# The Reactions of Tetrahydridotetrakis(methyldiphenylphosphine)-molybdenum(IV) and -tungsten(IV) with Acids †

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Neutral and cationic hydrido-complexes of molybdenum and tungsten have been prepared by interaction of the compounds $MH_4(PMePh_2)_4$ (M = Mo and W) with acids HX (X = $CF_3CO_2$, $p$-$MeC_6H_4SO_3$, $BF_4$, and $PF_6$). The reactions of $MoH_4(PMePh_2)_4$ are accompanied by hydrogen evolution and yield different $Mo^{IV}$ products that depend on the nature of the anion, namely neutral species $MoH_2X_2(PMePh_2)_3$ (X = $CF_3CO_2$ and $p$-$MeC_6H_4SO_3$) and cationic species $[MoH_3(PMePh_2)_3]X$ (X = $BF_4$ and $PF_6$). By contrast $WH_4(PMePh_2)_4$ is readily protonated to give the cationic pentahydrido-species $[WH_5(PMePh_2)_4]^+$. The corresponding trifluoroacetate isolated as $[WH_5(PMePh_2)_4][H(O_2CCF_3)_2]$·toluene loses hydrogen on melting to yield the neutral compound $WH_2(CF_3CO_2)_2(PMePh_2)_3$.

With hydrochloric acid $MoH_4(PMePh_2)_4$ gives a green compound $Mo_2Cl_4(PMePh_2)_4$ which readily transforms into a blue isomer, while $WH_4(PMePh_2)_4$ gives again the $WH_5(PMePh_2)_4{}^+$ ion. The compounds are characterised by i.r. and $^1H$ and $^{31}P$ n.m.r. spectroscopy.

POLYHYDRIDO-COMPLEXES of transition metals have been known for many years. $K_2ReH_9$, the first compound of this type, was prepared by Ginsberg *et al.*[1] Later,[2] three classes of complexes $ReH_7L_2$, $\{ReH_xL_2\}_2$ ($x < 7$) and $ReH_5L_3$ were isolated, the nature depending on the tertiary phosphine, L, used and the experimental conditions. Other polyhydrido-complexes of second and third row transition metals are now known.[3-7]

For tungsten $WH_6L_3$ (L = $PMe_2Ph$ or $PEt_2Ph$) was prepared by Moss and Shaw,[8] while Pennella [9] obtained the compounds $MoH_4L_4$ (L = $PMePh_2$ or $PEtPh_2$; $L_2$ = $Ph_2PCH_2CH_2PPh_2$) and subsequently Chatt *et al.*[10] reported the preparation of the tungsten analogues. Both the molybdenum and the tungsten tetrahydrides are stereochemically non-rigid, and the structure of $MoH_4(PMePh_2)_4$ has been determined by single-crystal *X*-ray analysis.[11]

Although $WH_6(PMe_2Ph)_3$ reacts with HCl to give $WCl_4(PMe_2Ph)_2$,[8] hydrido-species also formed could not be isolated. We report the reactions of $MH_4(PMePh_2)_4$ (M = Mo and W) with several acids which afford new neutral or cationic hydrido-complexes. An exception is the interaction of hydrochloric acid with $MoH_4(PMePh_2)_4$ which gives the binuclear complex $Mo_2Cl_4(PMePh_2)_4$, this reaction providing a new route to the compounds $Mo_2X_4(PR_3)_4$ which contain two quadruply-bonded molybdenum units.[12]

Spectroscopic data for new compounds are given in Table 1.

*Molybdenum.*—(1) *Trifluoroacetic,* p-*toluenesulphonic, tetrafluoroboric and hexafluorophosphoric acids.* The compound $MoH_4(PMePh_2)_4$ reacts with an excess of $CF_3CO_2H$ in toluene to give $MoH_2(CO_2CF_3)_2(PMePh_2)_3$ according to the following stoicheiometry:

$$MoH_4(PMePh_2)_4 + 2CF_3CO_2H \longrightarrow MoH_2(CO_2CF_3)_2(PMePh_2)_3 + 2H_2$$

The amount of hydrogen evolved was determined manometrically as 1.95 mol equiv. The compound is a red crystalline solid, moderately air-stable in the solid state and very sensitive in solution. Its i.r. spectrum (KBr disc) shows a weak band at 1 850 cm$^{-1}$ [ν(Mo–H)] and stronger absorptions at 1 705vs, 1 675vs, and 1 605m cm$^{-1}$ [$\nu(CO_2)$asym]. In dichloromethane solution only a broad, intense band centred at 1 675 cm$^{-1}$ and a smaller one at 1 608 cm$^{-1}$ can be observed in this region. Although the presence of other absorptions due to the phosphine ligands does not allow unambiguous assignment of $\nu(CO_2)$sym, a weaker band at 1 402 cm$^{-1}$ (which is not present in the spectra of other similar compounds without $CF_3CO_2{}^-$ groups reported here) can be attributed to this vibration. These observations, together with the molecular weight and conductivity data (Table 2) for this compound, suggest unidentate trifluoroacetate groups [13] although bidentate co-ordination by one of the $CF_3CO_2{}^-$ groups or the existence of a mixture of isomers cannot be excluded.

