Hexakis(trimethylphosphine)molybdenum Chemistry: Dinitrogen, Ethylene, Butadiene, η-Cyclopentadienyl, and Related Derivatives†

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Co-condensation of molybdenum atoms with trimethylphosphine gives octahedral [Mo(PMe$_3$)$_6$] (**1**) whose crystal structure has been determined. Treatment of (**1**) with dinitrogen, ethylene, carbon monoxide, iodine, or butadiene gives [Mo(N$_2$)(PMe$_3$)$_5$], *trans*-[Mo(η-C$_2$H$_4$)$_2$(PMe$_3$)$_4$], *fac*-[Mo(CO)$_3$(PMe$_3$)$_3$], *trans*-[MoI$_2$(PMe$_3$)$_4$], and *cis*-[Mo(η-C$_4$H$_6$)$_2$(PMe$_3$)$_2$] respectively. Protonation of *cis*-[Mo(η-C$_4$H$_6$)$_2$(PMe$_3$)$_2$] with tetrafluoroboric acid forms the compound *cis*-[$\overline{\text{Mo}(1-3\text{-}\eta\text{-H}}CH_2$CHCHCH$_2$)(η-C$_4H_6$)(PMe$_3$)$_2$]BF$_4$. The presence of the Mo–H–C bond is shown by low-temperature n.m.r. spectra, and variable-temperature n.m.r. shows that the agostic hydrogen can scramble between the four terminal carbons of the two C$_4$ ligands. The rate constants and activation parameters for the hydrogen-scrambling process have been determined and a mechanism is proposed. Reaction of *cis*-[Mo(η-C$_4$H$_6$)$_2$(PMe$_3$)$_2$] with trifluoroacetic acid gives [Mo(η-MeC$_3$H$_4$)(η-C$_4$H$_6$)(PMe$_3$)$_2$(O$_2$CCF$_3$)]. Treatment of [Mo(PMe$_3$)$_6$] with cyclopentadiene forms [MoH(η-C$_5$H$_5$)(PMe$_3$)$_3$] which reacts with aqueous tetrafluoroboric acid giving [MoH$_2$(η-C$_5$H$_5$)(PMe$_3$)$_3$]BF$_4$ and [Mo(η-C$_5$H$_5$)(PMe$_3$)$_2$O]BF$_4$. Reaction of [MoH(η-C$_5$H$_5$)(PMe$_3$)$_3$] with methyl iodide gives [MoH(η-C$_5$H$_5$)(PMe$_3$)$_2$I$_2$].

We wished to prepare the compound [Mo(PMe$_3$)$_6$] (**1**) since it was anticipated that it would be a highly electron-rich, reactive compound and a useful starting compound for the synthesis of a variety of derivatives of low-valent molybdenum compounds. Our interest in electron-rich molybdenum compounds arises in the context of their ability to activate carbon–hydrogen bonds and other normally inert systems such as dinitrogen. A preliminary communication of part of this work has been published.[1]

Results and Discussion

We have previously shown that co-condensation of molybdenum atoms with Me$_2$PCH$_2$CH$_2$PMe$_2$ gave [Mo(Me$_2$PCH$_2$CH$_2$PMe$_2$)$_3$] in high yield[2] and therefore it seemed possible that (**1**) might be accessible by reaction between molybdenum atoms and an excess of trimethylphosphine.

Molybdenum atoms were co-condensed with a large excess of trimethylphosphine; successive recrystallizations from cyclohexane gave analytically pure [Mo(PMe$_3$)$_6$] (**1**) in *ca.* 55% yield. In a typical experiment, 2.0 g of molybdenum atoms gave *ca.* 6.0 g of (**1**). Solutions of (**1**) are extremely air-sensitive although relatively inert to hydrolysis; the solid is pyrophoric in air. The mass spectrum of (**1**) showed a highest band at *m/e* (^{98}Mo) 478, with an isotope distribution pattern expected for a molybdenum monomer, assignable to [Mo(PMe$_3$)$_5$]$^+$. The fragmentation pattern indicated successive loss of PMe$_3$ molecules.

The ^{1}H n.m.r. spectrum of (**1**) showed that more than one species was present in solution. The main feature of the spectrum was an intense singlet at δ 1.36 assignable to 54 equivalent PMe$_3$ hydrogens of (**1**). There were also present two low-intensity bands at high field, a binomial quintet at δ −4.00, assignable to coupling with four equivalent PMe$_3$ ligands [J(P–H) = 45.2 Hz] and a binomial sextet at δ −5.22, which indicated coupling to five equivalent PMe$_3$ ligands [J(P–H) = 40.5 Hz]. These bands were consistently reproducible and appeared to be associated with bands assignable to P–CH$_3$ groups at *ca.* δ 1.37 and 1.41. Integration showed the hydride species to be *ca.* 5—10% of the total concentration. Free PMe$_3$ is also present in small concentration [δ 0.79, d, J(P–H) = 2.2 Hz].

The band at δ −5.22 may be identified by comparison with the spectrum of an authentic sample as being due to the presence of a small quantity (3—4%) of the dihydride [MoH$_2$(PMe$_3$)$_5$] (**2**).[3] The bands at δ −4.00, 1.37, and 1.41 may be assigned to the compound *trans*-[MoH(η^2-CH$_2$PMe$_2$)(PMe$_3$)$_4$] (**3**) by comparison with the spectrum of the tungsten analogue which has recently been described elsewhere.[4] Addition of excess PMe$_3$ to the solution of (**1**) causes the bands due to (**3**) to disappear but leaves those due to (**2**) unchanged except in *relative* intensity with respect to the band assigned to (**1**). Initially we incorrectly assigned the band at δ −5.22 to the compound [MoH(CH$_2$PMe$_2$)(PMe$_3$)$_4$] and those at δ −4.00 *etc.* to the compound [MoH$_2$(η^2-CH$_2$PMe$_2$)$_2$(PMe$_3$)$_2$] and suggested that these compounds were fluxional and that there was an equilibrium between (**1**) and these two compounds.[1] This arose since the anticipated multiplicity of the J(P–H) high-field hydrogens was consistent with the observed spectra, *i.e.*, a sextet for the MoP$_5$ species and a quartet for the 'MoP$_4$' compound. Further, the addition of excess PMe$_3$ caused the apparent MoP$_4$

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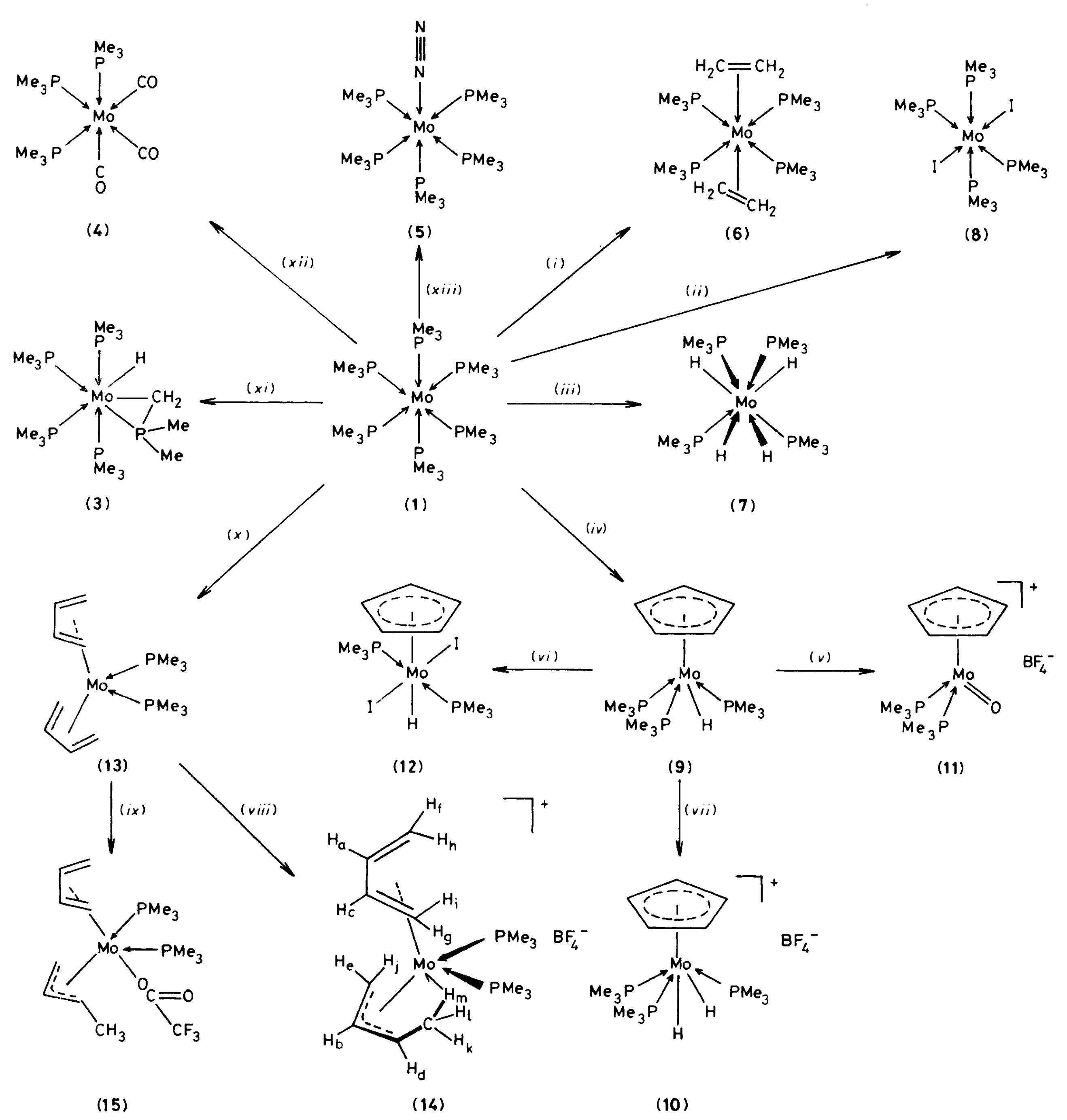
† *Supplementary data available* (No. SUP 56089, 3 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Non-S.I. units employed: atm = 101 325 Pa, cal = 4.184 J, eV ≈ 1.60 × 10^{-19} J, Torr = 133 Pa.



