Dinitrogen, Butadiene and Related Complexes of Molybdenum. Crystal Structures of $[Mo(N_2)(PMe_3)_5]$ and $[Mo(\eta^3\text{-}CH_3CHCHCH_2)(\eta^4\text{-}C_4H_6)(PEt_3)_2][BF_4]$†

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The sodium amalgam reduction of $[MoCl_3(PEt_3)_3]$ prepared *in situ*, under 2–3 atm of N_2, yielded the dimeric complex $[\{Mo(N_2)_2(PEt_3)_3\}_2(\mu\text{-}N_2)]$ **1**, which reacted with 3 and with 4 equivalents of PMe_3 to produce *trans*-$[Mo(N_2)_2(PMe_3)_3(PEt_3)]$ **2** and *trans*-$[Mo(N_2)_2(PMe_3)_4]$ **3**, respectively. In the presence of an excess of PMe_3 (> 5 equivalents, under Ar) the known $[Mo(N_2)(PMe_3)_5]$ **4a** was the final product. This synthetic methodology allowed the preparation, for the first time, of the pure *trans*-bis(dinitrogen) compound **3**. Complexes of the type $[Mo(N_2)(PMe_3)_3(L\text{–}L)]$ (L–L = $Me_2PCH_2PMe_2$ **4b**, $Me_2PCH_2CH_2PMe_2$ **4c** or $Et_2PCH_2CH_2PEt_2$ **4d**) and $[Mo(N_2)(PMe_3)\{N(CH_2CH_2PMe_2)_3\}]$ **4e** were also synthesized and structurally characterized by spectroscopic methods. Upon reaction with C_2H_4, under mild conditions, **1** gave the bis(butadiene) derivative $[Mo(\eta^4\text{-}C_4H_6)_2(PEt_3)_2]$ **5a**. Protonation of **5a**, and of its PMe_2Ph analogue **5b**, produced the cationic but-2-enyls $[Mo(\eta^3\text{-}CH_3CHCHCH_2)(\eta^4\text{-}C_4H_6)L_2][BF_4]$ (L = PEt_3 **6a** or PMe_2Ph **6b**) in which the butenyl ligand exhibits the classical η^3-allylic co-ordination in addition to an agostic Me–Mo interaction. Compounds **4a** and **6a** were structurally characterized by X-ray crystallography. The Mo atom of **4a** resides on a crystallographic mirror plane and is bound to the N_2 moiety with a Mo–N separation of 2.02(3) Å. The Mo–C and Mo–H separations within the agostic unit of **6a** are 2.48(2) and 1.9(2) Å, respectively.

The interaction of the comparatively inert dinitrogen molecule with transition-metal centres has continued to attract considerable attention in recent years, due to the implication of $M\text{–}N_2$ units in biochemical catalytic processes.[1,2] A number of $M\text{–}N_2$ co-ordination studies have focused upon the formation of complexes of Group 6 metals, particularly Mo and W. Apart from the well known complexes of the type *cis*- and *trans*-$[M(N_2)_2(PR_3)_4]$, mononuclear species having different numbers of co-ordinated N_2 and tertiary phosphine ligands are known, *e.g.* $[Mo(N_2)_3(PPr^n{}_2Ph)_3]$[3] and $[W(N_2)(PMe_3)_5]$.[4]

In the past few years our research interests have concentrated in part upon the chemistry of dinitrogen and olefin derivatives of Mo and W.[4,5] Herein we report the formation of the N_2-bridged dinuclear compound $[\{Mo(N_2)_2(PEt_3)_3\}_2(\mu\text{-}N_2)]$ **1**, as well as the outcome of its somewhat unusual reactions with PMe_3 and C_2H_4. The former proceeds in a stepwise manner, with substitution of PEt_3 by PMe_3, and sequential formation of *trans*-$[Mo(N_2)_2(PMe_3)_3(PEt_3)]$ **2**, *trans*-$[Mo(N_2)_2(PMe_3)_4]$ **3**, and the known $[Mo(N_2)(PMe_3)_5]$.[4a,5a] The latter transformation affords the butadiene complex $[Mo(\eta^4\text{-}C_4H_6)_2(PEt_3)_2]$ **5a**, which may also be prepared by the direct reaction of **1** with butadiene. Protonation of **5a**, and of the PMe_2Ph analogue **5b**, produces the agostic cationic but-2-enyls $[Mo(\eta^3\text{-}CH_3CHCHCH_2)(\eta^4\text{-}C_4H_6)L_2]^+$ (L = PEt_3 **6a** or PMe_2Ph **6b**) which have been isolated as their BF_4^- salts.