The reaction with $p$-toluenesulphonic acid (Htos) is similar, hydrogen being evolved [2 mmol per mmol of $MoH_4(PMePh_2)_4$]. The red crystalline compound $MoH_2(tos)_2(PMePh_2)_3$ may be isolated as a toluene solvate. This compound is similar to the trifluoroacetate but is more sensitive to air, especially in solution. Its i.r. spectrum shows weak bands at 1 880 and 1 830 cm$^{-1}$ [ν(Mo–H)] and other absorptions characteristic of the $p$-$MeC_6H_4SO_3{}^-$ and phosphine ligands. In the 1 300—1 000 cm$^{-1}$ region the spectrum consists of strong and rather broad bands from which no conclusions can be drawn regarding the nature of the tosylate groups. However, the solubility in non-polar solvents and failure to conduct in dichloromethane (Table 2) suggest that the anion is co-ordinated to molybdenum.

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† No reprints available.

[1] A. P. Ginsberg, J. M. Miller, and E. Koubek, *J. Amer. Chem. Soc.*, 1961, **83**, 4909.

[2] J. Chatt and R. S. Coffey, *Chem. Comm.*, 1966, 545; *J. Chem. Soc. (A)*, 1969, 1963.

[3] H. D. Kaesz and R. B. Saillant, *Chem. Rev.*, 1972, **72**, 231.

[4] D. Giusto, *Inorg. Chim. Acta Rev.*, 1972, 91.

[5] J. P. McCue, *Co-ordination Chem. Rev.*, 1973, **10**, 265.

[6] F. N. Tebbe, *J. Amer. Chem. Soc.*, 1973, **95**, 5823.

[7] R. R. Shrock, *J. Organometallic Chem.*, 1976, **121**, 373.

[8] J. R. Moss and B. L. Shaw, *Chem. Comm.*, 1968, 632; *J.C.S. Dalton*, 1972, 1910.

[9] F. Pennella, *Chem. Comm.*, 1971, 158; *Inorg. Synth.*, 1974, **15**, 42.

[10] B. Bell, J. Chatt, G. J. Leigh, and T. Ito, *J.C.S. Chem. Comm.*, 1972, 34.

[11] P. Meakin, L. J. Guggenberger, W. G. Peet, E. L. Muetterties, and J. P. Jesson, *J. Amer. Chem. Soc.*, 1973, **95**, 1467.

[12] F. A. Cotton, *Chem. Soc. Rev.*, 1975, **4**, 27, and references therein.

[13] C. D. Garner and B. Hughes, *Adv. Inorg. Chem. Radiochem.*, 1975, **17**, 1.

TABLE 1

Selected spectroscopic data for the molybdenum and tungsten complexes

| | | $^1$H n.m.r. | | | | | $^{31}$P n.m.r. | |
|---|---|---|---|---|---|---|---|---|
| | | Ligand resonances (P-Me) [b] | Hydride resonance | | | | | |
| Compound | Vibrational data [a] | | τ | Multiplicity | $J_{P-H}$ | $J_{W-H}$ | δ [c] | $J_{W-P}$ |
| $MoH_2(CO_2CF_3)_2(PMePh_2)_3$ | 1 850vw, ν(M–H); 1705vs, 1 675vs, 1 605m, $\nu(CO_2)$asym; 1 402, $\nu(CO_2)$sym | 8.4 | 11.35 | Quartet | 57 | | 51.9 | |
| $MoH_2(p\text{-}MeC_6H_4SO_3)_2(PMePh_2)_3\cdot C_7H_8$ | 1 880w, 1 830w, ν(M–H) | 8.2 | 11.65 | Quartet | 57 | | 51.7 | |
| $[MoH_3(PMePh_2)_3][BF_4]$ | 1 925w, 1 860w, ν(M–H) | 8.6 | 11.70 | Quartet | 56 | | 54.1, 53.3, 52.3, 51.5 | |
| $[MoH_4(PMePh_2)_3][PF_6]$ | 1 840vw, ν(M–H) | 8·3 | 11.60 | Quartet | 57 | | 54.1, 53.3, 52.3, 51.5 | |
| $Mo_2Cl_4(PMePh_2)_4$ (blue) | I.r.: 330s, 280m, ν(M–Cl)<br>Raman: 345, ν(M–M) | 7.9 | | | | | 5.7 | |
| $Mo_2Cl_4(PMePh_2)_4$ (green) | I.r.: 340w, 310m, 280vw, ν(M–Cl)<br>Raman: 345, ν(M–M) | 7.9 | | | | | 5.7 | |
| $[WH_5(PMePh_2)_4][H(CO_2CF_3)_2]\cdot C_7H_8$ | 1 890s, 1 840s, ν(M–H); 1 780vs, 1 735vs, $\nu(CO_2)$asym; 1 380, $\nu(CO_2)$sym | 8.1 | 9.63 | Quintet | 36.5 | 19.6 | 2.9 | 76.6 |
| $[WH_5(PMePh_2)_4][H(p\text{-}MeC_6H_4SO_3)_2]$ | 1 890s, 1 840s, ν(M–H) | 8.1 | 9.63 | Quintet | 36.5 | 19.6 | 2.9 | 76.6 |
| $[WH_5(PMePh_2)_4][BF_4]$ | 1 890s, 1 840s, ν(M–H) | 8.1 | 9.63 | Quintet | 36.5 | 19.6 | 2.9 | 76.6 |
| $[WH_5(PMePh_2)_4][PF_6]\cdot C_4H_8O$ | 1 890s, 1 840s, ν(M–H) | 8.1 | 9.63 | Quintet | 36.5 | 19.6 | 2.9 | 76.6 |
| $[WH_5(PMePh_2)_4]Cl\cdot C_4H_8O$ | 1 890s, 1 840s, ν(M–H) | 8.1 | 9.63 | Quintet | 36.5 | 19.6 | 2.9 | 76.6 |
| $WH_2(CO_2CF_3)_2(PMePh_2)_3$ [d] | 1 890vw, ν(M–H); 1 705s, 1 765vs, 1 650w, 1 600w, $\nu(CO_2)$asym; 1 385, $\nu(CO_2)$sym | 8.3 | 7.0 | Quartet | 48 | | 27.8, 27.6, 24.7, 24.3 | |