Scheme. (*i*) Ethylene (3 atm) for 18 h at room temperature, yield *ca.* 60%; (*ii*) iodomethane in toluene for 30 min, *ca.* 80%; (*iii*) H_2 (3 atm) for 3 d at room temperature, *ca.* 60%; (*iv*) cyclopentadiene (80 °C) for 3 d, *ca.* 70%; (*v*) wet acetone solution, photolyse (100 W medium-pressure Hg), *ca.* 80%; (*vi*) methyl iodide in toluene for 18 h, *ca.* 80%; (*vii*) HBF_4(aq) in diethyl ether, *ca.* 60%; (*viii*) HBF_4 (aq) methanol, *ca.* 80%; (*ix*) CF_3CO_2H in methanol at room temperature, *ca.* 10%; (*x*) butadiene (3 atm) for 12 h at room temperature, *ca.* 70%; (*xi*) equilibrium concentration in benzene solution with (**1**); (*xii*) carbon monoxide (2 atm) for 5 min, *ca.* 80%; (*xiii*) dinitrogen (15 atm) for 48 h at room temperature, *ca.* 90%

species to disappear and the MoP_5 to increase in relative intensity. In fact, the 'MoP_4' species is (**3**), which is converted to (**1**) in the presence of excess PMe_3, and the MoP_5 species (**2**) is unchanged but appears to decrease in intensity relative to (**1**).

Compound (**3**) is fluxional and in [$^2H_8$]toluene at -50 °C the binomial quintet at δ -4.00 becomes a double-doublet of triplets assignable in terms of a *trans* structure for (**3**). The structure proposed for (**3**) is shown in the Scheme. The tungsten compound $[WH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4]$, whose crystal structure has been determined,[4] shows a temperature-dependent n.m.r. spectrum closely analogous to that of (**3**) and the coupling between the WH proton and the ^{31}P of the $\eta^2\text{-}CH_2PMe_2$ group is not observed. Hence, the WH proton at room temperature appears as a quartet as observed for (**3**).[4]

The ^{31}P n.m.r. spectrum of (**1**), although poorly resolved, shows an intense band at -9.85 p.p.m. (^{31}P–^1H coupling was not observed). No bands assignable to (**2**) or (**3**) were observed at ambient temperature. Compound (**1**) was insufficiently soluble in benzene or toluene for a satisfactory ^{13}C n.m.r. study.

Crystals of (**1**) suitable for *X*-ray diffraction studies were

Table 1. Dimensions of some molybdenum– and tungsten–phosphine complexes

Complex	M–P/Å	P–C/Å	M–P–C/°	P–Mo–P/°	Ref.
$[Mo(PMe_3)_6]$	2.467(2)	1.884(4)	118.1(8)	90, 180	
		1.880(4)	126(1)		
$[Mo(C_4H_6)_2(PMe_3)_2]$	2.456(1), 2.465(1)			97.96(2)	
trans-$[MoCl_2(PMe_3)_4]$	2.496(3) (av.)				6
trans-$[Mo(C_2H_4)_2(PMe_3)_4]$	2.49(1) (av.)				6,7
trans,mer-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$	2.486(3) (av.)				6
P *trans* to CO	2.561(1)				
$[\{MoH(\mu\text{-}H)(PMe_3)_3\}_2]$	2.42(1) (av.)	1.83(1) (av.)	104.6(3)—129.0(4)		5
$[Mo(dmpe)_3]$	2.421(3)				2
$[Mo\{P(OMe)_3\}_5\{P(OMe)_2\}]PF_6$	2.248				*a*
P *trans* to $P(OMe)_2$	2.488				
$[Mo(CO)_4(PMe_3)_2]$	2.522(1)		114—123	97.5	13
$[Mo(CO)_4(PEt_3)_2]$	2.544(4)		112—118	100.3	13
$[Mo(CO)_4(PBu^n{}_3)_2]$	2.552(8)		110—122	99.3	13
$[W(CO)_5(PMe_3)]$	2.516(2)	1.85(2) (av.)	115.6(2)		*b*
$[W_2H_5(\mu\text{-}PMe_2)(PMe_3)_5]$	2.46(3)	1.80—1.89	112.2(6)—128.1(1)		5
μ-PMe_2 group	2.352(5), 2.446(5)				

[a] H. W. Choi and E. L. Muetterties, *J. Am. Chem. Soc.*, 1982, **104**, 153; E. L. Muetterties, W. J. Evans, P. L. Watson, S. Abdel-Meguid, I. Tavanaiepour, and V. W. Day, *Proc. Natl. Acad. Sci., USA*, 1978, **75**, 1054. [b] F. A. Cotton, D. J. Darensburg, S. Klein, and B. W. S. Kolthammer, *Inorg. Chem.*, 1982, **21**, 2661.

grown from benzene; the space group was found to be *Im*3*m*, which is the same as for $[Mo(dmpe)_3]$ [dmpe = 1,2-bis(dimethylphosphino)ethane].[2] $[Mo(PMe_3)_6]$ is not a true octahedral molecule because the PMe_3 groups have only three-fold symmetry. The phosphorus atoms of $[Mo(PMe_3)_6]$ lie on the four-fold axes of the crystallographic octahedron, on sites of 4*mm* symmetry, which requires the PMe_3 to be disordered over at least four positions. The disorder must result from the presence of *both* the three-fold symmetry of PMe_3 and the four-fold crystallographic symmetry. The final *R* value was 0.0518, *R'* 0.0690, for 12 parameters [Mo(1), C(1), and C(2) isotropic; P(1) anisotropic] and 228 observations.

Although it was necessary to model the torus of electron density instead of individual methyl groups, the derived parameters of the structure are quite precise. Those dimensions of (1) which are not fixed by symmetry are given in Table 1, along with the relevant dimensions of several other Group 6A compounds. The structure is shown in Figure 1. The M–P bond length in (1) [2.467(2) Å] is 0.047 Å longer than the M–P bonds [2.42(1) Å] of $[Mo(dmpe)_3]$ and $[\{MoH(\mu\text{-}H)(PMe_3)_3\}_2]$,[5] which is consistent with the facile dissociation of PMe_3 from $[Mo(PMe_3)_6]$. *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ also loses phosphine easily,[6,7] and its (average) M–P bond is even longer, 2.49(1) Å. However, ground-state bond strengths are not the only factor governing reactivity, as emphasized by the average M–P bond length [2.496(3) Å] for *trans*-$[MoCl_2(PMe_3)_4]$, and the exceptionally long Mo–P bond which is *trans* to CO in *trans,mer*-$[Mo(C_2H_4)_2(CO)(PMe_3)_3]$; neither of these two compounds has labile phosphines.[5,6] The large Mo(1)–P(1)–C(2) angle [126(1)°] in (1) is not unprecedented, as Table 1 shows, and it probably results from steric crowding. The P–Mo–P angles of (1) are constrained to be 90° (and 180°) by site symmetry, and this seems to be sterically undesirable, because the P–Mo–P angle increases to 98° when steric constraints are removed {*e.g.* in $[Mo(C_4H_6)_2(PMe_3)_2]$ and $[Mo(CO)_4(PMe_3)_2]$, see Table 1}.

The reaction of (1) with carbon monoxide gave a good yield of air-stable white platelets of the previously described[8] compound *fac*-$[Mo(CO)_3(PMe_3)_3]$ (**4**). The i.r. spectrum showed bands assigned to CO at 1 928 and 1 830 cm^{-1} corresponding to the *fac* isomer.

Treatment of (1) with N_2 (15 atm) causes displacement of one trimethylphosphine ligand giving air-sensitive yellow crystals of $[Mo(N_2)(PMe_3)_5]$ (**5**). Ethylene (3 atm) reacts readily with (**1**) giving the previously described complex *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$ (**6**).[6,9]

Compound (**1**) reacted with H_2 under mild conditions in the absence of excess trimethylphosphine giving $[MoH_4(PMe_3)_4]$ (**7**). The ^1H n.m.r. spectrum showed a band shape (five lines) characteristic for fluxional compounds of the class $[MoH_4(PR_3)_4]$ approaching the fast-exchange limit.[10] Compound (**1**) reacted rapidly with iodomethane giving air-stable, red crystals of the previously described paramagnetic complex *trans*-$[MoI_2(PMe_3)_4]$ (**8**).[6] The data characterising all the new compounds described in this work are given in Table 2.

