h the pressure was released and the solution filtered, concentrated, and cooled to give orange crystals. Yield: 0.37 g, 87.4%, m.p., 131 °C (decomp.) (Found: C, 26.5; H, 6.3; O, 12.4; P, 17.9. $C_{11}H_{31}O_4P_3W$ requires C, 26.2; H, 6.2; O, 12.7; P, 18.4%). I.r., 2 700w, 1 960—1 860w, 1 750w, 1 630w, 1 620s, 1 580s, 1 500w, 1 430m, 1 360m, 1 320m, 1 305m, 1 295m, 1 240w, 950s, 860m, 825w, 770w, 760w, 735m, 715m, 700w, 670m, and 480w cm^{-1}.

Heptahydridobis(trimethylphosphine)rhenium(VII)–*Aniline* (1/1).—To a stirred suspension of trichloro(phenylimido)bis(trimethylphosphine)rhenium(V)[12] (8.5 g, 15.9 mmol) in diethyl ether (400 cm^3) was added lithium aluminium hydride (6 g, 158 mmol). The colour of the mixture quickly changed from green to very pale yellow and hydrogen was evolved.

After stirring at room temperature for 1 h the mixture was cooled to −78 °C and methanol (26 cm^3 of a 1:1 solution in Et_2O) was added dropwise over 30 min. It is important to have efficient stirring at this stage as the reaction is quite exothermic, and any local rises in temperature appear to increase the amount of $Re_2H_8(PMe_3)_4$ produced. After stirring for a further 1 h at −78 °C the mixture was allowed to warm to room temperature, when there is further gas evolution and the colour changes to red-brown. After stirring for 1 h at room temperature and the mixture was centrifuged, the ether solution was evaporated, and the residue extracted with hexane (4 × 100 cm^3) to give a red solution which on reduction in volume and cooling affords several crops of white crystals. Any red $Re_2H_8(PMe_3)_4$ present can be removed by fractional crystallisation, as it is considerably more soluble in hexane than is $ReH_7(PMe_3)_2 \cdot PhNH_2$. The compound sublimes in vacuum at *ca.* 40 °C. Yield: 3.9 g, 56.2%; m.p. 78—80 °C (decomp.) (Found: C, 33.0; H, 7.3; N, 3.2; P, 14.3. $C_{12}H_{32}NP_2Re$ requires C, 33.0; H, 6.9; N, 3.2; P, 14.2%). I.r., 3 935w, 3 850w, 3 780w, 3 440s, 3 340s, 3 220w, 3 080w, 3 075w, 3 025w, 2 010w, 1 975s, 1 905s, 1 865s, 1 625s, 1 605s, 1 520w, 1 500s, 1 438s, 1 425s, 1 345w, 1 310w, 1 290s, 1 170s, 1 150w, 1 045w, 1 030w, 995w, 950s, 880m, 870s, 790s, 760s, 740s, 700s, 685s, 600m, and 515s cm^{-1}.

Heptahydridobis(trimethylphosphine)rhenium(VII).—The aniline adduct (1 g, 2.3 mmol) was warmed to 40 °C under vacuum in a Schlenk tube connected by a short tube to a trap cooled by liquid nitrogen. After 30 min a white condensate of aniline appears in the cold trap and small white crystals of the pure hydride started to form on the walls of the Schlenk tube. After 10 h no further aniline condenses and the pure hydride can be collected from the walls of the Schlenk tube. The compound sublimes in vacuum at *ca.* 40 °C. Yield: 0.64 g, 81.3%; m.p. 102 °C (decomp.) (Found: C, 21.2; H, 7.3; P, 18.3. $C_6H_{25}P_2Re$ requires C, 20.9; H, 7.3; P, 18.0%). I.r., 2 010w, 1 975s, 1 900s, 1 860s, 1 425s, 1 310m, 1 295s, 1 155w, 960s, 900w, 875s, 800s, 750s, 700s, and 600w cm^{-1}.