[a] In KBr discs or Nujol mulls. [b] Complex multiplet. [c] Chemical shifts are to high frequency of external 85% $H_3PO_4$. [d] $^1$H n.m.r. data corresponding to the spectrum at 75 °C.

TABLE 2

Analytical data and properties of the molybdenum and tungsten complexes

| | | Analysis [b] (%) | | | | | Λ [c] |
|---|---|---|---|---|---|---|---|
| Compound | M.p. ($\theta_c$/°C) [a] | C | H | P | Other | $M$ [b] | $\Omega^{-1}$ cm$^2$ mol$^{-1}$ |
| $MoH_2(CF_3CO_2)_2(PMePh_2)_3$ | 109—111 | 55.4 | 4.6 | 10.0 | | 860 | 0.9 [e] |
| | | (55.8) | (4.4) | (10.1) | | (924) | |
| $MoH_2(p\text{-}MeC_6H_4SO_3)_2(PMePh_2)_3\cdot C_7H_8$ | 89—91 | 62.5 | 5.8 | 7.6 | S 5.6 | 616 | 1.1 [e] |
| | | (63.6) | (5.6) | (8.2) | (5.6) | (1 132) | |
| $[MoH_3(PMePh_2)_3][BF_4]$ | 166—168 | 59.7 | 5.3 | 11.8 | | | 46 |
| | (decomp.) | (59.5) | (5.3) | (11.8) | | | |
| $[MoH_3(PMePh_2)_3][PF_6]$ | 104—107 | 55.9 | 5.1 | 14.3 | | | 59 |
| | | (55.4) | (5.0) | (14.7) | | | |
| $Mo_2Cl_4(PMePh_2)_4$ (blue) | 133 (decomp.) | 55.8 | 4.8 | 10.5 | Cl 12.2 | | |
| | | (55.0) | (4.6) | (10.9) | (12.5) | | |
| $Mo_2Cl_4(PMePh_2)_4$ (green) | 120 (decomp.) | 54.8 | 5.0 | 11.4 | 10.2 | | |
| $[WH_5(PMePh_2)_4][H(CO_2CF_3)_2]\cdot C_7H_8$ | 104—106 [d] | 57.3 | 5.0 | 9.8 | | | 70 |
| | | (57.8) | (5.0) | (9.5) | | | |
| $[WH_5(PMePh_2)_4][H(p\text{-}MeC_6H_4SO_3)_2]$ | 108—110 [d] | 58.7 | 5.6 | 8.0 | S 5.5 | | 57 [f] |
| | | (59.5) | (5.4) | (9.3) | (4.8) | | |
| $[WH_5(PMePh_2)_4][BF_4]$ | 162—167 [d] | 58.1 | 5.4 | 11.7 | | | 80 [f] |
| | | (58.0) | (5.3) | (11.5) | | | |
| $[WH_5(PMePh_2)_4][PF_6]\cdot C_4H_8O$ | 170—175 [d] | 54.9 | 5.4 | 12.7 | | | 77 |
| | | (55.7) | (5.4) | (12.8) | | | |
| $[WH_5(PMePh_2)_4]Cl\cdot C_4H_8O$ | 77—81 [d] | 60.6 | 5.7 | 11.4 | Cl 3.3 | | 58 |
| | | (61.3) | (5.9) | (11.3) | (3.2) | | |
| $WH_2(CF_3CO_2)_2(PMePh_2)_3$ | 106—109 | 51.1 | 4.3 | 9.1 | | 940 | 0.8 [e] |
| | | (51.0) | (4.1) | (9.2) | | (1 011.8) | |

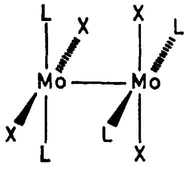
[a] In sealed capillary tubes. [b] Calculated values are given in parentheses. [c] In *ca.* $10^{-3}$M-solutions. [d] See text. [e] In $CH_2Cl_2$. In $CH_3NO_2$.