During the course of this work we became aware that Carmona *et al.*[6,7,9] had previously and independently synthesised the compounds (**5**), (**6**), and (**8**) using $[Mo(PMe_3)_3Cl_3]$ as the starting material. We discontinued our studies on these compounds in order to avoid duplication.

Treatment of (**1**) with excess cyclopentadiene in light petroleum (b.p. 100—120 °C) at 80 °C resulted in the formation of a volatile yellow-orange wax, $[MoH(\eta\text{-}C_5H_5)(PMe_3)_3]$ (**9**). Attempts to obtain crystals of (**9**) were unsuccessful. The solid is rapidly oxidized in air, although relatively inert to hydrolysis. Despite many attempts, a satisfactory analysis for (**9**) could not be obtained. The spectroscopic data suggested the presence of traces of small quantities of cyclopentadiene oligomers. However, the compound is well characterised spectroscopically, especially by the n.m.r. spectrum (Table 2) and by preparation of derivatives. The mass spectrum of (**9**) showed an intense band at *m*/*e* (^{98}Mo) 392, assignable to $[Mo(C_5H_5)(PMe_3)_3]^+$. The i.r. spectrum showed a band at 1 770 cm^{-1} assignable to a Mo–H stretch.

Treatment of (**9**) with an excess of aqueous HBF_4 gave, after crystallisation from water, golden platelets of $[Mo(\eta\text{-}C_5H_5)(PMe_3)_3H_2]BF_4$ (**10**), and from the mother-liquor a second red crystalline compound $[Mo(\eta\text{-}C_5H_5)(PMe_3)_2O]BF_4$ (**11**) was isolated. The 300 MHz ^1H n.m.r. spectrum of (**10**) at 20 °C showed a very broad feature at *ca.* δ −4, which on warming to 57 °C (90 MHz) sharpened to a binomial quartet, centred at δ −3.75 [*J*(P–H) = 45 Hz], thus confirming the presence of a Mo–H group. The quartet at δ 5.04 (relative intensity 5) and the doublet at δ 1.61 (relative intensity 27) were assigned to the protons of η-C_5H_5 and three PMe_3 ligands, respectively. The i.r. spectrum of (**11**) showed a strong band at 931 cm^{-1} assignable to ν(Mo=O) while the 300 MHz ^1H n.m.r. spectrum showed a

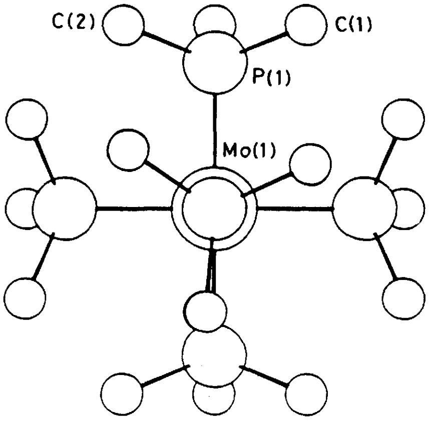


Figure 1. Molecular structure and labelling for [Mo(PMe$_3$)$_6$] (**1**)

band at δ 5.80 (relative intensity 5), assignable to the η-C$_5$H$_5$ group and a doublet at δ 1.86 [J(P–H) = 10 Hz, relative intensity 18] as expected for two equivalent PMe$_3$ ligands. Although (**11**) is formally a 16-electron species, the metal-bound oxygen atom may act as a four-electron donor *via* π donation {*cf.* the relatively short bond length in [Mo(O)(η-C$_5$H$_5$)(dmpe)]PF$_6$ of 1.70 Å}.[11]

Solutions of (**9**) in acetone proved to be photolytically unstable, with slow decomposition in sunlight giving a pale red solution (2 d). A solution of (**9**) in acetone irradiated with u.v. light (100 W Hg lamp) for 24 h gave a deep red solution together with the deposition of a very few black-purple crystals which were not characterised. The major product (80%) obtained from the solution was red crystals of the oxo-compound (**11**).

Compound (**9**) reacted with an excess of MeI affording a high yield of black, octahedral crystals of [MoH(η-C$_5$H$_5$)(PMe$_3$)$_2$I$_2$] (**12**). The i.r. spectrum of (**12**) showed a band at 1 890w cm^{-1}, indicating the presence of a Mo–H group. The ^{1}H n.m.r. spectrum of (**12**) (Table 2) supports the proposed formulation. The band assignable to the Mo–H proton is a triplet as expected [J(P–H) = 46.6] but interestingly it occurs at much lower fields than normally expected for transition metal hydrogens, at δ 5.21. Irradiation of the single band in the ^{31}P n.m.r. spectrum caused the triplet at δ 5.21 to collapse to a singlet. The line shape of the band at δ 1.51 assigned to the PMe$_3$ hydrogens indicates strong virtual coupling compatible with a *trans* disposition of the two PMe$_3$ groups. If the two PMe$_3$ groups adopt a *trans* configuration then there are two possible isomers of (**12**), namely where the hydrogen lies essentially coplanar with the two P atoms and *trans* to an iodine ligand, or, where the hydrogen lies on the Mo–C$_5$H$_5$ axis below an essentially planar *trans*-P$_2$I$_2$ system. The unusually low-field shift of the Mo–H suggests that it is the latter structure, as shown in the Scheme.

In a preliminary study, (**9**) in [^{2}H$_6$]benzene was irradiated by a 100 W medium-pressure mercury lamp. The reaction was monitored by ^{1}H n.m.r. spectroscopy and changes in relative intensities, when compared to an internal standard, clearly indicated that there was H/D exchange between the solvent and (**9**). For example, the band assigned to the P–CH$_3$ hydrogens steadily decreased in intensity, whilst the band assignable to C$_6$H$_6$ increased. The Mo–H proton was also seen to undergo H/D exchange. Surprisingly, in the duration of the experiment (100 h), no H/D exchange was observed for the cyclopentadienyl ring. The mass spectrum of (**9**) recovered after deuteriation showed a broad band corresponding to the presence of partially deuteriated species. Analysis of the spectrum showed the highest band corresponding to the ion [MoD(η-C$_5$H$_5$){P(CD$_3$)$_3$}]$^+$ (*m/e* 420, 2%).

The reaction of [Mo(PMe$_3$)$_6$] with an excess of dry butadiene afforded yellow, air-sensitive crystals of compound (**13**). The 300 MHz ^{1}H and 75.4 MHz ^{13}C n.m.r. data for (**13**) are summarised in Table 2. The single ^{1}H and ^{13}C resonances from the two PMe$_3$ groups suggest they are equivalent. The observation of only four ^{13}C signals and a set of six ^{1}H resonances for the two butadiene ligands indicate that they occupy equivalent sites. These data are consistent with an octahedral complex possessing C_2 symmetry. The solid-state structure of (**13**) confirms this geometry (see below). The chemical shift and coupling constants determined by double-resonance experiments are assigned based on the labelling scheme shown in the Scheme. Chemical shifts and coupling constants determined are consistent with those observed for other transition metal butadiene complexes.[12] The complexity of the spectrum of (**13**) is in contrast to that of the analogous [Mo(η-C$_4$H$_6$)$_2$(CO)$_2$][13] where fluxionality gives rise to an AA′BB′CC′ spectrum at room temperature which separates to an ABCDXY spectrum on cooling to 180 K. It can be inferred that the activation energy for fluxional isomerisation of the butadiene ligands of (**13**) is substantially greater than for [Mo(η-C$_4$H$_6$)$_2$(CO)$_2$].[12] [A lower limit for isomerisations of (**13**) can be set as $\Delta G^{\ddagger} > 16$ kcal mol^{-1}.]

The crystal structure of (**13**) has been determined. Selected bond lengths, angles and least-squares best planes are given in Table 3. A non-crystallographic two-fold axis bisects the angle subtended by P(1)–Mo–P(2). The structure is shown in Figure 2.

Both the butadiene ligands are bound in an η^4 mode with an essentially planar skeleton. The average distance between the internal carbon atoms is 1.398(5) Å and is shorter (by 0.015 Å) than the average distance between the terminal and internal carbon atoms [1.413(5) Å], a small but significant difference. Also the average internal Mo–C distance [2.223(3) Å] is shorter (by 0.066 Å) than the terminal carbon atom to Mo distance, 2.289(3) Å. These trends are general features of most diene complexes[14] and represent the η^4-bonding mode exemplified by [Fe(CO)$_3$(diene)] complexes.

One terminal metal–carbon bond length on both butadiene molecules [involving C(4) and C(8)] is longer than the other [C(1),C(5)] by 0.018 Å and may be the result of a small *trans* effect, as the longer bond is *trans* to the PMe$_3$ phosphorus atom. This may explain the slight asymmetry in the *cis*-butadiene, *i.e.* the C(2)–C(3)–C(4) angle [118.7(2)°] is 3.8° larger than C(1)–C(2)–C(3), 114.9(2)° [the difference is 3° for C(5)–C(6)–C(7) and C(6)–C(7)–C(8)].