Octahydridotetrakis(trimethylphosphine)dirhenium(IV).—To a stirred suspension of rhenium pentachloride (4 g, 11 mmol) in diethyl ether (200 cm^3) at −100 °C was added trimethylphosphine (2.5 cm^3, 25 mmol) and lithium aluminium hydride (4 g, 105.4 mmol). The dark purple reaction mixture was allowed to warm slowly to room temperature. *Care is required* as the reaction is *very exothermic*, and between *ca.* −20 °C and 0 °C the reaction was very vigorous and a large volume of hydrogen evolved. After stirring for *ca.* 12 h at room temperature the yellow-orange mixture was cooled to −78 °C and methanol (18 cm^3 of 1:1 solution in diethyl ether) was added dropwise over 30 min. After stirring for 1 h at −78 °C the reaction mixture was allowed to warm to room temperature. At 0 °C the solution goes deep red; it was then stirred for 2 h at room temperature, centrifuged, and the red solution evaporated. The dark red powder was extracted with hexane (250 cm^3); the filtered solution on reduction in volume and cooling to −20 °C affords several crops of dark red crystals. Yield: 2.0 g, 53.1%; m.p. 110 °C (Found: C, 20.2; H, 5.8; P, 17.5. $C_{12}H_{44}P_4Re_2$ requires C, 21.0; H, 6.5; P, 18.1%). I.r., 2 800w, 1 930s, 1 420s, 1 295s, 1 270s, 940s, 860s, 850s, 790s, 715s, 685s, 670s, and 575m cm^{-1}.

Tetrahydridotetrakis(trimethylphosphine)tungsten(IV).—To a suspension of tetrachlorotris(trimethylphosphine)tungsten(IV)[5] (5 g, 9.03 mmol) in tetrahydrofuran (50 cm^3) at −78 °C in a pressure bottle was added sodium amalgam (2 g Na in 20 cm^3 Hg). The bottle was pressurised with hydrogen (7 atm) and allowed to warm to room temperature. After stirring overnight the orange solution was depressurised, transferred to a flask, and evaporated. The residue was extracted with hexane (2 × 50 cm^3) which was filtered, concentrated, and cooled to −20 °C to yield white crystals. Yield: 2.67 g, 80.2% (maximum theoretical yield is 0.75 of 9.03 mmol, *i.e.* 6.77 mmol); m.p. 80 °C (Found: C, 29.1; H, 8.2; P, 25.1. $C_{12}H_{40}P_4W$ requires C, 29.3; H, 8.2; P, 25.2%). I.r., 1 760s, 1 720s, 1 435m, 1 415s, 1 295s, 1 275s, 940s, 850s, 715s, 700s, and 660s cm^{-1}.

Tetrahydridotetrakis(trimethylphosphine)molybdenum(IV).— To a suspension of tetrachlorobis(tetrahydrofuran)molybdenum(IV)[16] (5 g, 13.1 mmol) in tetrahydrofuran (50 cm^3) at −78 °C was added trimethylphosphine (5.2 cm^3, 52 mmol). The mixture was transferred cold to a pressure bottle containing magnesium turnings (3 g). The bottle was pressurised with hydrogen (*ca.* 7 atm) and allowed to warm to room temperature. After stirring for *ca.* 12 h the brown-orange solution was depressurised, transferred to a flask, and evaporated. The residue was extracted with hexane, which was concentrated and cooled to give white crystals. Yield: 4.30 g, 81.2%; m.p. 74 °C (Found: C, 35.4; H, 9.9; P, 30.4. $C_{12}H_{40}MoP_4$ requires C, 35.6; H, 10.0; P, 30.6%). I.r., 1 712s, 1 675s, 1 440m, 1 420s, 1 300s, 1 280s, 1 100w, 940s, 860s, 720s, 670s, and 540w cm^{-1}.

Acknowledgements

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