Results and Discussion

As part of our investigations on the formation and chemistry of dinitrogen complexes of Mo and W containing PMe_3 ligands[4,5] we examined the effect of increasing both the basicity and the steric requirements of the tertiary phosphine by using PEt_3. Reduction of $[MoCl_3(PEt_3)_3]$, prepared *in situ*, with sodium amalgam, under 2–3 atm of N_2, resulted in a change from the initial red to green and then to dark, red-brown. Work-up of the reaction mixture, followed by crystallization from acetone, yielded analytically pure red crystals of complex **1** (Scheme 1).

$$[MoCl_3(thf)_3] \xrightarrow{(i)} [MoCl_3(PEt_3)_3] \xrightarrow{(ii)} \underset{\mathbf{1}}{[\{Mo(N_2)_2(PEt_3)_3\}_2(\mu\text{-}N_2)]}$$

Scheme 1 (*i*) PEt_3, tetrahydrofuran (thf); (*ii*) Na–Hg, N_2, thf

The solution IR spectrum of **1** showed a strong band at *ca.* 1950 cm^{-1}, together with a weaker absorption at 1980 cm^{-1}. Multinuclear NMR studies (^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$) were in accord with the proposed formulation. For instance, an AX_2 pattern (δ_A 22.7, δ_X 19.6, $^2J_{AX}$ = 16 Hz) was observed in the $^{31}P\text{-}\{^1H\}$ NMR spectrum, consistent with the proposed

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton. Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: atm = 101 325 Pa.

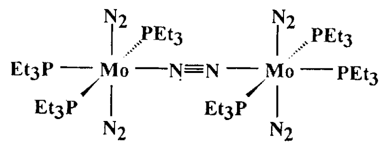
meridional distribution of the PEt_3 groups. Assignment of structure **I** to this complex found additional support in the similarity of the spectroscopic data with those reported for $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$, which was prepared and structurally characterized by X-ray methods by Richards and co-workers.[6] Other spectroscopic data were also in agreement with the above proposal. For instance, the ^1H NMR spectrum revealed the existence of two mutually *trans* molecules of PEt_3 and of a third *cis* to the others, a conclusion based upon the observation of a quartet of triplets (12 H, $^3J_{HH} = 7.5$, $J_{HP_{app}} = 2$ Hz) and a quartet of doublets (6 H, $^3J_{HH} = 8$, $^2J_{HP} = 4.5$ Hz) for the methylenic protons.

A number of substitution reactions of dinitrogen complexes have been shown to proceed with displacement of the co-ordinated N_2 ligands. In some cases, however, the M–N_2 bond may be sufficiently stable for replacement of the co-ligands to occur without dissociation of N_2. A rather unusual example in this regard is the complex *trans*-$[Mo(N_2)_2(PMe_2Ph)_4]$ which has allowed a variety of substitution reactions to ensue without loss of the N_2 ligands.[7] Other examples of M–N_2 complexes which undergo similar coligand displacements are *trans*-$[W(N_2)_2(PMe_2Ph)_4]$,[7a] and *trans*-$[ReCl(N_2)(PMe_2Ph)_4]$. The latter complex converted into *trans*-$[ReCl(N_2)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) upon reaction with the chelating phosphine, although rather forcing conditions were necessary (toluene under reflux for 4 h).[8]

A smooth reaction commenced when complex **1** was treated with an excess of PMe_3 (Scheme 2). Stirring a 1 : 3.5 mixture of **1** and PMe_3 at room temperature, over a period of 3 h, caused partial substitution of the PEt_3 ligands and formation of the mixed PEt_3–PMe_3 complex **2**. The proposed formulation for this complex found support in the appearance of a strong IR absorption at *ca.* 1950 cm^{-1} as well as in the observation of an AM_2X spin system in the $^{31}P\text{-}\{^1H\}$ NMR spectrum (see Experimental section). Compound **2** reacted in turn overnight, with an additional equivalent of PMe_3, to give *trans*-$[Mo(N_2)_2(PMe_3)_4]$ **3**. As expected, **3** also formed in the direct reaction of **1** with a five-molar excess of PMe_3 over a period of *ca.* 16 h.

It is worth mentioning that this rather unusual substitution reaction has allowed the isolation for the first time of the *trans*-bis(dinitrogen) complex **3** in an analytically pure form. Some years ago we found that the sodium-dispersion reduction of $[MoCl_3(PMe_3)_3]$ gave *cis*-$[Mo(N_2)_2(PMe_3)_4]$.[5] The analogous reaction using Na–Hg as the reducing agent gave instead a product initially formulated as *trans*-$[MoCl(N_2)(PMe_3)_4]$, which was shown to consist[9] of a cocrystallized mixture of *trans*-$[Mo(N_2)_2(PMe_3)_4]$ and *trans*-$[MoCl_2(PMe_3)_4]$. Attempts to isolate **3** from these mixtures by crystallization proved fruitless although conclusive spectroscopic and chemical evidence was gained in favour of its formulation as the *trans*-bis(dinitrogen) species.

During the progress of this work we obtained orange crystals of complex **3** by crystallization from Et_2O solutions. In agreement with the proposed *trans* geometry they exhibited a strong IR absorption at *ca.* 1930 cm^{-1}, as well as ^1H and $^{13}C\text{-}\{^1H\}$ resonances characteristic of approximately planar $Mo(PMe_3)_4$ units.[10] The $^{31}P\text{-}\{^1H\}$ NMR spectrum (C_6D_6) consisted of a singlet at δ 0.34. Complex **3** slowly isomerized to the thermodynamically more stable *cis* isomer. Thus, after standing at 30 °C for 48 h, a 3 : 1 *cis* : *trans* mixture was obtained, together with small amounts of $[Mo(N_2)(PMe_3)_5]$ which resulted from partial decomposition of the *cis* complex. Prolonged standing (25 °C, 6 weeks) converted individual samples of both pure *cis*- and *trans*-$[Mo(N_2)_2(PMe_3)_4]$ into the same mixture of *cis*-$[Mo(N_2)_2(PMe_3)_4]$, $[Mo(N_2)(PMe_3)_5]$ and other unidentified species. Similar isomerization reactions have been studied recently by George and co-workers,[11a] although in their case the final reaction mixture contained *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$ and *trans*-$[Mo(N_2)_2(PMe_2Ph)_4]$ in a *ca.* 2.5 : 1 ratio. Compound **3** reacted with C_2H_4 to yield the known



