Synthesis of Hexakis(trimethylphosphine)molybdenum using Molybdenum Atoms and its *X*-Ray Crystal Structure

F. Geoffrey N. Cloke,[a] Kevin P. Cox,[a] Malcolm L. H. Green,*[a]
Jim Bashkin,[b] and Keith Prout*[b]

[a] *Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.*
[b] *Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD, U.K.*

Co-condensation of molybdenum atoms with an excess of trimethylphosphine gives hexakis(trimethylphosphine)molybdenum which crystal structure studies show to have an octahedral MoP_6 unit; it is highly reactive to substitution by dinitrogen, olefins, and dihydrogen, forming a variety of derivatives.

Transition metal compounds which have high energy (electron-rich) centres frequently are reactive towards normally inert systems such as carbon–hydrogen bonds and dinitrogen. Amongst the monodentate tertiary phosphines, trimethylphosphine combines strongly electron-releasing properties with relative compactness of size. We set out to synthesise a compound of the type $Mo(PMe_3)_n$ using the method of metal vapour synthesis.

In a typical experiment, molybdenum atoms (1 g) were co-condensed with an excess of trimethylphosphine (50 cm^3) using the apparatus recently described.[1] After removal of the volatile trimethylphosphine and recrystallisation of the red-orange residue from cyclohexane, orange crystals of $Mo(PMe_3)_6$ **(1)** were obtained in *ca.* 55% yield.

The compound **(1)** has been characterised by crystal structure determination and microanalysis [Found Mo: 17.6%; **(1)** requires 17.4%]. The mass spectrum shows a highest band assignable to the cation $[Mo(PMe_3)_5]^+$.

Crystal data: $C_{18}H_{54}MoP_6$, $M = 551.97$, cubic, space group $Im3m$, $a = 11.319(2)$ Å, $U = 1450$ Å^3, $Z = 2$, $D_c = 1.26$ g cm^{-3}. Intensities of 1622 reflections were measured ($2\theta_{max}$ 60°) on a CAD-4 diffractometer using Mo-K_α radiation. The structure was solved by Patterson and difference-Fourier methods, and refined by full-matrix least squares using 224 independent reflections [$I > 3\sigma(I)$], not corrected for absorption [μ(Mo-K_α) 7.3 cm^{-1}].†

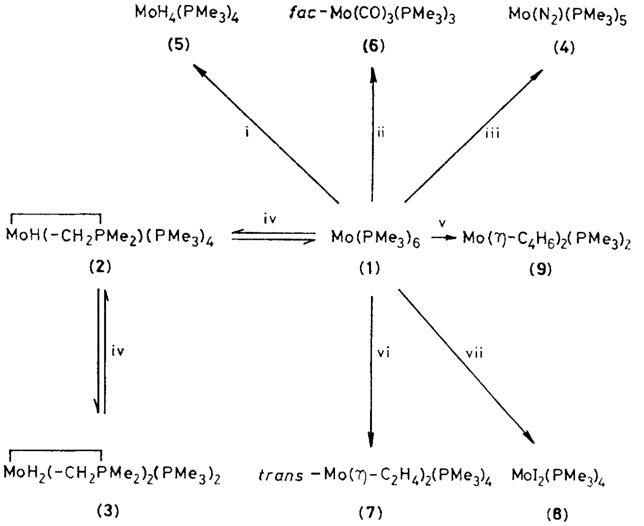
The P atoms lie on sites of crystallographic $4mm$ symmetry, requiring at least four-fold disorder for the methyl groups. The disorder was modelled by placing two independent carbons on the mirror-planes at (x,y,y) and $(x,y,0)$. C(1) and C(2) were given a relative occupancy of 2:1 in accord with difference-Fourier peak heights and cell symmetry, and were refined with isotropic temperature factors. Symmetry requires that Mo(1) be refined isotropically as well, but P(1) was allowed anisotropic temperature factors. The R-value is 0.052, and R_w is 0.069.

The molecule has an octahedral arrangement of the six phosphorus atoms about the central Mo, with a separation Mo(1)–P(1) of 2.467(2) Å. This is considerably longer than the Mo–P bond-length of 2.421(3) found in another zero-valent Mo–phosphine compound, $Mo(Me_2PCH_2CH_2PMe_2)_3$,[2] and may reflect steric pressure caused by the bulky PMe_3 ligands. The angles Mo(1)–P(1)–C(1) and Mo(1)–P(1)–C(2) are 118.1(8) and 126(1)°, respectively; the P(1)–C(1) bond length is 1.884(4) Å, and the distance P(1)–C(2) is 1.880(4) Å.