The hydrogen atoms of the butadiene ligands have been located. The terminal *anti* hydrogens are displaced away from the molybdenum, out of the least-squares best plane, by an average of 0.560 Å. This may be indicative of some rehybridization of the terminal carbon atoms, from sp^2 to sp^3. Similar distortions have been noted in the structure of [Mn(C$_4$H$_6$)$_2$(CO)].[15]

The He-I and He-II photoelectron (p.e.) spectra of (**13**) are shown in Figure 3. Assignments of the various bands (Table 4) are based on intensity variations with photon energy and comparison with the p.e. spectra reported for [Mo(η-C$_4$H$_6$)$_3$][16] and [Mo(η-C$_6$H$_6$)$_2$].[17] Band (d) shows a smaller He-II/He-I cross-section ratio than (a), (b), or (c), indicating that it contains ionisations from the PMe$_3$ donor electron pairs. The ionisation energy (i.e.) of free PMe$_3$ occurs at 8.5 eV. Intensity and i.e. considerations suggest that ionisations from the lowest π levels (Ψ_1) of the diene ligands also comprise band (d). Band (c) is assigned to ionisations from the top filled π level (Ψ_2) of the dienes, which act as donors to the molybdenum. Band (b) is assigned to ionisations from a composite molecular orbital, which represents back-donation from the molybdenum to the Ψ_3 the lowest occupied molecular orbital (l.u.m.o.) of the diene ligands. Though the Mo atom is formally d^6 in this complex,

Table 2. Analytical and spectroscopic data

Compound	Colour	Analysis[a] (%) C	H	Selected i.r. data[b]	N.m.r. data[c]
(1)	Orange	*d*		926s[e]	1.36 (s, 18Me)[f]
(5)	Yellow	35.4 (35.7)	8.7[g] (8.9)	1 942s[h] 927s[e]	1.40 (s, **36**, PMe *cis* to N_2), 1.11 [d, *J*(P–H) = 4, **9**, PMe *trans* to N_2][f]
(7)	Yellow	*i*		*j*	1.40 (s, **36**, PMe), −3.99 [five lines, *J*(P–H) = 34.8, **4**, 4 Mo–H][f]
(9)	Yellow-orange	*k*		1 770w, br[l] 953s[e]	4.47 (s, **5**, η-C_5H_5), 1.28 (narrow multiplet with sharp outer lines, **27**, PMe), −8.37 [q, *J*(P–H) = 52.6, **1**, Mo–H][f]
(10)	Red	34.8 (35.1)	7.1 (7.1)	1 880w, br 1 800w, br 952s[e]	20 °C: 5.04 [q, *J*(P–H) = *ca.* 2, **5**, η-C_5H_5], 1.61 [d, *J*(P–H) = 8.3, **27**, PMe], *ca.* −4 (vbr, **2**, Mo–H) 57 °C: η-C_5H_5 and PMe as above, −3.75 [q, *J*(P–H) = 45, Mo–H][m]
(11)	Red	31.6 (31.7)	5.5 (5.5)	950s[e] 931[n]	5.80 (s, **5**, η-C_5H_5), 1.86 [d, *J*(P–H) = 10, **18**, PMe][m]
(12)	Black	23.0 (23.2)	4.2[o] (4.2)	1 890w[l] 943s	5.21 [t, *J*(P–H) = 46.6, **1**, Mo–H], 4.43 (s, **5**, η-C_5H_5), 1.51 (doublet with broad centre, **18**, PMe)[f]
(13)	Yellow-orange	47.0 (47.2)	8.4[p] (8.4)		4.21 (m, **2**, =CH_2–), 3.50 [q, *J*(H–H) = 5.7, **2**, =CH–], 1.16 [dddd, *J*(H–H) = 1.5, 2.6, 7.2, *J*(P–H) = 20.5, **2**, *syn* =CH_2], 1.01 [d, *J*(P–H) = 6.7, **18**, PMe], 0.72 [d, *J*(H–H) = 6.7, **2**, *syn* =CH_2], −0.73 [qd, *J*(H–H) = 2.6, 6.1, *J*(P–H) = 6.7, **2**, *anti* =CH_2], −0.82 [t, *J*(H–H) = 6.7, *J*(P–H) = 6.7, **2**, *anti* =CH_2] ^{13}C-n.m.r. (75.4 MHz, C_6H_6, off-resonance coupled): 80.6 (d, =CH–), 69.7 (d, =CH–), 43.3 (t, =CH_2), 35.1 (t, =CH_2), 20.5 (m, P–CH_3)[f]
(14)	Yellow	37.9 (37.9)	7.1 (7.0)		5.66, (q, $J_{av.}$ = 7.4, **1**, H_a), 5.30 (m, **1**, H_b), 4.70 (q, $J_{av.}$ = 6.3, **1**, H_c), 3.90 (m, **1**, H_d), 2.56 [ddq, *J*(P–H) = 18.4, **1**, H_e], 2.12 (m, dd, **1**, H_f), 1.70 [d, *J*(P–H) = 8.8, **9**, PMe], 1.52 [d, *J*(P–H) = 8.1, **9**, PMe], *ca.* 1.50 (m, **1**, H_g), 0.8 (s, **1**, H_k or H_l), 0.39 (t, $J_{av.}$ = 6, **1**, H_h), −0.18 (t, $J_{av.}$ = 8.8, **1**, H_i), −0.40 (m, **1**, H_j), −0.8 (s, **1**, H_k or H_l), −9.16 (br s, **1**, H_m)[j,q] ^{13}C-n.m.r. (at −90 °C, off-resonance decoupled): 82.49 (d, *J* = 172, =CH–), 81.36 (d, *J* = 169, =CH–), 80.2 (d, *J* = 171, =CH–), 73.38 (d, *J* = 175, =CH–), 55.98 (t, *J* = 155, =CH_2), 50.73 (t, *J* = 154, =CH_2), 43.8 (t, *J* = 158, =CH_2), 18.66 [q, *J*(P–C) = 27, PMe], 18.6 [m, *J*(P–C) = 31, PMe], −3.9 (dt,[r] *J* = 84.0 and 141, –CH_3)[j,s]
(15)	Yellow	41.2 (40.9)	6.6 (6.6)	1 690s[t] 1 672s[t]	6.36 (q, $J_{av.}$ = 6.7, **1**, H_a), 6.05 (q, $J_{av.}$ = 5.6, **1**, H_b), 4.24 (tt, **1**, H_c), 3.15 (m, **1**, H_d), 2.61 (sextet, J_{eg} = 6.1, J_{ec} = 11.7, **1**, H_e), 1.64 [dd, *J*(H^fP) = 19.1, J_{fb} = 7.2, H_f], 1.23 (d, J_{ge} = 6.1, **3**, H_g), 0.83 [d, *J*(P–H) = 7.8, **9**, PMe], 0.52 [d, *J*(P–H) = 6.7, **9**, PMe], *ca.* 0.53 (H_h, obscured by PMe), 0.25 (m, **2**, H_i and H_j), −1.27 (m, **1**, H_k) ^{13}C-n.m.r. (75.4 MHz, [$^2H_8$]toluene, ^1H coupled): 161.0 (C=O), 116.3 [q, *J*(C–F) = 293, –CF_3], 95.3 [d, *J*(C–H) = 156, =CH–], 94.8 [dd, *J*(C–H) = 167, *J*(P–C) = 9, =CH–], 87.5 [d, *J*(C–H) = 161, =CH–], 79.9 [d, *J*(C–H) = 179, =CH–], 61.2 [td, *J*(C–H) = 158, *J*(C–P) = 9, =CH_2], 55.7 [t, *J*(C–H) = 152, =CH_2], 45.5 [td, *J*(C–H) = 154, *J*(C–P) = 18, =CH_2], 19.0 [m, *J*(C–P) = 25, PMe], 18.0[u] (–CH_3), 16.5 [m, *J*(C–P) = 25, PMe][f,u]

[a] Calculated values are given in parentheses. [b] Measured as Nujol mulls; values in cm^{-1}. [c] ^1H Unless stated otherwise. Given as chemical shift δ (multiplicity, *J* in Hz, **relative intensity**, assignment). [d] Mo: 17.6(17.4)%. *m/e* ^{98}Mo: 478 (M^+ − PMe_3), 402 (M^+ − $2PMe_3$), 387 (M^+ − $2PMe_3$ − CH_3), 326 (M^+ − $3PMe_3$). Compound (**3**) is only observed as a minor equilibrium component in the ^1H n.m.r. spectrum; −4.0 [quintet, *J*(P–H) = 45.2 Hz], 1.37 (shoulder), 1.41. [e] P–C stretch. [f] In C_6D_6. [g] N: 5.4(5.6)%. *m/e*, ^{98}Mo: 506 (M^+), 478 (M^+ − N_2), 458, 430 (M^+ − PMe_3), 400 (M^+ − N_2 − PMe_3 − 2H), 326 (M^+ − N_2 − $2PMe_3$ − 2 H). [h] ν(N_2). [i] Mass spectrum (*m/e*, ^{98}Mo): 400 (M^+ − 6H, 42%), 324 (M^+ − 6H − PMe_3). [j] ν(Mo–H) 1 720m br, 1 672m br. [k] Analysis unsatisfactory, see text. *m/e* ^{98}Mo: 392 (M^+), 314 (M^+ − PMe_3 − 2H). [l] ν(Mo–H). [m] In $(CD_3)_2CO$. [n] ν(Mo=O). [o] I: 45.7(44.7)%. *m/e*, ^{98}Mo: 568 (M^+ − H, 40%; M^+ − 2H, 51%), 503 (M^+ − 2H − C_5H_5), 492 (M^+ − 2H − PMe_3), 441 (M^+ − 2 H − I). A weak band at *m/e* 702 exhibits an isotope distribution pattern consistent for a Mo_2 species. [p] *m/e* ^{98}Mo: 358 (M^+), 302 (M^+ − C_4H_6), 282 (M^+ − PMe_3), 226 (M^+ − C_4H_6 − PMe_3). [q] At −90 °C in CD_3OD. At room temperature (r.t.) the bands at δ −9.16, −0.8, and 0.8 are absent and there is a new band at δ −3.05 (br s, **3**, CCH_3). The ^1H n.m.r. spectrum of the mono-deuteriated cation shows a new band at δ −3.66 of relative intensity 1 compared to the band at δ −3.05 assignable to a CH_2D group. ^{31}P-{^1H} n.m.r. in $(CD_3)_2CO$: two doublets centred at 21.4 and 33.26 p.p.m., separation 27.9 Hz. [r] The ^{13}C n.m.r. spectrum at r.t. shows the band centred at −3.53 p.p.m. as a binomial quartet (*J* = 123 Hz). [s] The diene/allylic carbon atom assignments were ambiguous. [t] ν(CO). [u] Seen clearly in the broad-band decoupled spectrum.