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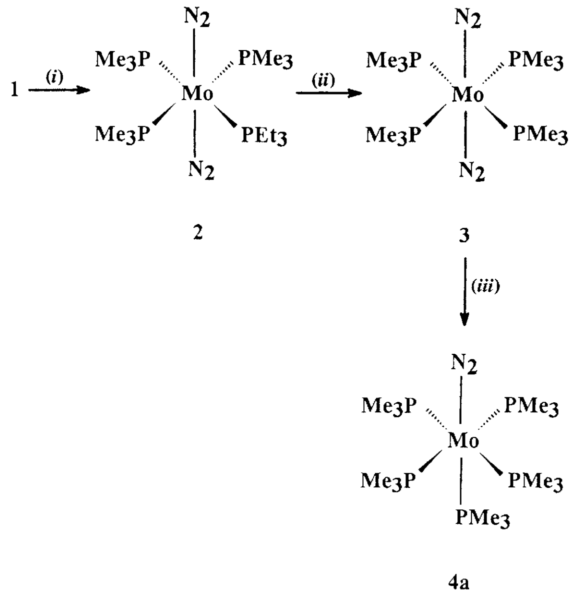


Scheme 2 (*i*) 3.5 equivalents PMe_3, 3 h; (*ii*) PMe_3, 12 h; (*iii*) PMe_3, Ar, 48 h

$$cis\text{-}[Mo(N_2)_2(PMe_3)_4] + L\text{–}L \xrightarrow{Ar} [Mo(N_2)(PMe_3)_3(L\text{–}L)] + PMe_3 + N_2$$

Scheme 3 L–L = dmpm **4b**, dmpe **4c** or depe **4d**

bis(ethylene) derivative *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$[5a] and with PMe_3, under Ar, to produce $[Mo(N_2)(PMe_3)_5]$ **4a**.[4a] Qualitative evidence suggested these reactions proceeded through the intermediacy of the *cis*-bis(dinitrogen) isomer.

Compounds of the type $M(N_2)L_5$ which contain a single N_2 molecule and five P-bound phosphorus-containing ligands co-ordinated to a Group 6 metal are rather uncommon members within the family of dinitrogen complexes. The first compounds of this type were the $[M(N_2)(PMe_3)_5]$ derivatives (Mo and W), independently prepared by our group and by Green and co-workers.[4a,12] Subsequently, other related complexes have been reported.[13] In an effort to further our knowledge of monodinitrogen complexes of molybdenum we have prepared several new derivatives containing chelating phosphines. In addition, we discuss in full the structural characterization by X-ray methods of the complex $[Mo(N_2)(PMe_3)_5]$ a preliminary report of which has been published.[4a]

The addition of the bidentate phosphines dmpm ($Me_2P\text{-}CH_2PMe_2$), dmpe ($Me_2PCH_2CH_2PMe_2$) and depe ($Et_2PCH_2\text{-}CH_2PEt_2$) to solutions of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ maintained under argon caused the disappearance of the two IR absorptions characteristic of the *cis* dinitrogen species at 2010 and 1965 cm^{-1} and the concomitant observation of a new band in the range 1970–1930 cm^{-1}, indicating the formation of a new monodinitrogen species (Scheme 3). The reactions were essentially complete in about 30 min (20 °C) after which time the resulting products **4b**–**4d** could be isolated as yellow crystalline solids. The use of $[Mo(N_2)(PMe_3)_5]$ as the starting material [equation (1)] also provided complexes **4b**–**4d** but the reactions required heating at 50 °C for several hours to reach

$$[Mo(N_2)(PMe_3)_5] + L\text{–}L \xrightarrow{Ar} [Mo(N_2)(PMe_3)_3(L\text{–}L)] + 2PMe_3 \quad (1)$$

4a **4b–4d**

completion, yields were significantly lower and the resulting compounds were often contaminated by decomposition products. Under similar experimental conditions, the analogous reactions aimed at the preparation of the related $[Mo(N_2)(PMe_3)(L\text{–}L)_2]$ by using 2 equivalents of bidentate phosphine proved unsuccessful.