Addition of methanolic solutions of $HBF_4$ and $HPF_6$ to $MoH_4(PMePh_2)_4$ in tetrahydrofuran results again in hydrogen evolution and from the red–brown solutions salts of the ion $[MoH_3(PMePh_2)_3]^+$ can be isolated. Both are air sensitive, the hexafluorophosphate particularly so. Their i.r. spectra (Table 1) show weak absorptions in the metal–hydride stretching region. Both compounds are conducting in $CH_2Cl_2$ and in $CH_3NO_2$. For the fluoroborate, over the concentration range $10^{-2}$—$5 \times 10^{-4}$M, plots of $\Lambda_o - \Lambda_e$ *vs.* $\sqrt{c}$ gave a straight line passing through the origin with a slope of 160, which is somewhat greater than the expected for a 1 : 1 electrolyte. The ion $[MoH_3(PMePh_2)_3]^+$ has also been isolated as tetracarbonylcobaltate(—I) salt by anion exchange with $Na[Co(CO)_4]$.

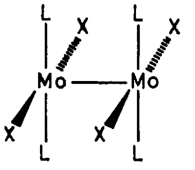
(2) *Hydrochloric acid.* The reactions of HCl with $ReH_5(PEt_2Ph)_3$ and $ReH_7(PEt_2Ph)_2$ give $ReCl_3(PEt_2Ph)_3$ and $ReCl_4(PEt_2Ph)_2$ respectively;[2] $OsH_4(PMe_2Ph)_3$ gives $[OsH_5(PMe_2Ph)_3]^+$ though no salts could be isolated.[14]

The complex $MoH_4(PMePh_2)_4$ reacts with an excess of hydrochloric acid to give the known[15] complex β-$MoCl_3(PMePh_2)_3$. However, addition of aqueous HCl to a tetrahydrofuran solution of $MoH_4(PMePh_2)_4$ (2 : 1 molar ratio HCl : Mo) gives a yellow-red solution which becomes deep green. From the solution the dimer $Mo_2Cl_4(PMePh_2)_4$ can be isolated. This green compound is difficult to purify since it changes irreversibly to the blue isomer $Mo_2Cl_4(PMePh_2)_4$, but on several occasions good analytical samples have been obtained. The blue compound is a member of the series of dinuclear complexes $Mo_2X_4(PR_3)_4$ [16a,b,17] and was synthesized independently[17] during the progress of this work, from the reaction of $K_4Mo_2Cl_8$ with an excess of phosphine. The Raman spectra of both compounds show an intense sharp band at 345 cm$^{-1}$ assignable to the metal–metal stretching vibration[18] by analogy with studies on $Mo_2X_4L_4$. The electronic absorption spectrum ($\varepsilon_{max.}$ *ca.* 600 nm) corresponds to the $\delta \rightarrow \delta^*$ transition[19] and is responsible for the intense colour.

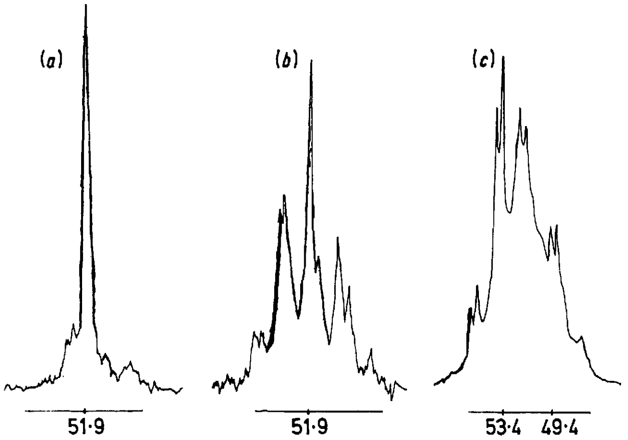
The i.r. spectrum of the blue compound in the low frequency region is similar to spectra of other $Mo_2X_4L_4$ compounds[16] and the structure is by analogy, clearly (I). The i.r. spectrum of the green isomer has a medium intensity band at *ca.* 310 cm$^{-1}$ and a weaker absorption at 340 cm$^{-1}$, a spectrum typical of the *cis*-complexes $Mo_2X_4(LL)_2$ (LL = bidentate alkyl sulphides, bipyridine) as found also for $Mo_2Cl_4L_4$ (L = MeCN and $Me_2NCHO$). The similarity of the $^1$H n.m.r. spectra and the identity of the $^{31}$P n.m.r. spectra of both green and blue compounds rules out a *cis*-structure for the former. Since the blue → green conversion does not occur either thermally or photochemically, structure (II) seems reasonable for the green isomer.



