

Tetrahydrido-complexes of Molybdenum

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Summary The synthesis and spectral characteristics of the complexes $(\text{PR}_3)_4\text{MoH}_4$ (PR_3 = tertiary phosphine) are described.

TERTIARY phosphine- and arsine-hydrido-complexes containing more than three hydrogen ligands bonded to the metal have been described for several third-row transition metals.^{1,2} For second-row metals only one such complex, $(\text{Ph}_3\text{P})_3\text{RuH}_4$, has been reported,³ but apparently it was not isolated. We have now prepared the molybdenum hydrido-complexes $(\text{PR}_3)_4\text{MoH}_4$ (PR_3 = MePh_2P , EtPh_2P) and $(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2\text{MoH}_4$ by the reaction of *cis*- $(\text{PR}_3)_2\text{MoCl}_4$ and an excess of ligand in ethanolic NaBH_4 . The complexes, recrystallized from C_6H_6 - MeOH , are yellow, soluble in non-polar solvents and moderately stable in air. They have been characterized by chemical analysis, magnetic measurements, and i.r. and n.m.r. spectra.

The compounds are diamagnetic. They are characterized as hydrido-complexes by their i.r. spectra ($\nu_{\text{M-H}}$ in the 1700—1850 cm^{-1} region and $\delta_{\text{M-H}}$ in the 600—800 cm^{-1} region); thus $(\text{MePh}_2\text{P})_4\text{MoH}_4$ shows bands at 1800, 1714, 775, and 640 cm^{-1} , which in the deuteride are shifted to 1293, 1235, 558, and 460 cm^{-1} , respectively. The diphosphine complex was insufficiently soluble for n.m.r. measurements. The high-field n.m.r. spectra of the monodentate phosphine complexes in C_6D_6 show a quintet pattern with an intensity

ratio 1:4:6:4:1, which for $(\text{EtPh}_2\text{P})_4\text{MoH}_4$ is centred at τ 12.20, $J_{\text{P,H}}$ 34 Hz. Intensity measurements indicate 4 hydridic hydrogens per molybdenum.

Identical chemical shifts for all hydride ligands and splitting patterns indicating magnetic equivalence of the phosphorus nuclei have also been observed for the phosphine polyhydrido-complexes of third-row metals.^{1,2} The high-field spectra¹ of $(\text{PR}_3)_3\text{WH}_6$, $(\text{PR}_3)_3\text{ReH}_5$, and $(\text{PR}_3)_3\text{OsH}_4$ show quartet patterns, but the hexacoordinated $(\text{PR}_3)_3\text{IrH}_3$ complexes give spectra which allow determination of their stereochemistry.² Among hydrido-complexes of the second-row metals, $(\text{Ph}_3\text{P})_3\text{RuH}_4$ shows only a broad signal in the high-field region with the loss of fine structure resulting from ligand dissociation in solution.⁴ The rhodium homologues of the molybdenum tetrahydride $(\text{PR}_3)_4\text{RhH}$ [PR_3 = MePh_2P ,⁵ $\text{P}(O\text{-aryl})_3$,⁶] also show a quintet pattern, while the hexacoordinated ruthenium homologue $(\text{MePh}_2\text{P})_4\text{RuH}_2$ gives a spectrum which characterizes its stereochemistry.⁵

The apparent magnetic equivalence of the hydride ligands, which has been attributed¹ to strong phosphorus-phosphorus coupling or to rapid intramolecular rearrangement of the hydride ligands, seems to be a phenomenon widespread among transition metal complexes other than tetra- or hexacoordinated.

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¹ P. G. Douglas and B. L. Shaw, *J. Chem. Soc. (A)*, 1970, 334 and references therein.

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³ T. Ito, S. Kitazume, A. Yamamoto, and S. Ikeda, *J. Amer. Chem. Soc.*, 1970, **92**, 3011 and references therein.

⁴ F. Pennella and M. R. Rycheck, unpublished results.

⁵ K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, 1968, **7**, 546.

⁶ J. J. Levison and S. D. Robinson, *Chem. Comm.*, 1968, 1405.