four of the '*d*' electrons appear to be substantially delocalised onto the butadiene ligands, as was found for [Mo(η-C_4H_6)$_3$].[16] The remaining band (a) represents the other two '*d*' electrons. The i.e. of bands (b), (c), and (d) are all lower than the corresponding bands in the p.e. spectrum of [Mo(η-C_4H_6)$_3$], presumably as a result of the electron-donating property of the PMe_3 ligands. Band (a) does not show an increase in relative intensity in the He-II spectrum as would be expected for ionisations of electrons principally localised on the metal. It may well be that the associated electrons, though less tightly bound, are also delocalised onto the diene groups.

The bonding in η^4-butadiene complexes can be represented by (I) and (II). Both (I) and (II) are resonance hybrids of two limiting structures, in which all the diene carbons are involved in the bonding. Representation (I) emphasises a bonding mode involving, principally, the donation of electrons from the filled orbitals of butadiene (Ψ_1 and Ψ_2) to the metal, while (II) reflects substantial occupation of the l.u.m.o. (Ψ_3) of butadiene from

Table 3. Selected distances, angles, and planes for compound **(13)**

(*a*) Distances (Å) and angles (°)

Mo(1)–C(1)	2.279(3)	Mo(1)–C(6)	2.217(3)	C(1)–C(2)	1.406(5)	P(1)–Mo(1)–P(2)	97.96(2)
Mo(1)–C(2)	2.223(3)	Mo(1)–C(7)	2.228(3)	C(2)–C(3)	1.395(5)	C(1)–C(2)–C(3)	114.98(29)
Mo(1)–C(3)	2.223(3)	Mo(1)–C(8)	2.294(3)	C(3)–C(4)	1.413(5)	C(2)–C(3)–C(4)	118.74(30)
Mo(1)–C(4)	2.299(3)	Mo(1)–P(1)	2.456(1)	C(5)–C(6)	1.409(5)	C(5)–C(6)–C(7)	115.19(29)
Mo(1)–C(5)	2.277(3)	Mo(1)–P(2)	2.465(1)	C(6)–C(7)	1.397(5)	C(6)–C(7)–C(8)	118.24(33)
				C(7)–C(8)	1.413(5)		

(*b*) Least-squares planes of the form $PX + QY + RZ = S$, where X, Y, and Z are fractional co-ordinates

Plane	Atoms	P	Q	R	S
1	C(1), C(2), C(3), C(4)	10.487	−8.090	−5.407	−3.693
2	C(5), C(6), C(7), C(8)	11.967	−5.135	3.012	5.221
3	Mo(1), P(1), P(2)	12.512	−1.766	−2.382	2.396

Distances (Å) of atoms from planes; atoms included in the least-squares plane are in square brackets

Plane	
1	Mo(1) 1.845, [C(1) −0.003, C(2) 0.007, C(3) −0.007, C(4) 0.003]
2	Mo(2) −1.842, [C(5) 0.005, C(6) −0.010, C(7) 0.010, C(8) −0.005]

Angles (°) between planes
1—2, 35.2; 1—3, 24.6; 2—3, 23.7

Table 4. Ionization energies for transition metal diene and arene complexes

Complex	Band energy,[a] eV (assignments)				Ref.
(13)	5.91	7.10	8.39	9.31	*b*
	(d^2)	($d + \Psi_3$)	(Ψ_2)	(Ψ_1, P)	
$[Mo(\eta\text{-}C_4H_6)_3]$	—	[7.23] 7.44	9.10	10.49	16
		(Ψ_3)	(Ψ_2)	(Ψ_1)	
$[Fe(CO)_3(C_4H_6)]$	—	[8.16] 8.62	9.82	11.43	*c*
		($d + \Psi_3$)	(Ψ_2)	(Ψ_1)	
$[Mo(\eta\text{-}C_6H_6)_2]$	5.52	6.59	9.47	10.15	17

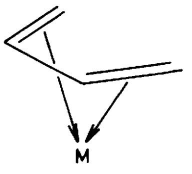
[a] Values in square brackets indicate a shoulder. [b] This work. [c] J. A. Conner, L. M. R. Derrick, M. B. Hall, I. H. Hillier, M. F. Guest, B. R. Higginson, and D. R. Lloyd, *Mol. Phys.*, 1974, **28**, 1193.

Table 5. Spin-saturation-transfer and T_1 (longitudinal relaxation) experiments on **(14)** at 320 K (saturation of band at δ −3.05)

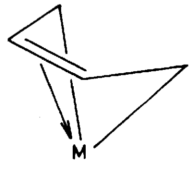
Signal	$T_1{}^a$/s	$M(0)/M(\infty)$	k^b/s^{-1}	$\Delta G^\ddagger$/kJ mol^{-1}
(a)	4.09	1	0	
(b)	4.04	1	0	
(c)	3.80	1	0	
(d)	3.85	1	0	
(e)	2.02	2.33	0.731	80
(f)	1.33	1.67	0.391	82
(g)	obscured			
(h)	1.33	1.88	0.513	81
(i)	1.81	4.68	2.26	77
(j)	1.86	1.79	0.469	82
(k)	1.69	—		

[a] T_1 pulse sequence 180–τ–90: T_1 from a computer fitting to $Y = A3 - A2\ \exp\ (-\tau/T_1)$; Y = intensity (observed), $A2$ = pre-exponential constant, $A3$ = constant (intensity at t_∞); $A2$, $A3$, T_1 varied. [b] $k = 1/T_{1A}\{[M(0)/M(\infty)] - 1\}$: $T_{1A} = T_1$ of the site to which saturation is being transferred; $M(0)$ = instantaneous intensity (peak height) at $t = 0 : M(\infty)$ at $t = \infty$.

metal electron back-donation. The relative weighting of these forms, *i.e.* the degree of occupation of the Ψ_3 orbital, depends largely on the nature of the metal and additional ligands. Representation (I) prevails if the diene group competes for metal electrons with good π-acceptor ligands, *e.g.* CO, restricting the back-donation. Conversely, poorer π-acceptor ligands, *e.g.* $\eta\text{-}C_5R_5$ (R = H or CH_3), or strongly electron-releasing ligands, *e.g.* tertiary phosphines, would favour (II).[18]



(I)



(II)

The crystal structure data show that the carbon–carbon bond distances of the butadiene ligand are closely similar. Strong back-donation is indicated, giving a situation intermediate between (I) and (II). The p.e. spectrum, as discussed, indicates that four metal electrons are strongly involved in metal–ligand bonding. The values of J = 2.6 Hz for $=CH_2$ of the butadiene are consistent with a slight move from sp^2 to sp^3 hybridisation.[19]

[Mo(butadiene)$_3$] shows apparently anomalous behaviour. M.o. calculations predict extensive back-donation between metal and butadiene ligands[16] and hence the equalization of the carbon–carbon bond lengths. However, *X*-ray crystallographic data show the internal carbon–carbon bonds to be longer than those of the internal terminal carbons [1.560(8) and 1.336(11) Å respectively]. This phenomenon has yet to be understood fully.

Addition of a methanol solution of aqueous HBF_4 to **(13)** gives orange-red crystals of $[\overline{M(1\text{—}3\text{-}\eta\text{-}H}CH_2CHCHCH_2)(\eta^4\text{-}C_4H_6)(PMe_3)_2]BF_4$ **(14)**. The low-temperature ^1H and ^{13}C n.m.r. spectral data of **(14)** at −90 °C are given in Table 2 together with assignments. The assignments correspond to the proposed structure shown in the Scheme. Comprehensive double-resonance experiments are entirely consistent with the proposed structure. The presence of the agostic[20] methyl group is shown by the observation at −90 °C of three bands assignable to the methyl hydrogens, at δ 0.8, −0.8, and −9.16.