Compounds **4b–4d** displayed solubility and other physical properties similar to those reported for the PMe_3 derivative **4a**.[5a] For example, they exhibited a single, strong IR absorption in the range 1970–1930 cm^{-1}, *i.e.* in the region found for other monodinitrogen complexes (*e.g.* 1950 cm^{-1}, $[Mo(N_2)(PMe_3)_5]$;[5a] 1978 cm^{-1}, $[Mo(N_2)\{PhP(CH_2CH_2PPh_2)_2\}(PMe_2Ph)_2]$;[13c] 1925 cm^{-1}, $[Mo(N_2)(PMe_3)\{N(CH_2CH_2PPh_2)_3\}]$[13a]). NMR studies were also in support of the indicated structures. Thus, the doublet splitting observed for the Me protons of the PMe_3 ligands in **4c** (δ 1.41, $^2J_{HP}$ = 4.5, 2 PMe_3; δ 1.39, $^2J_{HP}$ = 5 Hz, PMe_3) was taken as evidence of a facial distribution of these P atoms. Since the Me groups of the dmpe ligand gave rise to two doublets at δ 1.22 ($^2J_{HP}$ = 4 Hz) and 0.98 ($^2J_{HP}$ = 4 Hz), structure **II** was advanced for these complexes. In excellent accord with the above, a pattern of lines characteristic of an AA′MXX′ spin system was present in the $^{31}P\text{-}\{^1H\}$ NMR spectrum of **4b–4d**. Computer simulation of the spectral data gave the NMR parameters which are collected in the Experimental section. While the above methyl- or ethyl-substituted diphosphines afforded clean reaction products, **4b–4d**, the analogous transformations involving the more sterically encumbered ligands $Ph_2P(CH_2)_nPPh_2$ (n = 1, dppm; n = 2, dppe) and $Pr^i_2P(CH_2)_2PPr^i_2$, dippe, did not provide any isolable complexes.

The polydentate phosphine $N(CH_2CH_2PMe_2)_3$[14] afforded a related monodinitrogen adduct **4e**, according to equation (2).

$$cis\text{-}[Mo(N_2)_2(PMe_3)_4] + N(CH_2CH_2PMe_2)_3 \xrightarrow{60\,°C} [Mo(N_2)(PMe_3)\{N(CH_2CH_2PMe_2)_3\}] + 3PMe_3 \quad (2)$$

Structure **III** was proposed for this derivative on the basis of the following observations: (*i*) a single, low-energy N–N stretching at *ca.* 1890 cm^{-1}; (*ii*) two virtually coupled triplets (δ 1.58 and 1.28) and a doublet (δ 0.98) for the Me groups of the $N(CH_2CH_2PMe_2)_3$ ligand, as well as another doublet at δ 1.48 for the PMe_3 protons; (*iii*) an A_2MX spin system for the four ^{31}P nuclei.

Structural characterization of a complex of type **4** was considered appropriate and the PMe_3 derivative **4a** was chosen for convenience. An ORTEP[15] view is shown in Fig. 1, and interatomic distances and angles and atomic parameters are collected in Tables 1 and 4, respectively. The complex is isostructural with the tungsten analogue[4b] and consists of distorted-octahedral molecules that reside on a crystallographic mirror plane containing the atoms Mo, P(1), P(2), P(3), N(1), N(2), C(3) and C(5). As in $[W(N)_2(PMe_3)_5]$, C(1) was found to be disordered about that mirror plane. The structural parameters for the $Mo\text{–}N_2$ linkage are similar to those found for other dinitrogen complexes of Mo and W. Thus, the N_2 molecule is bonded to the metal centre *via* N(1) at a Mo–N separation of 2.02(3) Å, which is identical (within experimental error) to that found for $[W(N_2)(PMe_3)_5]$ [2.04(2) Å].[4b] Similarly, the N–N bond length of 1.12(3) Å compares well with that found in the isostructural tungsten complex [1.11(2) Å][4b] and in other dinitrogen complexes of molybdenum {*e.g.* 1.118(8) Å in *trans*-$[Mo(N_2)_2(dppe)_2]$,[7a] 1.087(18) Å in *trans*-$[Mo(CO)(N_2)(dppe)_2]\cdot0.5\,C_6H_6$[16]}. The Mo–N(1)–N(2) group is linear [179(2)°] as is normally observed in complexes of this type. Predictably, the Mo–P distance *trans* to the dinitrogen ligand was found to be somewhat longer at 2.483(7) Å than the average of the four Mo–P distances in the equatorial plane [2.460(5) Å]. Corresponding distances in $[W(N_2)(PMe_3)_5]$ are 2.473(4) and 2.444(7) Å, respectively.

As reported previously, the N_2 molecules of the dinitrogen complex *cis*-$[Mo(N_2)_2(PMe_3)_4]$ are displaced readily by C_2H_4 with formation of *trans*-$[Mo(C_2H_4)_2(PMe_3)_4]$.[5a] In view of the interesting reactivity exhibited by the latter complex[17] we attempted the preparation of related derivatives of the bulkier and more basic PEt_3. Treatment of **1** with C_2H_4 (20 °C, 2 atm) gave a colourless crystalline material **5a**, for which analytical and spectroscopic data were not in support of its formulation as a $Mo\text{–}C_2H_4$ compound. Rather, they revealed the presence of

Table 1 Selected bond lengths (Å) and angles (°) for $[Mo(N_2)(PMe_3)_5]$ **4a**

Mo–P(1)	2.483(7)	Mo–P(2)	2.460(7)
Mo–P(3)	2.456(7)	Mo–P(4)	2.456(5)
Mo–N(1)	2.02(3)	P(1)–C(1)	1.86(3)
P(1)–C(2)	1.84(3)	P(2)–C(3)	1.89(4)
P(2)–C(4)	1.86(3)	P(3)–C(5)	1.86(3)
P(3)–C(6)	1.88(2)	P(4)–C(7)	1.90(2)
P(4)–C(8)	1.86(2)	P(4)–C(9)	1.19(2)
N(1)–N(2)	1.12(3)		
P(1)–Mo–P(2)	88.9(3)	P(1)–Mo–P(3)	93.4(2)
P(2)–Mo–P(3)	177.7(3)	P(1)–Mo–P(4)	96.4(1)
P(2)–Mo–P(4)	92.0(1)	P(3)–Mo–P(4)	87.8(1)
P(4)–Mo–P(4A)*	166.6(6)	P(2)–Mo–N(1)	87.8(6)
P(1)–Mo–N(1)	176.7(6)	P(4)–Mo–N(1)	83.7(1)
P(3)–Mo–N(1)	89.9(6)		

* Symmetry code $x, \frac{1}{2} - y, z$.

