Trimethylphosphine Hydrides of Molybdenum(II), Tungsten(VI), and Rhenium(VII): *X*-Ray Crystal Structure of Pentakis(trimethylphosphine)dihydridomolybdenum(II)

Michael B. Hursthouse,[a] **David Lyons,**[b] **Mark Thornton-Pett,**[a] **and Geoffrey Wilkinson**[b]
[a] *Chemistry Department, Queen Mary College, Mile End Road, London E1 4NS, U.K.*
[b] *Chemistry Department, Imperial College, London SW7 2AY, U.K.*

The reduction of bis(tetrahydrofuran)tetrachloromolybdenum by magnesium under hydrogen in the presence of trimethylphosphine produces $MoH_2(PMe_3)_5$ whose structure has been determined by *X*-ray diffraction; the hydrides $WH_6(PMe_3)_3$ and $ReH_6(NHPh)(PMe_3)_2$ have also been synthesised.

Since the discovery of tungsten polyhydrides with tertiary phosphine ligands by Moss and Shaw,[1] many compounds of the type $MH_n(PR_3)_m$ for both M = W and Mo have been made.[2] We now report the first structural characterisation of an $MH_2(PR_3)_5$ complex; other examples are $CrH_2[P(OMe)_3]_5$,[3] $MoH_2[P(OMe)_3]_5$,[4] $WH_2[P(OMe)_3]_5$,[4] and $WH_2(PMe_3)_5$[5] but the geometries, although indicated by n.m.r. spectra, have not been determined with certainty.

Interaction of $MoCl_4(thf)_2$ in tetrahydrofuran (thf) in the presence of trimethylphosphine and magnesium under hydrogen (3 atm) gives high yields of yellow $MoH_2(PMe_3)_5$;† crystals suitable for *X*-ray study were obtained from petroleum.

Crystal data: $C_{15}H_{47}MoP_5$, $M = 478.32$, triclinic, $a = 18.020(3)$, $b = 16.767(7)$, $c = 9.650(2)$ Å, $\alpha = 105.29(2)$, $\beta = 93.25(1)$, $\gamma = 110.97(2)°$, $U = 2589$ Å^3, space group $P\bar{1}$, $Z = 4$ (2 per asymmetric unit), $D_c = 1.23$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 7.30$ cm^{-1}, $\lambda(\text{Mo-}K_\alpha) = 0.71069$ Å, temperature = 295 K.

The structure was solved using standard heavy-atom procedures and refined by full-matrix least squares (2 blocks, one for each molecule) with anisotropic temperature factors for non-hydrogen atoms and isotropic for hydrogen atoms (all of which were experimentally located and refined). The final R and R_w values are 0.0247 and 0.0242, respectively.‡

The co-ordination geometries of the two crystallographically independent molecules are equal within the limits of experimental error and correspond to a pentagonal bipyramid with deformation of the equatorial angles due to differing steric size of the two hydrogens and three phosphines which constitute the girdle. A diagram of one molecule is given in Figure 1, along with selected, averaged geometry parameters. It may be noted that the phosphine ligands with the longest Mo–P distances, P(13), P(14), are most nearly '*trans*' to the hydrido ligands, whereas P(11), which is unique, has the shortest Mo–P distance. These effects may be due to the strong *trans* effects of hydride, or less likely, to purely steric factors.

A dihydrido molybdenum(II)trimethylphosphine complex has been made previously, but this was the dimer $Mo_2H_2(\mu\text{-}H)_2(PMe_3)_6$.[6] Both the ^1H and $^{31}P\{^1H\}$ n.m.r. spectra of $MoH_2(PMe_3)_5$ are consistent with a fluxional structure; the former shows a binominal sextet at δ −5.23, $J_{P-H} = 40.41$ Hz, the latter a singlet; in the ^1H coupled ^{31}P spectrum there is a

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† All new compounds reported here gave satisfactory elemental analyses.

‡ Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

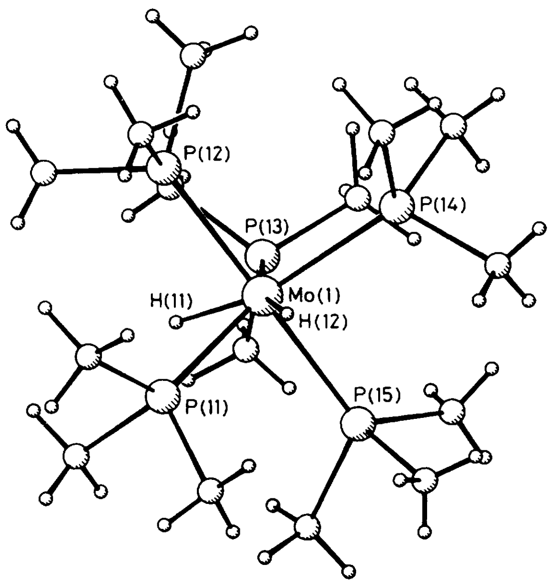

Figure 1. The structure of one of the two crystallographically independent molecules of $MoH_2(PMe_3)_5$. The pentagonal girdle comprises H(11), H(12), P(11), P(13), P(14). Selected bond lengths (Å) and angles (deg.) are: Mo–H 1.68(4), 1.67(3); Mo–P(12), P(15) 2.426(3), 2.424(3); Mo–P(11) 2.403(3); Mo–P(13), P(14) 2.469(3), 2.478(3); P(13)–Mo–P(14) 99.2(1); P(13), P(14)–Mo–H 59(1), 66(1); P(11)–Mo–H 70(1), 66(1); H–Mo–H 135.9(2).

triplet at δ 3.07 p.p.m., $J_{P-H} = 40.16$ Hz. No change occurs in the spectrum down to 190 K. The infrared spectrum has bands at 1945, 1920, 1670, and 1605 cm^{-1} that can be assigned to Mo–H. $MoH_2(PMe_3)_5$ is very reactive towards $HBF_4.Et_2O$, methanol, ethylene, methylacetylene, *etc.*, and these studies will be reported later.

By interaction of lithium aluminium hydride with $WCl_4(PMe_3)_3$[7] or $ReCl_3(NPh)(PMe_3)_2$[8] followed by methanol hydrolysis at low temperatures, we have isolated, respectively, $WH_6(PMe_3)_3$, a member of the well known $WH_6(PR_3)_3$ series known for other phosphines,[1,2] and $ReH_6(NHPh)(PMe_3)_2$, no analogues of which are known, although other nine-co-ordinate rhenium(VII) hydrides, $[ReH_9]^{2-}$ and $[ReH_7(PR_3)_2]$ exist.[9] The ^1H n.m.r. spectrum of $ReH_6(NHPh)(PMe_3)_2$ in the hydride region shows a triplet at δ −5.73, J_{P-H} 20.99 Hz; there is also a broad resonance at δ 2.73 that can be assigned to the N–H proton. The $^{31}P\{^1H\}$ spectrum shows a singlet at δ −30.9 p.p.m.; the i.r. spectrum shows bands in the region 2010—1865 cm^{-1}, due to Re–H, and bands at 3440, 3340, and 3220 cm^{-1} due to N–H.

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