

Synthesis and Crystal Structure of Hexakstrimethylphosphine(dihydrido)- μ -dihydrido-dimolybdenum(II)(Mo-Mo)†

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Summary The interaction of dimolybdenum tetra-acetate, $\text{Mo}_2(\text{O}_2\text{CMe})_4$, with sodium amalgam in tetrahydrofuran in the presence of an excess of trimethylphosphine under hydrogen (3 atm) yields the dimeric phosphine hydride $(\text{Me}_3\text{P})_3\text{HMo}(\mu\text{-H})_2\text{MoH}(\text{PMe}_3)_3$, whose structure has been determined by X-ray diffraction methods

ALTHOUGH many dinuclear transition metal phosphine hydrides containing both bridging and terminal M-H bonds are known,¹ none has previously been reported for molybdenum. For molybdenum, however, there are some dinuclear hydrides having $\eta\text{-C}_5\text{H}_5$,² CO,³ or Cl⁴ ligands as well as mononuclear species with tertiary phosphines such as $\text{MoH}_4(\text{PMePh}_2)_4$ ⁵

The interaction of dimolybdenum(II) tetra-acetate, $\text{Mo}_2(\text{O}_2\text{CMe})_4$, with sodium amalgam in tetrahydrofuran in the presence of an excess of trimethylphosphine under hydrogen (3 atm) yields the dimeric phosphine hydride $(\text{Me}_3\text{P})_3\text{HMo}(\mu\text{-H})_2\text{MoH}(\text{PMe}_3)_3$, (1), in high yield. Using $\text{Ru}_2(\text{O}_2\text{CMe})_4\text{Cl}$ or $[\text{Ru}_3\text{O}(\text{O}_2\text{CMe})_6(\text{H}_2\text{O})_3]\text{OAc}$ instead of $\text{Mo}_2(\text{O}_2\text{CMe})_4$ under similar conditions only monomeric *cis*- $\text{RuH}_2(\text{PMe}_3)_4$ is obtained, while $\text{Cr}_2(\text{O}_2\text{CMe})_4$, $\text{Rh}_2(\text{O}_2\text{CMe})_4$, and $\text{Re}_2(\text{O}_2\text{CMe})_4\text{Cl}_2$ decomposed.

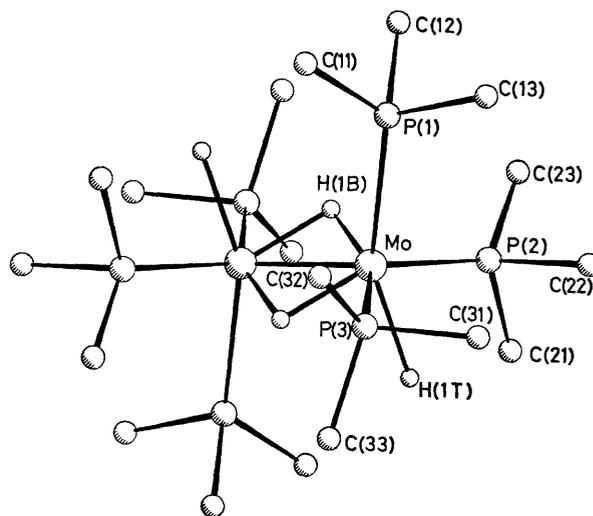
Unlike the moderately air stable Mo^{IV} hydrides,⁵ (1) is pyrophoric in the solid state and it reacts readily with alkyl halides, CO, olefins, acetylenes, and H_2S . Although H_2 is rapidly liberated on treatment with HBF_4 (40%, aq) and the salt $(\text{HPMe}_3)\text{BF}_4$ formed, no molybdenum-containing species have so far been isolated. The structure of this yellow crystalline material has been determined by an X-ray diffraction study.

Crystal data $\text{C}_{18}\text{H}_{18}\text{Mo}_2\text{P}_6$, M 652.39. Orthorhombic, space group $Pbca$, $a = 12.133(6)$, $b = 14.892(4)$, $c = 17.692(5)$ Å, $U = 3196.7$ Å³, $Z = 4$, $D_c = 1.36$ g cm⁻³,

† No reprints available

‡ The 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.

$F(000) = 1360$, $\mu(\text{Mo-K}\alpha) = 9.9$ cm⁻¹. The structure was solved and refined by standard methods, using 3129 unique intensity data recorded on a CAD4 diffractometer in a manner described previously.⁶ Non-hydrogen atoms were refined anisotropically, hydrogen atoms were located on difference maps and refined isotropically. The final R value is 0.0362 for 2388 data with $I > 1.5\sigma(I)$ ‡



(1)

FIGURE The molecular structure of $\text{Mo}_2\text{H}_4(\text{PMe}_3)_6$. Some important bond lengths Mo-Mo 2.194(3), Mo-P(1) 2.430(3), Mo-P(2) 2.430(3), Mo-P(3) 2.413(3), Mo-H(1B) 1.43(2), Mo-H(1T) 1.61(3), Mo-H(1T) 1.82(4) Å

The structure analysis confirms the dimeric nature of the molecule and the presence of two bridging and two terminal hydrides. Neglecting the Mo—Mo interaction, which at 2.19 Å is well in the region of values found for quadruply bonded Mo^{II}—Mo^{II} species, the metal atom co-ordination geometry can be regarded as distorted octahedral, with two phosphines and the bridging hydrogens forming the equatorial and one phosphine and the terminal hydrogen at the axial sites. The Mo—H distances to the bridging hydride are unequal and apparently very short. This is not unusual for structures determined by X-ray methods,³ although the shortness is more emphasised here than in any other structure. It is almost certain however, that this hydrogen atom position is subject to some uncertainty

since it consistently refines with a negative temperature factor coefficient. The terminal hydrogen seems to be better defined, having a reasonable temperature factor and giving a 'normal' Mo—H distance of ca 1.8 Å.

One other important feature in the structure are the values of the Mo—P distances where the Mo—P(3) bond *trans* to the 'short' Mo—H (bridge) bond is shorter than the other two, which are equal. It is interesting to note that both these latter phosphines are '*trans*' to hydrogen atoms which, in spite of their different geometrical (and electronic) environments have similar Mo—H distances.

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¹ See for example, Pt G Bracher, D M Grove, P S Pregosin and L M Venanzi, *Angew Chem, Int Ed Engl*, 1979, **18**, 155, Ir R Crabtree, *Acc Chem Res*, 1979, **12**, 331, Co and Fe P Dapporto, S Midollini, and L Sacconi *Inorg Chem*, 1975, **14**, 1643, Re R Bau, W E Carroll R G Teller, and T F Koetzle, *J Am Chem Soc* 1977, **99** 3872

² N J Cooper M L H Green, C Couldwell, and K Prout, *J Chem Soc, Chem Commun*, 1977, 145, J C Smart and C J Curtis, *Inorg Chem* 1978, **17**, 3290

³ See R Bau, R G Teller, S W Kirtley, and T F Koetzle, *Acc Chem Res*, 1979, **12**, 176 (Also for M—H—M carbonylates and derivatives)

⁴ E g A Bino and F A Cotton, *Angew Chem, Int Ed Engl*, 1979, **18**, 332

⁵ For references see E Carmona Guzman and G Wilkinson, *J Chem Soc Dalton Trans* 1977, 1716

⁶ M B Hursthouse, R A Jones, K M A Malik, and G Wilkinson, *J Am Chem Soc*, 1979, **101**, 4128