(I)
(blue)



(II)
(green)



$^{31}$P N.m.r. spectra of $MoH_2(CF_3CO_2)_2(PMePh_2)_3$ at various temperatures: (a) room temperature; (b) —10 °C; (c) —40 °C

(3) *N.m.r. spectra.* The $^1$H n.m.r. spectra of the hydrido-complexes show a 1 : 3 : 3 : 1 quartet due to coupling of the hydrido-protons to the phosphines. The equivalence of the hydrogens is doubtless due to non-rigidity as is well established for hydrido-species.[2,7,14]

The $^1$H and especially the $^{31}$P n.m.r. spectra of $MoH_2(CO_2CF_3)_2(PMePh_2)_3$ suggest the presence in solution of different isomers. At 35 °C the $^1$H n.m.r. spectrum shows a complex multiplet centred at *ca.* τ 8.4 due to the methylphosphine protons, and a sharp quartet centred at τ 11.35. On cooling to 10 °C a doublet appears at τ 7.9 while the multiplet at 8.4 p.p.m. becomes more complex with new absorptions superimposed on its high field side. At —30 °C the doublet centred at τ 7.9 becomes sharper and more intense, and in the multiplet at 8.4 p.p.m. a pseudo-triplet at 8.4 p.p.m. and absorptions at 8.7 and 8.78 can be clearly observed. The hydride protons still appear as a quartet although considerably broader. Further cooling does not essentially modify the spectrum though it causes considerable broadening of the absorptions, the hydrido-resonances being very broad at —90 °C.

$^{31}$P N.m.r. spectra at different temperatures are shown in the Figure. The room-temperature spectrum consists

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[14] P. G. Douglas and B. L. Shaw, *J. Chem. Soc.* (*A*), 1970, 334.

[15] M. W. Anker, J. Chatt, G. J. Leigh, and G. Wedd, *J.C.S. Dalton*, 1975, 2639.

[16] (*a*) J. San Filippo, jun., *Inorg. Chem.*, 1972, **11**, 3140; (*b*) J. San Filippo, jun., H. J. Sniadoch, and R. L. Grayson, *Inorg. Chem.*, 1974, **13**, 2121.

[17] H. D. Glicksman, A. D. Hanur, T. J. Smith, and R. A. Walton, *Inorg. Chem.*, 1976, **15**, 2205.

[18] J. San Filippo, jun., and H. J. Sniadoch, *Inorg. Chem.*, 1973, **12**, 2326.

[19] F. A. Cotton, B. A. Frenz, B. R. Stults, and T. R. Webb, *J. Amer. Chem. Soc.*, 1976, **98**, 2768; J. San Filippo, jun., and H. J. Sniadoch, *Inorg. Chem.*, 1976, **15**, 2209.

mainly of a sharp singlet at 51.9 p.p.m.* that is converted into a 1 : 2 : 1 triplet on selectively decoupling the ligand protons; this confirms the formulation as the dihydrido-complex $MoH_2(CO_2CF_3)_2(PMePh_2)_3$. Some other, considerably smaller absorptions are also observed at ambient temperature and they become more intense as the temperature is lowered, becoming at −40 °C the more intense resonances in the spectrum. Cooling to −80 °C causes broadening of the peaks and a further diminution in the intensity of the 51.9 p.p.m. resonance. These results can be interpreted in terms of an equilibrium between two isomeric interconverting species (A) and (B). At room and higher temperatures the equilibrium is shifted towards (A), which is fluxional and gives rise to the pseudotriplet at 8.4 p.p.m. and the quartet at 11.4 p.p.m. in the $^1H$ n.m.r. spectrum, and to the singlet at 51.9 p.p.m. in the $^{31}P$ n.m.r. spectrum. Upon lowering the temperature isomer (B) begins to predominate. This compound has non-equivalent phosphines, its $^1H$ n.m.r. spectrum consisting of a doublet at 7.9 p.p.m. due to a *cis*-phosphine ($J_{P-H}$ 8.7 Hz) and a ' virtually coupled ' triplet centred at $\tau$ 8.7 arising from two mutually *trans*-phosphines through virtual coupling ($J_{P-H} + J_{P'-H}$ 9.3 Hz). Integration of the doublet *vs.* the complex multiplet at $\tau$ 8.4 is higher than the theoretical 1 : 2 ratio that would be expected if only a species with a *cis*- and two *trans*-phosphines were present in solution. The $^{31}P$ n.m.r. spectrum of (B) can be interpreted in terms of an $AB_2$ system ($\nu_A = 49.4$ p.p.m.; $\nu_B = 54.4$ p.p.m.; $J_{AB}$ 75 Hz).

The $^{31}P$ n.m.r. spectrum of $MoH_2(tos)_2(PMePh_2)_3$ shows an intense and somewhat broad peak at 51.7 p.p.m. and a smaller, also broad, resonance at −26.1 p.p.m. due to free phosphine, indicating dissociation with slow phosphine exchange on the n.m.r. time scale.