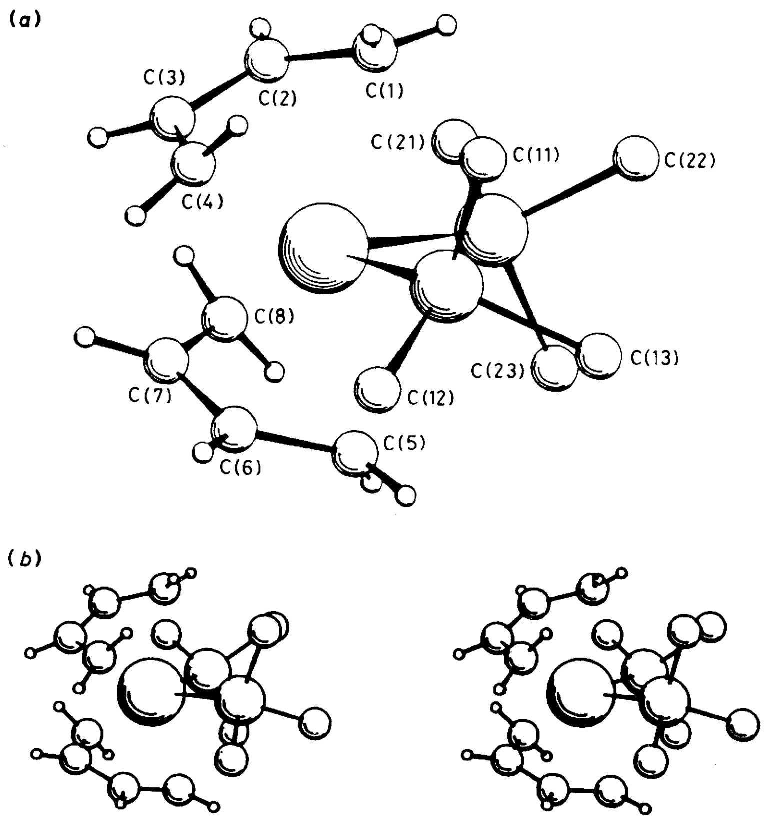


Figure 2. Molecular structure and labelling for [Mo(η-C_4H_6)$_2$(PMe_3)$_2$] (**13**). (*a*) Viewed along P(1)–P(2); (*b*) stereoscopic view

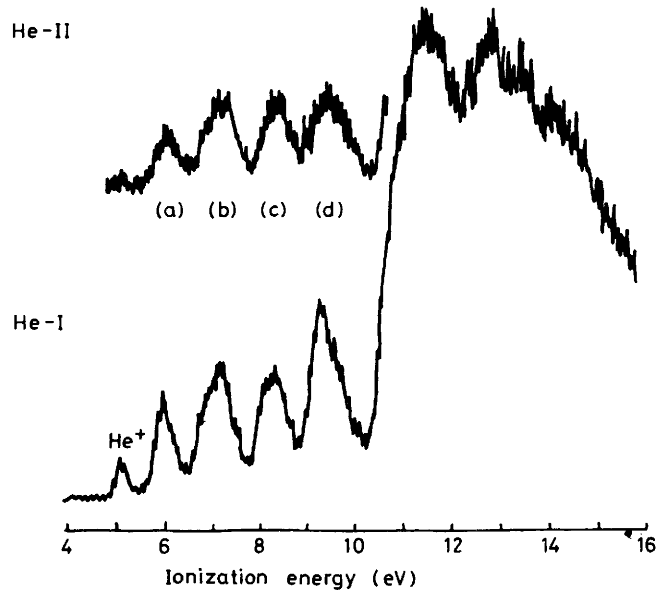


Figure 3. Photoelectron spectra of [Mo(η-C_4H_6)$_2$(PMe_3)$_2$] (**13**)

The high-field band is in the region associated with agostic hydrogens bonded to transition metal centres with d^n ($n > 0$) electrons.[20] The ^{13}C n.m.r. spectrum (−90 °C) is especially diagnostic of the presence of the agostic hydrogen since the band assigned to the agostic methyl occurs as a doublet of triplets with the value of J(C–$H_{agostic}$) = 84.0 Hz and J(C–H_l) = J(C–H_k) = 144 Hz. These values are similar to those found for analogous agostic alkyl groups.[20] The ^{13}C n.m.r. spectrum of the Mo–HCH_2 fragment of (**14**) at −90 °C is shown in Figure 4.

N.m.r. line-broadening and spin-saturation-transfer experiments indicate two different intramolecular hydrogen-scrambling processes. One process concerns interchange of the agostic H with the two normal hydrogens of the Mo–H–CH_2 group. As the temperature is raised above −90 °C the three bands assigned to the agostic hydrogen[20] and to the two other methyl hydrogens collapse and in the room temperature spectrum merge to a singlet at the expected weighted mean average position, namely (0.8 − 0.8 − 9.16)/3 = δ −3.05. The hydrogens of the agostic methyl are presumably exchanged by rotation about the C–C (methyl) bond. Analysis of the linewidth gives the value k(Me rotation, −90 °C) = 90 ± 10 s^{-1} and $\Delta G^{\ddagger}$ = *ca.* 37.2 kJ mol^{-1}.

Evidence for the second scrambling process was first apparent from the ^1H n.m.r. spectrum of the product formed by deuteriation of (**14**) giving the monodeuteriated methyl analogue (**14**–D) which showed substantial incorporation of ^1H from the two C_4 ligands into the methyl site. The details of this exchange process were investigated by spin-saturation-transfer experiments. Irradiation of the band at δ −3.05 caused a decrease in intensity of bands assigned to H_f, H_h, H_i, H_g, H_e, H_j, and H_d. Quantitative saturation-transfer experiments including relaxation time (T_1) measurements were carried out and the results, including rates and activation energies for the scrambling processes, are given in Table 5. The data show that there is no exchange of hydrogens with internal sites. Hydrogen exchange to all terminal carbons is observed but occurs preferentially to one end of the other C_4 ligand. This may be compared to the analogous system [M(1—3-η-HCHCH_2-CH_2CH⋯CH⋯CH)(CO)$_3$] where a similar exchange

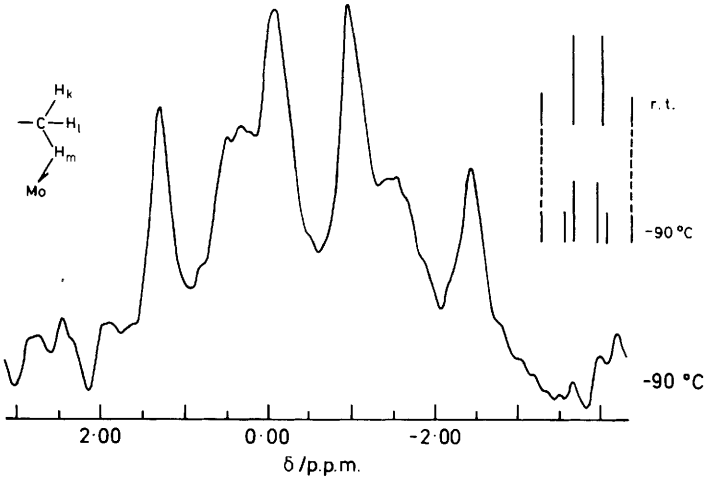


Figure 4. Carbon-13 n.m.r. spectrum of the Mo–HCH$_2$ fragment of (**14**) at −90 °C and at room temperature (top insert)

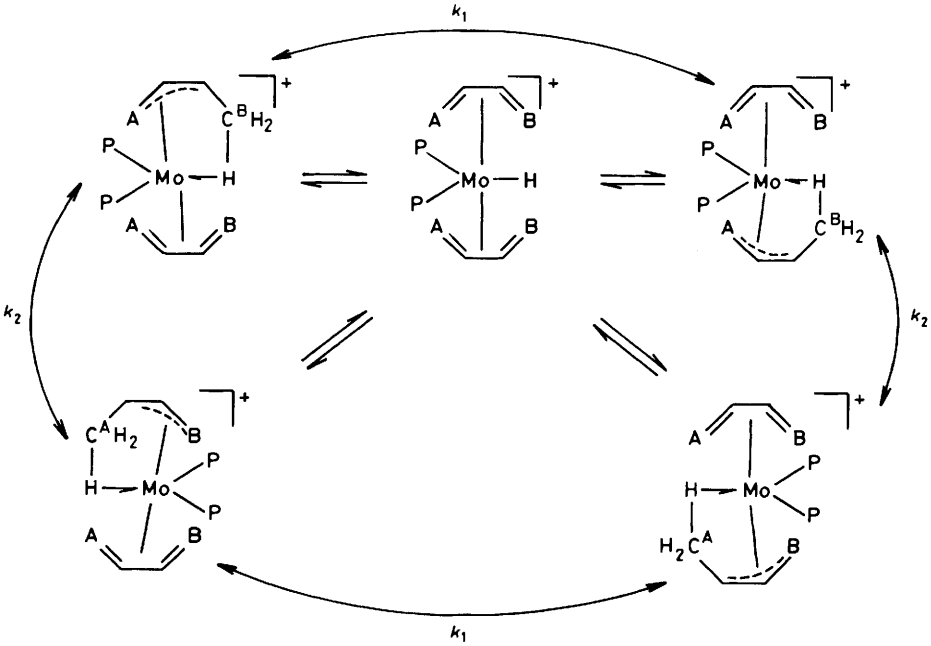


Figure 5. Mechanism proposed for the hydrogen-exchange equilibria in (**14**). $K_{exch.}$ for H_B = 2 s^{-1}, $\Delta G^{\ddagger}$ = 77.2 kJ mol^{-1}; $K_{exch.}$ for $H_{A(av.)}$ = 0.5 s^{-1}, $\Delta G^{\ddagger}$(av.) = 81 kJ mol^{-1}

process was found to have an activation barrier of *ca.* 60 kJ mol^{-1}.[21] The mechanism shown in Figure 5 is proposed and involves exchange *via* a diene–hydride intermediate.