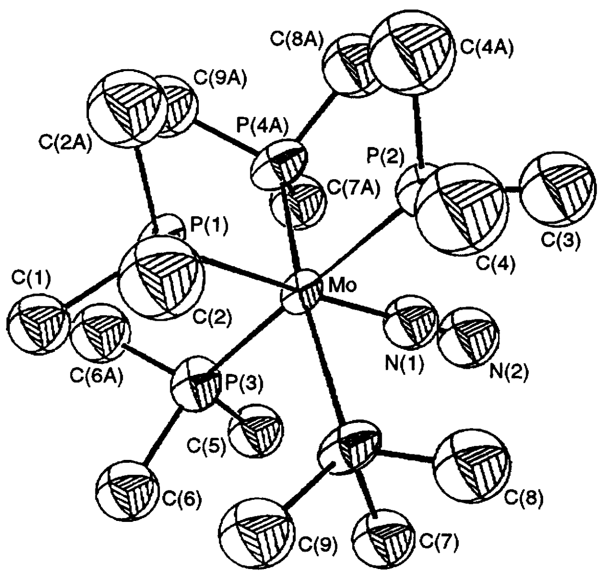
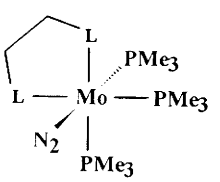
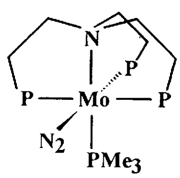


Fig. 1 An ORTEP diagram and atomic numbering scheme for complex **4a**



II



III

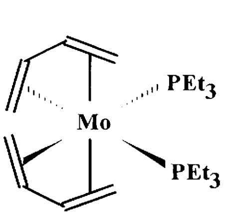
two symmetry-related olefinic four-carbon chains (^{13}C-{^1H} signals were detected at δ 81.6 (CH), 68.4 (CH), 41.5 (CH_2) and 36.9 (CH_2) and corresponding ^1H multiplets of equal relative intensity at δ 3.40, 4.27, 1.32 and −0.92, 0.88 and −0.74) and of only two PEt_3 groups. From the information available (see Experimental section) and taking into account the close similarity of the spectral data obtained for **5a** with those reported for the butadiene complex [Mo(η^4-C_4H_6)$_2$-(PMe_3)$_2$],[12b] structure **IV** was anticipated for this complex and its formation proposed to proceed as hinted by equation (3). Compound **5a** was alternatively synthesized by the direct

$$\mathbf{1} \xrightarrow[20\,^{\circ}C]{C_2H_4,\ 2\ atm} 2[Mo(\eta^4\text{-}C_4H_6)_2(PEt_3)_2] + 2PEt_3 + 5N_2 + \ldots \quad (3)$$
5a

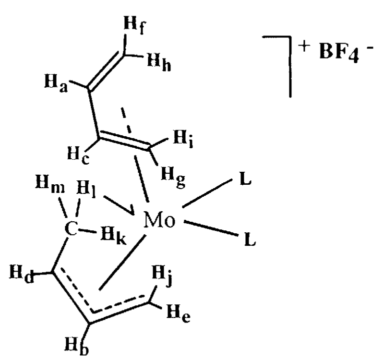
reaction of **1** with butadiene and also by reduction of [$MoCl_3$-(PEt_3)$_3$] under C_2H_4. The latter procedure gave, however, poor yields of this species (less than 20%).

The transformation of the hydrocarbon fragment represented in equation (3) corresponds to the dimerization of ethylene to butadiene, with concomitant trapping of the latter molecule by the resulting metal fragment. No attempts were made to investigate the fate of the two H atoms lost during this conversion. Although the dimerization of C_2H_4 to butenes is well known,[18] the formation of C_4H_6 is less common. The generation of C_4H_6 and C_2H_6 from C_2H_4 is catalysed by some transition-metal compounds[19] and the stoichiometric production of C_4H_6 from C_2H_4 in reactions involving for instance zirconium[20a] and ditungsten[20b] complexes is also known. A relevant example in connection with the present work is the formation of [W(C_4H_6)$_2$(PMe_3)$_2$] upon treatment of [WH-(CH_2PMe_2)(PMe_3)$_4$][12c] with C_2H_4, a reaction which involves, in addition, the formation of but-1-ene. The bis(ethylene) derivative *trans*-[W(C_2H_4)$_2$(PMe_3)$_4$], a possible intermediate in this transformation, gave in fact the above bis(butadiene) complex when treated with C_2H_4 under appropriate conditions. Nevertheless both reactions required heating at 60–70 °C for several days and gave very low yields of the butadiene product. This is in contrast with the conversion of **1** into **5a** [equation (3)] which takes place under mild conditions in fairly high yields (*ca.* 80%). The related compound *trans*-[Mo(C_2H_4)$_2$(P-Me_2Ph)$_4$][21] failed to undergo a similar transformation in the presence of C_2H_4. It would seem, therefore, that the C_2H_4 to C_4H_6 dimerization requires a very electron-rich metal centre. Notwithstanding, compound **5b**, the PMe_2Ph analogue of **5a**, was prepared by the straightforward reaction of *trans*-[Mo(C_2H_4)$_2$(PMe_2Ph)$_4$] and C_4H_6 [equation (4)]. Spectroscopic data for **5b** are collected in the Experimental section and need no further comment.