As expected, $[MoH_3(PMePh_2)_3]^+$ salts have identical $^{31}P$ n.m.r. spectra consisting of a complex multiplet of four lines, the sharp outer at 54.1 and 51.5 p.p.m., the inner, broader and complex centred at 53.3 and 52.3 p.p.m. At 0 °C the apparent quartet is very broad, and cooling at −90 °C only causes another broad resonance to appear at slightly higher field. At 45 °C the multiplet resembles a quartet, the outer peaks being very sharp and the inner still broad. At 60 °C the spectrum is essentially the same though extensive decomposition and dissociation of phosphine has taken place. Variable-temperature $^1H$ n.m.r. studies are not more informative, only broadening of the peaks being observed at low temperatures. No conclusions about the structure of this compound can be drawn.

*Tungsten Complexes.*—On addition of acid to a solution of $WH_4(PMePh_2)_4$ protonation occurs leading to the cationic species $[WH_5(PMePh_2)_4]X$ (X = $CF_3CO_2$, tos, $BF_4$, $PF_6$, and Cl). The reactions are reversible and addition of methanolic KOH to methanol solutions precipitates the free base. The compounds are white crystalline solids air-stable in the solid state but more sensitive in solution. The $[BF_4]^-$ and the $[PF_6]^-$ salts turn blue slowly or on heating but only partial decomposition has evidently occurred. We have been unable to isolate the blue material but e.s.r. spectra show that a paramagnetic species is present [$g_z = 2.00$, $g_y = 1.94$, $g_x = 1.81$ with poorly resolved doublet structure along $g_x$ (3 mT) and $g_y$ (3 mT) consistent with interaction with only one H atom].

The trifluoroacetate and tosylate turn brown at *ca.* 100 °C and melt to red-brown liquids. For the former, thermal decomposition gives the red crystalline neutral complex $WH_2(CO_2CF_3)_2(PMePh_2)_3$ whose i.r. spectrum suggests, but does not prove, the presence of unidentate carboxylate.

The n.m.r. spectra of the $[WH_5(PMePh_2)_4]^+$ salts are (apart from solvating molecules) identical. The hydride resonance is a sharp 1 : 4 : 6 : 4 : 1 quintet centred at $\tau$ 9.63, $J_{P-H}$ 36.5 Hz with satellite lines due to $^1H-^{183}W$ coupling ($^{183}W$, 14.4% abundance). This coupling constant, 19.6 Hz, is significantly lower than the values of 31 and 30 Hz found for the tetrahydrides $WH_4(PMe_2Ph)_4$ and $WH_4\{P(OEt)_2Ph\}_4$ respectively.[11] This fairly large decrease can be attributed to a lowering of the *s*-electron character of the metal–hydrogen bond due to an increase in the co-ordination number of the metal.[20] No changes were observed upon cooling at −90 °C although both the methyl-phosphine and the hydride resonances became considerably broader. The $^{31}P$ n.m.r. spectra of the ions are a sharp singlet at 2.9 p.p.m. flanked by two satellites due to coupling to $^{183}W$ ($J_{W-H}$ 76.6 Hz). No variations in the spectra were observed upon cooling at −90 °C. $^{31}P$-$\{^1H\}$ n.m.r. decoupling gives unequivocal evidence for the number of hydrido-protons, as the singlet at 2.9 p.p.m. characteristic of the $[WH_5P_4]^+$ cation split into a sharp, slightly distorted sextet upon selectively decoupling the phenyl-phosphine protons.

$^1H$ and $^{31}P$ n.m.r. studies of $WH_2(CO_2CF_3)_2(PMePh_2)_3$, as for $MoH_2(CO_2CF_3)_2(PMePh_2)_3$, suggest the presence in solution of two isomers. The $^1H$ n.m.r. spectrum consists at 35 °C in the $\tau$ 5—10 region of a complex multiplet centred at $\tau$ 8.3, with some weaker absorptions superimposed on its high field side (*ca.* $\tau$ 8.48 and 8.56), and several weak and rather broad resonances at $\tau$ 7.68 and 7.52 (doublet), 7.3, 6.6, 6.35, and 5.8. On increasing the temperature the broad resonances sharpen and at 75 °C the spectrum shows only a broad unresolved signal centred at 8.3 p.p.m., a weak broad absorption at *ca.* $\tau$ 7.6, and three sharp resonances that constitute the low field part of a 1 : 3 : 3 : 1 quartet centred at *ca.* $\tau$ 7 ($J_{P-H}$ 48 Hz) arising from the coupling of the hydrido-protons to the phosphines. On lowering the temperature, the hydride signals broaden and at 15 °C each peak is split into two, giving rise to two quartets approximately centred at $\tau$ 6.8 and 7.2 respectively. Assignment is only approximate since the broad and weak resonance appearing at $\tau$ 7.6 in the spectrum at 75 °C gives now a sharp doublet, and only five of the expected eight peaks can be clearly observed, the remaining three being hidden under the

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* $^{31}P$ Chemical shifts are to high frequency of external 85% $H_3PO_4$.