Based on the isotopic probe developed by Calvert and Shapley,[22] the bridging interaction in (**14**) is confirmed by noting the large upfield shift (at 25 °C) of the CH$_2$D group (δ −3.66) relative to the CH$_3$ group (δ −3.05). This arises from the preferential occupation of ^{1}H in the bridging site and the consequent upfield shift of the weighted-average resonance.

The reaction of (**13**) with CF$_3$COOH in methanol or toluene gave air-stable red-orange crystals of (**15**). The i.r. spectrum of (**15**) showed bands at 1 690s, 1 672s; and 1 195s, 1 169s, 1 120s cm^{-1}, assigned to metal-bound CF$_3$COO– (C–O and C–F respectively). A weak band at 1 569 cm^{-1} was thought to result from an allylic species. The 300 MHz ^{1}H n.m.r. spectrum of (**15**) can be fully assigned, with the assistance of extensive double-resonance experiments, in terms of the structure shown in the Scheme.

Experimental

All preparations and reactions were carried out under an atmosphere of purified argon. Solvents were dried and purified by reflux over a suitable drying agent under dinitrogen, followed by distillation under dinitrogen. Benzene, tetrahydrofuran (thf), light petroleum (b.p. 60—80 °C), and cyclohexane were dried over potassium; toluene and light petroleum (b.p. 100–120 °C) were dried over sodium; light petroleum (b.p. 30—40 °C) and diethyl ether were dried over sodium–potassium alloy. Butadiene was purified by distillation over solid potassium hydroxide and then 4A molecular sieves. All other reagents were used as supplied. Microanalyses were performed by the analytical department of this laboratory or by Alfred Bernhardt Ltd.

Infrared spectra were recorded on a Pye-Unicam SP2000 double-beam grating spectrophotometer or a Perkin-Elmer 457 double-beam grating spectrophotometer.

Nuclear magnetic resonance spectra were recorded on a

JEOL PMX60 (^1H, 60 MHz), a Bruker WH300 (^1H, 300 MHz; ^{13}C, 75.4 MHz), a Bruker WH90 (^1H, 90 MHz; ^{31}P, 36.43 MHz), and a Bruker WH400 (^1H and ^{13}C). Multiplicities are abbreviated as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet. Solvent bands were used as internal standards. Mass spectra were recorded on an A.E.I. MS 902 spectrometer. Synthesis experiments involving Mo atoms were carried out using the apparatus previously described.[23] Photoelectron spectra were measured on a PES Laboratories 0078.

Hexakis(trimethylphosphine)molybdenum, (**1**).—In a typical experiment, molybdenum atoms (2.0 g, 0.02 mol) were evaporated from a pre-melted ingot (15 g) at 3.0 kW (6 kV at 500 mA) and co-condensed with pure PMe_3 (100 cm^3) over a period of four hours. A red matrix was formed. On completion of metal evaporation and warming to ambient temperature, the product solution in neat PMe_3 was dichroic red-green, with small crystallites on the walls of the receiver. Before extraction with the washing solvent, excess PMe_3 was recovered by distillation under reduced pressure. An average of 70% recovery of the excess of trimethylphosphine was achieved. The residue was extracted with hot cyclohexane (600 cm^3, 70 °C) and the extract was immediately filtered through a bed of Celite to remove unreacted metal. Concentration of the filtrate (to 100 cm^3) under reduced pressure gave an olive-green solution. This was cooled to 7 °C for 3 d, giving impure orange crystals which were recrystallized three times from cyclohexane. This gave analytically pure hexakis(trimethylphosphine)molybdenum; yield 6.0 g, *ca.* 55%. Recrystallization from benzene gave single crystals suitable for *X*-ray diffraction studies.

Tricarbonyltris(trimethylphosphine)molybdenum, (**4**).—The compound $[Mo(PMe_3)_6]$ (0.20 g, 0.0004 mol) in light petroleum (b.p. 40—60 °C; 50 cm^3) was pressurized with carbon monoxide to 2 atm. After 5 min at 25 °C the orange solution had become pale yellow and there was a small quantity of a brown precipitate. The supernatant liquor was separated by filtration and the volatile components removed under reduced pressure, affording a yellow solid. This was recrystallized from a concentrated solution in hot light petroleum (b.p. 60—80 °C). After *ca.* 18 h white platelets were deposited from solution. These were collected and dried *in vacuo*, giving pure $[Mo(CO)_3(PMe_3)_3]$; yield *ca.* 80%.

Dinitrogenpentakis(trimethylphosphine)molybdenum, (**5**).—The compound $[Mo(PMe_3)_6]$ (0.2 g, 0.0004 mol) in light petroleum (b.p. 40—60 °C; 30 cm^3) was pressurized with N_2 to 15 atm in a pressure bottle. After 48 h at 25 °C, with stirring, the solution had changed from orange to yellow. The volatile components were removed under reduced pressure and the resulting orange solid was recrystallized from a concentrated solution (15 cm^3) in light petroleum (b.p. 40—60 °C) at −30 °C, giving yellow needles of $[Mo(N_2)(PMe_3)_5]$; yield *ca.* 90%.

Bis(η-ethylene)tetrakis(trimethylphosphine)molybdenum, (**6**).—The compound $[Mo(PMe_3)_6]$ (0.15 g, 0.0003 mol) in light petroleum (b.p. 100—120 °C; 50 cm^3) was pressurized to 3 atm with ethylene. After *ca.* 18 h at 25 °C the orange solution had become pale yellow. Removal of the volatile components under reduced pressure gave a waxy yellow-brown solid. This was purified by sublimation (80 °C, 5 × 10^{-2} Torr) onto a liquid N_2 cooled probe affording the slightly air-sensitive (stable for minutes), pale yellow $[Mo(\eta\text{-}C_2H_4)_2(PMe_3)_4]$; yield *ca.* 60%.

Tetrahydridotetrakis(trimethylphosphine)molybdenum, (**7**).—The compound $[Mo(PMe_3)_6]$ (0.15 g, 0.003 mol) in light petroleum (b.p. 100—120 °C) was pressurized to 3 atm with H_2 gas (250 cm^3). After 3 d at 25 °C a small amount of brown powder had settled from a yellow solution. The reaction was considered to be complete at this stage. The volatile components were removed under reduced pressure; the resultant brown oily solid was purified by sublimation (80 °C, 5 × 10^{-2} Torr) onto a liquid N_2 cooled probe giving an air-sensitive, pale yellow solid; yield *ca.* 60%.

trans-*Di-iodotetrakis(trimethylphosphine)molybdenum*, (**8**).—The compound $[Mo(PMe_3)_6]$ (0.15 g, 0.0003 mol) in light petroleum (b.p. 40—60 °C; 50 cm^3) was treated with an excess of iodomethane in toluene (0.10 g in 25 cm^3). After *ca.* 30 min at 25 °C a white flocculent precipitate had settled from an orange-red solution. The supernatant liquor was separated by filtration and the volatile components removed under reduced pressure. The resultant red solid was recrystallized from a concentrated toluene solution (30 cm^3) at −30 °C, affording red-orange, orthorhombic crystals; yield *ca.* 80%.

(η-Cyclopentadienyl)hydridotris(trimethylphosphine)molybdenum, (**9**).—The compound $[Mo(PMe_3)_6]$ (0.25 g, 0.0005 mol) and freshly distilled cyclopentadiene (0.1 g, 0.002 mol) in light petroleum (b.p. 100—120 °C; 80 cm^3) were heated to 80 °C for 3 d. The yellow solution thus formed was separated from a small amount of a black amorphous solid by filtration. The volatile components were removed under reduced pressure, affording a viscous orange oil. Attempts to recrystallize this oil from common organic solvents were unsuccessful. Sublimation (40 °C, 5 × 10^{-2} Torr) onto a liquid N_2 cooled probe gave a waxy, very air-sensitive solid. Attempts to obtain crystals and chromatography on silica led to decomposition. The compound was not isolated in an analytically pure form. However, spectral data led to characterization as $[MoH(\eta\text{-}C_5H_5)(PMe_3)_3]$; yield *ca.* 70%.

(η-Cyclopentadienyl)dihydridotris(trimethylphosphine)molybdenum Tetrafluoroborate, (**10**) *and (η-Cyclopentadienyl)oxobis(trimethylphosphine)molybdenum Tetrafluoroborate*, (**11**) (*Method* 1).—The compound $[MoH(\eta\text{-}C_5H_5)(PMe_3)_3]$ (0.15 g, 0.0004 mol) in diethyl ether (50 cm^3) was treated with a slight excess of aqueous HBF_4 (50%) in diethyl ether. A pink flocculent precipitate formed immediately and addition continued until the solution became colourless. The solid was isolated by filtration, washed with diethyl ether and dried *in vacuo*. Crystallization from methanol at −30 °C gave a mixture of white and red crystals. Recrystallization of these from hot water gave off-white platelets, which were deposited from a red solution. The supernatant liquor was decanted, the crystals were washed with cold water and dried *in vacuo*, affording the air-stable compound (**10**); yield *ca.* 60%.