The ^1H and ^{31}P n.m.r. spectra of solutions of **(1)** in C_6H_6 show that partial dissociation of trimethylphosphine has occurred and that **(1)** is in equilibrium with small quantities of two hydrido-compounds. The spectra may be interpreted in terms of an equilibrium between the compounds **(2)** and **(3)** shown in Scheme 1; for both molecules the phosphorus nuclei are made equivalent by a rapid fluxional process involving reversible C–H addition of a methyl group to the molybdenum centres. {Partial ^1H n.m.r. data (C_6D_6) are for **(1)** 8.64 τ (s, no P–H coupling owing to rapid exchange of PMe_3 groups); for **(2)** 15.67 τ [sext., J(P–H) 40.5 Hz, MoH]; for **(3)** 14.0 τ [quint., J(P–H) 45.2 Hz, MoH_2]}

In accord with the long Mo–P distances, the trimethylphosphine ligands of **(1)** are highly labile and **(1)** very readily undergoes ligand substitutions.

Treatment of solutions of **(1)** in light petroleum with dinitrogen at 15 atm forms the compound $Mo(PMe_3)_5N_2$ **(4)**. Similarly, treatment of **(1)** with hydrogen, carbon monoxide, ethylene, or butadiene causes in each case a smooth displacement of two or more trimethylphosphine ligands and the reactions and structure proposed for the products, namely **(5)**—**(7)**, **(9)**, respectively, are shown in Scheme 1. Treatment of **(1)** with methyl iodide gives the di-iodo-compound **(8)**. The compounds **(4)**, **(6)**, **(7)**, and **(8)** have been independently prepared and characterised.[3,5] The compounds **(4)**—**(9)** have been characterised by microanalysis, mass spectra, and by n.m.r. spectroscopy.



Scheme 1. *Conditions and yields*: i, hydrogen at 2 atm and 20 °C in light petroleum, >60%; ii, CO at 2 atm and 20 °C in light petroleum, >90%; iii, dinitrogen at 15 atm and 20 °C in light petroleum, $\nu(N_2)$ 1950 cm^{-1} (mull), >90%; iv, solution in benzene at 20 °C, reversible dissociation of a PMe_3 group, followed by C–H metallation; v, excess of butadiene at 20 °C in light petroleum, >60%; vi, ethylene at 2 atm and 20 °C in light petroleum, >60%; vii, excess of methyl iodide at 20 °C in light petroleum, >60%.

There is a very marked difference between the reactivity of **(1)** and that of the previously described analogue containing the bis(1,2-dimethylphosphino)ethane ligand, namely $Mo(Me_2PCH_2CH_2PMe_2)_3$,[2,4] which is very inert to substitution and, for example, protonates with hydrogen chloride forming the dihydrido-derivative $[MoH_2(Me_2PCH_2CH_2PMe_2)_3]^{2+}$.[6] Further, the compound $Mo[P(OMe)_3]_6$ is inert to substitution except when photolysed.[7]

The molybdenum centre in **(1)** is probably highly electron-rich and this, together with the steric overcrowding, can account for the exceptional lability and ease of substitution of the PMe_3 ligands. The compound **(1)** is clearly a useful precursor to a wide variety of low valent derivatives.

We thank the Science Research Council for a grant (to K.P.C.), the Ramsey Memorial Fellowship for support (to F.G.N.C.), and the Petroleum Research Fund, administered by the American Chemical Society, for partial support.

Received, 18th January 1982; Com. 046

References

1 F. G. N. Cloke and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1981, 1938.
2 F. G. N. Cloke, P. J. Fyne, M. L. H. Green, M. J. Ledoux, A. Gourdon, and K. Prout, *J. Organomet. Chem.*, 1980, **198**, C69.
3 M. S. Arabi, R. Mathieu, and R. Poilblanc, *J. Organomet. Chem.*, 1976, **104**, 323.
4 J. Chatt and J. R. Watson, *J. Chem. Soc.*, 1962, 1343.
5 E. Carmona, J. M. Marin, M. L. Poveda, J. L. Atwood, R. D. Rogers, and G. Wilkinson, personal communication. We are very grateful to Professor Carmona for providing unpublished experimental details for his compounds.
6 V. C. Gibson, unpublished observations.
7 E. L. Muetterties, J. F. Kirner, W. J. Evans, P. L. Watson, S. Abdel-Meguid, I. Tavanaipour, and V. W. Day, *Proc. Natl. Acad. Sci., USA*, 1978, **75**, 1065.

---

† 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.