[20] E. L. Muetterties, ed., ' Transition Metal Hydrides,' Marcel Dekker Inc., New York, 1971, ch. 4.

methyl-phosphine resonances. At this temperature, a ' virtually-coupled ' triplet-like structure can also be observed on the high field side of the multiplet at 8.3, centred at *ca.* $\tau$ 8.48. On further cooling the complexity of the spectrum increases and at −30 °C the low field part of the hydrido-resonances becomes very complex. On the other hand, the intensities of the doublet at $\tau$ 7.6 and the triplet at 8.48 have increased considerably. These features can be explained by the existence of two interconverting isomeric forms (A) and (B). At temperatures higher than room temperature, form (A) predominates. This species is fluxional and at 75 °C the two hydrido-protons interchange rapidly on the n.m.r. time scale coupling equally to the three phosphines giving a 1 : 3 : 3 : 1 quartet. Upon cooling (A) becomes non-fluxional and at 15 °C the two hydrido-protons are no longer equivalent and give rise to two quartets with slightly different chemical shifts. No coupling between the two hydrogens has been observed. Below −15 °C the equilibrium seems to shift towards form (B) which has non-equivalent phosphines, the doublet at $\tau$ 7.6 due to a *cis*-phosphine ($J_{P-H}$ 8.6 Hz) and the apparent triplet at *ca.* 8.5 arising from two *trans*-phosphines through virtual coupling ($J_{P-H} + J_{P'-H}$ 8.3 Hz). For this isomeric form, the two hydrido-protons will not probably be equivalent and would, therefore, give a complex pattern in coupling to the three phosphines. As before, integration of the doublet and multiplet areas does not give the theoretical 1 : 2 ratio that would be expected if only a single species with one *cis*- and two *trans*-phosphines were present in solution. Further confirmation of the presence of two species comes from variable-temperature $^{31}P$ n.m.r. studies. The room temperature spectrum consists mainly of a sharp singlet at 24.7 p.p.m. and other smaller absorptions at 30.6 (very weak), 27.8, 27.6, 24.3, and 21.7 (very weak). Upon cooling the last resonances increase their intensities at the expense of the one at 24.7 p.p.m. The situation is reversed on warming, the absorption at 24.7 p.p.m. again becoming the strongest. At 60 °C the spectrum consists mainly of a single, rather broad resonance at 24.7 p.p.m., the broadening being probably due to the partial decomposition of the compound that occurs at that temperature with dissociation of phosphine. These observations are also consistent with a temperature-dependent equilibrium between isomers (A) and (B), form (A) predominating at room and higher temperatures its spectrum consisting of a single line at 24.7 p.p.m. in the temperature range studied (−90 °C to 60 °C). As the temperature is lowered, (A) is converted into (B) which shows a spectrum characteristic of an $AB_2$ system ($\nu_A = 22$ p.p.m.; $\nu_B = 29$ p.p.m.; $J_{AB}$ 67 Hz).

## EXPERIMENTAL

Microanalyses were by Imperial College, Butterworth Microanalytical Consultancy Limited, Middlesex, and Pascher, Bonn, microanalytical laboratories.

Molecular weights were measured cryoscopically in benzene under $N_2$ atmosphere. The following spectroscopic instruments were used: u.v., Perkin-Elmer model 402; i.r., Perkin-Elmer models 457 and 257; n.m.r., Perkin-Elmer R12A ($^1H$ n.m.r.) and Varian XL100-12 ($^{31}P$ n.m.r.); Raman spectra were recorded on a Spex Ramalog V spectrometer as described elsewhere.[18] E.s.r. spectra were obtained at *X*-band frequencies using a Varian E12 spectrometer. Conductivities were measured in nitromethane solutions with a Mullar conductivity bridge type E7566/3.

$MoH_4(PMePh_2)_4$ [9] and $WH_4(PMePh_2)_4$ [11] were prepared as previously described. Freshly prepared acid solutions were used: $CF_3CO_2H$ (toluene); $HBF_4$ and $HPF_6$ (methanol); HCl (methanol or tetrahydrofuran); solid *p*-$MeC_6H_4SO_3H\cdot H_2O$. The light petroleum used had b.p. 30—40 °C unless otherwise stated. All preparations and other operations were carried out under oxygen-free nitrogen and using conventional Schlenk-tube techniques.

*Dihydridotris(methyldiphenylphosphine)bis(trifluoroacetato)molybdenum*(IV).—$CF_3CO_2H$ (0.9 ml of a *ca.* 1.3M-toluene solution) was added to a solution of $MoH_4(PMePh_2)_4$ (0.46 g, 0.5 mmol) in benzene (20 ml) and the solution stirred at room temperature for 1—2 h. The solvent was removed *in vacuo*, the residue washed with light petroleum and the *complex* recrystallised twice from toluene–dichloromethane, as red-orange crystals; yield 80%.