$$trans\text{-}[Mo(C_2H_4)_2(PMe_2Ph)_4] + 2C_4H_6 \longrightarrow [Mo(\eta^4\text{-}C_4H_6)_2(PMe_2Ph)_2] + 2PMe_2Ph + 2C_2H_4 \quad (4)$$
5b



IV



V

Protonation of complexes **5** with HBF_4 produced the cationic species [Mo(η^3-$CH_3CHCHCH_2$)(η^4-C_4H_6)L_2]BF_4 (L = PEt_3 **6a** or PMe_2Ph **6b**) in the form of red crystals in high yield [equation (5)]. Proton and ^{13}C-{^1H} NMR data suggested

$$[Mo(\eta^4\text{-}C_4H_6)_2L_2] + HBF_4 \longrightarrow [Mo(\eta^3\text{-}CH_3CHCHCH_2)(\eta^4\text{-}C_4H_6)L_2][BF_4] \quad (5)$$
6a, **6b**

that the proton has become attached to a CH_2 terminus of one of the C_4H_6 ligands and that the resulting allylic butenyl moiety exhibited in addition an agostic[22] Mo–Me interaction. High-field proton and carbon resonances for this agostic methyl appeared at δ −3.31 and −3.0 (**6a**) and −3.51 and −2.1 (**6b**), respectively. At −70 °C the high-field region of the ^1H NMR spectrum of, for example **6b**, contained three signals at δ 0.70, −1.40 and −9.60, the latter corresponding to the Mo-bound hydrogen atom of the agostic structure. These and other data were closely reminiscent of those found by Green and co-workers[12b] for the analogous PMe_3 derivative and will not be discussed any further.

The molecular geometry proposed for these complexes (structure **V**) was later confirmed by X-ray studies carried out on **6a**, the results of which are presented in Fig. 2 and Tables 2 and 5. The cationic part of this molecule contains the protonated buta-1,3-diene moiety co-ordinated to the Mo(C_4-H_6)(PEt_3)$_2$ fragment in the already described manner, *i.e.* by means of an allylic interaction [through atoms C(5), C(6) and C(7)] and an agostic bond involving C(8) and H(82). This co-ordination mode is similar to that observed in other η^3-enyl complexes.[12b,23] The Mo–C(8) bond length, while somewhat longer than the Mo–C(allylic) bonds, is well within bonding distance. For comparison, in the agostic acetyls [Mo{(C(O)CH_3)}-(L–L)(CO)(PMe_3)$_2$] (L–L = monoanionic, bidentate sulfur ligand[24]) the Mo–C separation was in the range 2.60–2.76 Å. In turn, the Mo–H(82) bond length of 1.9(2) Å fitted in the lower end of the 2.06–2.56 Å interval found for the above agostic acetyls. The butadiene entity of this complex is bound in the typical sym-*cis* η^4 fashion,[25] and it has an essentially planar skeleton which forms a dihedral angle of 40.5(8)° with the allylic C(5)–C(6)–C(7) plane.

Experimental

Microanalyses were by Pascher Microanalytical Laboratory, Remagen, Germany, and by the Microanalytical Service of the

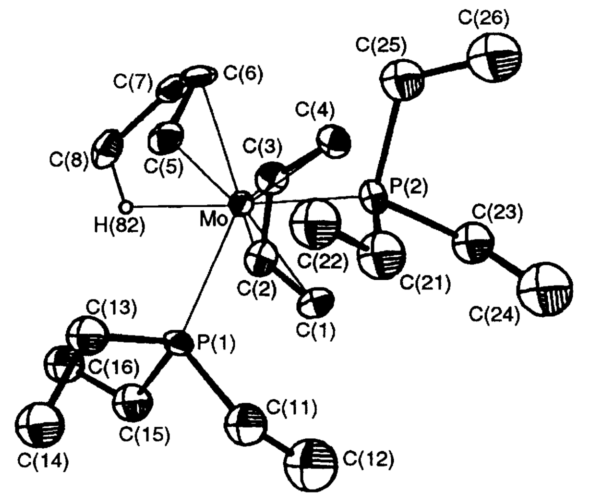


Fig. 2 Molecular structure of the cation of complex **6a** showing the atom numbering scheme