The water was removed from the red mother-liquor under reduced pressure and the resultant red oil was dissolved in a minimum volume of methanol. Cooling to −30 °C for 24 h gave red needles of compound (**11**); yield *ca.* 30%.

(η-Cyclopentadienyl)oxobis(trimethylphosphine)molybdenum Tetrafluoroborate, (**11**) (*Method* 2).—The compound $[MoH(\eta\text{-}C_5H_5)(PMe_3)_3]$ (0.06 g, 0.0001 mol) in wet acetone was irradiated using a 100 W medium-pressure Hg lamp for 24 h. A very small quantity of black-purple crystals was deposited from a red solution. The supernatant liquor was decanted and the solvent was removed under reduced pressure. The residue was recrystallized from methanol at −30 °C. After 18 h, small red crystals separated which were collected and dried *in vacuo*; yield *ca.* 80%.

(η-Cyclopentadienyl)hydridodi-iodobis(trimethylphosphine)molybdenum, (**12**).—The compound $[MoH(\eta\text{-}C_5H_5)(PMe_3)_3]$

Table 6. Atomic fractional co-ordinates and molecular parameters* for (**1**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	0.0000	0.0000	0.0000
P(1)	−0.218 0(2)	0.0000	0.0000
C(1)	−0.292(2)	0.103 8(8)	0.103 8(8)
C(2)	−0.316(3)	0.134(2)	0.0000

* Mo(1)–P(1) 2.467(2), P(1)–C(1) 1.880(4), P(1)–C(2) 1.884(4) Å; Mo(1)–P(1)–C(1) 110.1(8), Mo(1)–P(1)–C(2) 126(1)°.

(0.10 g, 0.0003 mol) in toluene (50 cm^3) was reacted with methyl iodide (0.20 g, 0.0041 mol) in toluene (30 cm^3). After 5 min the solution was observed to darken and after 18 h at 25 °C a buff coloured precipitate had settled from the dark red solution. The solution was separated by filtration and the volatile components removed under reduced pressure, affording a black-red solid. Recrystallization from hot (*ca.* 80 °C) light petroleum (b.p. 100—120 °C) gave large, black octahedral crystals; yield *ca.* 80%. Compound (**12**) could be sublimed (200 °C, 5 × 10^{-2} Torr) without decomposition.

Bis(η-butadiene)bis(trimethylphosphine)molybdenum, (**13**).—The compound [Mo(PMe$_3$)$_6$] (0.25 g, 0.0005 mol) in light petroleum (b.p. 40—60 °C; 50 cm^3) was pressurized to 3 atm with butadiene in an ampoule (250 cm^3). After *ca.* 5 min at 25 °C a fine suspension had formed, which after 12 h had settled from a yellow solution. The reaction was considered to be complete at this stage. The supernatant liquor was decanted and the volatile components removed under reduced pressure, leaving a brown solid. Sublimation (80 °C, 5 × 10^{-2} Torr) onto a liquid N$_2$ cooled probe afforded a yellow, air-sensitive solid. Attempts to recrystallize this solid from light petroleum were unsuccessful; however, from a concentrated solution in methanol at −30 °C, yellow-orange crystals were deposited. The supernatant liquor was removed by filtration, the crystals washed with cold methanol, and dried *in vacuo*; yield *ca.* 70%.

η-Butadiene[1—3-η-butenyl-C$^{1-3}$H(C^4)]bis(trimethylphosphine)molybdenum Tetrafluoroborate, (**14**).—The compound [Mo(η-C$_4$H$_6$)$_2$(PMe$_3$)$_2$] (0.10 g, 0.0003 mol) in methanol (50 cm^3) was treated, dropwise, with a solution of aqueous HBF$_4$ (1 cm^3) in methanol (30 cm^3). Immediately the yellow solution became orange and eventually a red-orange colour persisted. Concentration of this solution under reduced pressure afforded small orange crystals; precipitation was completed by cooling to −30 °C. The orange crystals were isolated by filtration, washed with cold methanol, and dried *in vacuo*; yield *ca.* 80%.

η-Butadiene(1—3-η-butenyl)trifluoroacetatobis(trimethylphosphine)molybdenum, (**15**).—(*i*) *In methanol.* The compound [Mo(η-C$_4$H$_6$)$_2$(PMe$_3$)$_2$] (0.15 g, 0.0004 mol) in methanol (50 cm^3) was treated with a solution of anhydrous trifluoroacetic acid (1 cm^3) in methanol (30 cm^3). The reaction was considered to be complete when the solution had become dark red. The methanol and excess acid were removed under reduced pressure, giving a black-red oil. Attempts to recrystallize the product from methanol and toluene, in which it was very soluble, were unsuccessful. Extraction with hot light petroleum (b.p. 60—80 °C; 100 cm^3) afforded a red solution from which red-orange crystals separated on cooling and were washed with cold light petroleum (b.p. 30—40 °C) and dried *in vacuo*; yield *ca.* 10%.

Crystal Structure Determinations.—Data reduction, structure solution, and refinement were carried out with the Oxford CRYSTALS package.[24] The Oxford CHEMGRAF[25] system was used for diagrams and molecular modelling. Scattering factors for non-hydrogen atoms were taken from Cromer and Mann;[26] the hydrogen scattering factors were taken from ref. 27. Final atomic co-ordinates for compounds (**1**) and (**13**) are given in Tables 6 and 7.

Table 7. Atomic fractional co-ordinates (× 10^4) for compound (**13**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mo(1)	3 253.6(1)	3 572.3(1)	4 382.9(1)
P(1)	3 088.7(6)	4 285.2(4)	2 987.9(5)
P(2)	2 956.8(5)	2 384.7(3)	3 704.6(4)
C(1)	1 465(2)	3 542(2)	4 378(2)
C(2)	1 849(3)	3 436(2)	5 264(2)
C(3)	2 449(3)	3 998(2)	5 611(2)
C(4)	2 636(3)	4 600(2)	5 053(2)
C(5)	4 902(2)	3 473(2)	3 797(3)
C(6)	4 898(2)	3 937(2)	4 552(3)
C(7)	4 577(3)	3 628(2)	5 371(3)
C(8)	4 255(3)	2 905(2)	5 363(2)
C(11)	1 839(3)	4 710(2)	2 726(3)
C(12)	3 943(3)	5 069(2)	2 934(3)
C(13)	3 376(4)	3 894(2)	1 885(2)
C(21)	2 463(3)	1 721(2)	4 496(2)
C(22)	2 017(3)	2 269(2)	2 781(3)
C(23)	4 061(3)	1 899(2)	3 212(3)

Crystal data for (**1**). C$_{18}$H$_{54}$MoP$_6$, M = 551.97, cubic, *Im*3*m*, a = 11.319(2) Å, U = 1 450 Å^3, Z = 2, D_c = 1.26 g cm^{-3}, $F(000)$ = 588, λ(Mo-K_α) = 0.710 69 Å μ(Mo-K_α) = 7.3 cm^{-1}.

The intensities of 1 622 reflections were measured ($2\theta_{max.}$ = 60°), and the data were corrected for extinction but not absorption. A total of 224 independent, observed reflections [$I > 3\sigma(I)$] were used for structure solution and refinement; the structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares. The methyl carbons are highly disordered, resulting in a torus of electron density at approximately 1.85 Å from the phosphorus atoms. After several models for the methyl disorder had been investigated unsuccessfully, it was decided to fix one carbon on each of the two independent mirrors that pass through P(1). The occupancies were set to Mo(1) 0.020 83, P(1) 0.125, C(1) 0.25, C(2) 0.125, and refinement converged with R = 0.0518, R' = 0.0690 for 12 parameters, 224 reflections, and four constraints. A five-term Chebyshev series was used to calculate the weights; the coefficients are 13.46, 3.30, −5.73, 2.21, and 10.41. The final difference Fourier map was featureless.

Crystal data for (**13**). C$_{14}$H$_{30}$MoP$_2$, M = 356.24, orthorhombic, *Pbca*, a = 12.7373(15), b = 18.7094(26), c = 14.7060(18) Å, U = 3 504.55 Å^3, Z = 8, D_c = 1.35 g cm^{-3}, $F(000)$ = 1 488, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 8.98 cm^{-1} The intensities of 9 305 reflections were measured ($2\theta_{max.}$ = 30°), and the data were corrected for extinction but not for absorption. A total of 2 722 independent, observed reflections [$I > 3\sigma(I)$] were used for structure solution and refinement. The structure was solved by Patterson and Fourier methods, and refined by least squares using the large-block approximation. All hydrogen atoms were located and their positions were refined subject to 'soft' restraints. A three-term Chebyshev series was used to calculate the weights; the coefficients are 38.99, 53.11, and 15.14. The refinement converged with R = 0.0237, R' = 0.0316 for 247 parameters. The final difference Fourier map was featureless. $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R' = \sqrt{(\Sigma w||F_o|-|F_c||^2/\Sigma w|F_o|^2)}$ for both (**1**) and (**13**).

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