*Dihydridotris(methyldiphenylphosphine)bis(*p*-toluenesulphonato)molybdenum*(IV).—To a tetrahydrofuran solution of $MoH_4(PMePh_2)_4$ (0.46 g, 0.5 mmol; 20 ml) solid Htos (0.19 g, 1 mmol) was added. The resulting dark-red solution was stirred at room temperature for 30 min. The solution was taken to dryness by pumping at room temperature for 1—2 h. To the residue was added dry, deoxygenated toluene (10 ml) and the solution stirred for 10—15 min. The red-orange *complex* which precipitated was collected, washed with light petroleum and recrystallised from toluene–dichloromethane; yield, 70%.

*Trihydridotris(methyldiphenylphosphine)molybdenum*(IV) *Tetrafluoroborate and Hexafluorophosphate*.—Excess of $HBF_4$ or $HPF_6$ in methanol was added to $MoH_4(PMePh_2)_4$ (0.46 g) dissolved in tetrahydrofuran (20 ml). The solution was stirred at room temperature for 6—8 h, evaporated to dryness, methanol (5—10 ml) then added, and the resulting solution stirred at room temperature for 15—20 min. The red-brown *salt* which precipitated was collected, thoroughly washed with methanol (3 × 5 ml) and recrystallised from methanol–dichloromethane; yields 40 – 60%. The hexafluorophosphate salt is more soluble than the tetrafluoroborate, and the methanolic solution is best cooled at −20 °C overnight. The salt $[MoH_3(PMePh_2)_3][Co(CO)_4]$ was prepared from the $BF_4$ salt and $Na[Co(CO)_4]$ in refluxing tetrahydrofuran (Found: C, 57.5; H, 5.2; P, 10.8. Calc. for $C_{43}H_{42}CoMoO_4P_3$: C, 59.3; H, 4.83; P, 10.7%).

*Reaction of Tetrahydridotetrakis(methyldiphenylphosphine)-molybdenum with Hydrochloric Acid*.—A freshly prepared tetrahydrofuran solution of *ca.* 1M aqueous HCl (1 ml) was syringed dropwise onto a tetrahydrofuran solution of $MoH_4(PMePh_2)_4$ (0.46 g; 20 ml). The initial yellow colour changed first to red–yellow and then darkened to become green after being stirred for a few minutes. The resulting solution was stirred at room temperature for 8—10 h and then reduced *in vacuo* to 3—5 ml. Slow addition of light petroleum caused precipitation of a green solid. Attempts to purify this compound usually yielded mixtures of the green and blue isomers (see text).

Upon addition of an excess of HCl to a solution of $MoH_4(PMePh_2)_4$ a yellow-red solution was obtained from which the yellow paramagnetic complex $MoCl_3(PMePh_2)_3$

could be isolated on addition of methanol. This was identical with the compound β-$MoCl_3(PMePh_2)_3$ [15] (m.p., i.r., and analysis).

*Pentahydridotetrakis(methyldiphenylphosphine)tungsten*(VI) *Hydrogenbis(trifluoroacetate)–Toluene and Hydrogenbis-*(p-*toluenesulphonate*).—The trifluoroacetate salt was obtained when $WH_4(PMePh_2)_4$ (0.49 g, 0.5 mmol) dissolved in toluene (25 ml) was treated with a *ca.* 1.3M-solution of $CF_3CO_2H$ in toluene (0.9 ml). After the mixture had been stirred at room temperature for 15—30 min the resulting white solid was filtered off, washed with light petroleum (3 × 5 ml) and dried *in vacuo*. Recrystallisation from toluene–dichloromethane gave white crystals; yield, 90%.

The *p*-toluenesulphonate was obtained similarly by using tetrahydrofuran as solvent [0.49 g of $WH_4(PMePh_2)_4$; 0.19 g Htos·$H_2O$; 20 ml of tetrahydrofuran]. After the mixture had been stirred for 10—15 min at room temperature the volume was reduced to 8—10 ml; when cooled at −20 °C white *crystals* were obtained; yield, 80%.

*Pentahydridotetrakis(methyldiphenylphosphine)tungsten*(VI) *Tetrafluoroborate, Hexafluorophosphate, and Chloride*.—To a solution of $WH_4(PMePh_2)_4$ in tetrahydrofuran (0.49 g, 0.5 mmol; 20 ml), at −10 °C, was added a *ca.* 1M-methanolic solution of the acid (0.5 ml). The *hexafluorophosphate* salt precipitated after the mixture had been stirred at −10 °C for a few minutes. For the *tetrafluoroborate* and *chloride*, removal of some solvent and cooling overnight at −20 °C were needed. The compounds could be recrystallised from methanol–dichloromethane or tetrahydrofuran–dichloromethane. Storage of these products should be at *ca.* −20 °C; yields, 60 to 80%.

*Dihydridotris(methyldiphenylphosphine)bis(trifluoroacetato)tungsten*(IV).—$[WH_5(PMePh_2)_4][H(O_2CCF_3)_2]$·toluene (0.25 g) was heated at 90 °C under $N_2$ and the colour started to change to brown after a few minutes. The reaction was completed at 100 °C *in vacuo* after 10—15 min. The red-brown residue was washed with light petroleum (5 × 10 ml) and recrystallised twice from toluene–dichloromethane to give red *crystals*; yield, 80%.

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