Table 2 Selected bond lengths (Å) and angles (°) for complex **6a**

Mo–P(1)	2.563(4)	Mo–C(8)	2.48(2)
Mo–P(2)	2.537(4)	C(1)–C(2)	1.45(2)
Mo–C(1)	2.34(1)	C(2)–C(3)	1.38(2)
Mo–C(2)	2.24(1)	C(3)–C(4)	1.41(2)
Mo–C(3)	2.23(2)	C(5)–C(6)	1.43(2)
Mo–C(4)	2.30(2)	C(6)–C(7)	1.40(2)
Mo–C(5)	2.28(1)	C(7)–C(8)	1.49(2)
Mo–C(6)	2.25(2)	Mo–H(82)	1.9(2)
Mo–C(7)	2.22(2)	C(8)–H(82)	1.1(2)
P(1)–Mo–P(2)	95.4(1)	C(8)–Mo–P(2)	150.9(4)
C(8)–Mo–P(1)	95.5(4)	C(7)–Mo–P(2)	119.1(4)
C(7)–Mo–C(8)	36.5(6)	C(6)–Mo–P(2)	87.7(4)
C(6)–Mo–P(1)	119.4(4)	C(6)–Mo–C(8)	63.5(6)
C(6)–Mo–C(7)	36.5(6)	C(5)–Mo–P(2)	84.0(4)
C(5)–Mo–P(1)	83.3(4)	C(5)–Mo–C(8)	70.6(6)
C(5)–Mo–C(7)	64.2(6)	C(5)–Mo–C(6)	36.7(5)
C(4)–Mo–P(2)	79.6(4)	C(4)–Mo–P(1)	148.8(4)
C(3)–Mo–P(2)	113.4(4)	C(3)–Mo–P(1)	128.0(5)
C(2)–Mo–P(2)	117.0(4)	C(2)–Mo–P(1)	92.9(4)
C(1)–Mo–P(2)	84.9(4)	C(1)–Mo–P(1)	77.9(4)
P(2)–Mo–H(82)	155(5)	P(1)–Mo–H(82)	72(5)
C(8)–Mo–H(82)	24(5)	C(7)–Mo–H(82)	60(5)
C(6)–Mo–H(82)	81(5)	Mo–H(82)–C(8)	110(12)
C(5)–Mo–H(82)	73(5)		

Table 3 Crystal and refinement data for compounds **4a** and **6a** *

	4a	**6a**
Formula	$C_{15}H_{45}MoN_2P_5$	$C_{20}H_{43}BF_4MoP_2$
M	504.4	528.25
Crystal symmetry	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/n$
a/Å	22.063(6)	27.655(4)
b/Å	12.106(4)	8.125(3)
c/Å	9.745(4)	11.107(1)
β/°		98.18(1)
U/Å^3	2603(2)	2470(1)
D_c/g cm^{-3}	1.29	1.42
F(000)	1064	1104
μ/cm^{-1}	8.04	6.79
Crystal size/mm	0.45 × 0.54 × 0.75	0.2 × 0.2 × 0.4
2θ range/°	2–36	11–26
Data collected	$+h, +k, +l$	$\pm h, +k, +l$
Unique data	950	2722
Observed data	730 ($I > 3\sigma I$)	1827 ($I > 2\sigma I$)
Decay (%)	±2	⩽5
R	0.074	0.080
R'	0.082	0.091

* Details in common: $Z = 4$; 22 °C; Enraf-Nonius CAD_4 diffractometer; graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å); ω–2θ scans; $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; refinement based on *F*.

Table 4 Final fractional coordinates for complex **4a**

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.385 98(9)	0.25	0.277 5(2)
P(1)	0.355 4(3)	0.25	0.032 3(7)
P(2)	0.492 7(3)	0.25	0.204 4(7)
P(3)	0.280 8(3)	0.25	0.360 2(7)
P(4)	0.385 9(2)	0.452 2(4)	0.306 9(5)
N(1)	0.416(1)	0.25	0.474(3)
N(2)	0.433(1)	0.25	0.581(3)
C(1)	0.277(2)	0.295(3)	−0.012(4)
C(2)	0.380(1)	0.364(2)	−0.080(2)
C(3)	0.552(2)	0.25	0.345(4)
C(4)	0.528(1)	0.359(2)	0.096(3)
C(5)	0.273(1)	0.25	0.550(3)
C(6)	0.226 2(9)	0.365(2)	0.323(2)
C(7)	0.358 3(9)	0.500(2)	0.482(2)
C(8)	0.456(1)	0.537(2)	0.311(2)
C(9)	0.338 6(9)	0.552(2)	0.200(2)

Table 5 Final fractional coordinates for complex **6a**

Atom	*X/a*	*Y/b*	*Z/c*
Mo	0.152 48(4)	0.159 58(14)	0.856 39(10)
C(1)	0.097 39(53)	−0.045 75(166)	0.893 94(144)
C(2)	0.124 88(63)	−0.091 34(168)	0.796 90(144)
C(3)	0.174 93(62)	−0.099 54(184)	0.826 56(151)
C(4)	0.195 52(56)	−0.061 27(181)	0.947 05(147)
C(5)	0.181 65(53)	0.420 50(170)	0.842 32(142)
C(6)	0.221 48(47)	0.308 01(211)	0.861 02(155)
C(7)	0.220 90(51)	0.182 72(219)	0.774 13(153)
C(8)	0.184 84(68)	0.191 65(231)	0.660 74(146)
P(1)	0.069 89(12)	0.296 02(44)	0.784 20(32)
C(11)	0.025 26(69)	0.334 42(269)	0.888 13(169)
C(12)	0.002 44(106)	0.216 68(377)	0.940 00(242)
C(13)	0.072 51(66)	0.504 55(236)	0.730 80(159)
C(14)	0.023 32(76)	0.590 97(272)	0.686 41(184)
C(15)	0.032 63(67)	0.184 06(251)	0.659 03(166)
C(16)	0.054 22(67)	0.168 41(265)	0.546 34(169)
P(2)	0.153 84(15)	0.231 82(48)	1.079 05(31)
C(21)	0.119 03(79)	0.410 19(291)	1.128 54(192)
C(22)	0.131 62(79)	0.576 00(290)	1.091 89(194)
C(23)	0.132 01(69)	0.073 04(249)	1.175 69(172)
C(24)	0.106 21(103)	0.111 60(368)	1.276 78(251)
C(25)	0.216 94(74)	0.267 39(265)	1.149 95(186)
C(26)	0.227 64(95)	0.274 77(349)	1.281 24(240)
B	0.862 56(127)	0.334 91(463)	0.541 44(309)
F(1)	0.849 20(60)	0.191 96(207)	0.480 30(146)
F(2)	0.834 80(66)	0.433 16(237)	0.478 99(162)
F(3)	0.836 47(72)	0.272 96(247)	0.630 88(167)
F(4)	0.899 95(74)	0.349 13(266)	0.593 22(176)
H(82)	0.150(6)	0.21(2)	0.69(1)

University of Seville. Infrared spectra were recorded on Perkin-Elmer model 683 and 883 spectrometers, NMR spectra on Varian XL-200 and Bruker AMX-300 and AMX-500 spectrometers. All preparations and manipulations were carried out under oxygen-free nitrogen or argon following conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. The complexes $[MoCl_3(thf)_3]$, *trans*-$[Mo(C_2H_4)_2(PMe_2Ph)_4]$ [21] and *cis*-$[Mo(N_2)_2(PMe_3)_4]$ [5a] and all the mono- and poly-phosphines [14] employed in this work were prepared according to literature methods. The light petroleum used had b.p. 40–60 °C.

Syntheses.—$[\{Mo(N_2)_2(PEt_3)_3\}_2(\mu\text{-}N_2)]$ **1**. The complex $[MoCl_3(thf)_3]$ (2.8 g, 5 mmol) was suspended in thf (100 cm^3) and 3 equivalents of PEt_3 (2.3 cm^3, 15 mmol) were added. The mixture was transferred to a Fischer–Porter pressure vessel containing an excess of 1% sodium amalgam (0.6 g of Na). The vessel was pressurized with 3 atm of N_2 and the reaction mixture stirred for 6 h at room temperature. The initial red colour took on a greenish tone after a few minutes, gradually becoming dark, red-brown. After 6 h of stirring the mixture was centrifuged and the volatiles removed under reduced pressure. The residue was extracted with light petroleum and the resulting solution evaporated under vacuum. Crystallization from acetone gave red crystals of complex **1** in *ca.* 50% yield (Found: C, 41.5; H, 9.0; N, 13.6. $C_{36}H_{90}Mo_2N_{10}P_6$ requires C, 41.5; H, 8.7; N, 13.4%). IR (Nujol mull): $\nu(N_2)$ 1980w and 1950vs cm^{-1}. NMR (C_6D_6): ^1H (200 MHz), δ 1.78 [q of t, 12 H, $^3J_{HH} = 7.5$, $J_{HP,app} = 2$, 2 $P(CH_2CH_3)_3$ *trans*], 1.53 [q of d, 6 H, $^3J_{HH} = 8$, $^2J_{HP} = 4.5$, 1 $P(CH_2CH_3)_3$], 1.10 [m, 18 H, 2 $P(CH_2CH_3)_3$ *trans*] and 0.95 [dt, 9 H, $^3J_{HP} = 13$, $^3J_{HH} = 8$, 1 $P(CH_2CH_3)_3$]; ^{31}P-$\{^1H\}$ (81 MHz, AX_2 spin system), δ_A 22.7, δ_X 19.6, $^2J_{AX} = 16$; ^{13}C-$\{^1H\}$ (50 MHz), δ 21.5 [d, 3 C, 1 $P(CH_2CH_3)_3$, $^1J_{CP} = 15$], 18.3 [pseudo-triplet, 2 $P(CH_2CH_3)_3$

trans, $J_{CP_{app}}$ = 8 Hz], 8.3 (s, 1 $P(CH_2CH_3)_3$], and 7.8 [2 $P(CH_2CH_3)_3$ *trans*].

Reactions of complex **1** *with* PMe_3 *to give trans*-$[Mo(N_2)_2(PMe_3)_3(PEt_3)]$ **2** *and trans*-$[Mo(N_2)_2(PMe_3)_4]$ **3**. Trimethylphosphine (1.2 mmol, 1.2 cm^3 of a 1 mol dm^{-3} solution in Et_2O) was added to a stirred solution of complex **1** (0.2 g, 0.2 mmol) in light petroleum (30 cm^3) and the resulting mixture stirred at room temperature for 3 h. Volatiles were removed under vacuum and the residue was extracted with light petroleum Et_2O (1:3). Upon cooling overnight at −20 °C the complex *trans*-$[Mo(N_2)_2(PMe_3)_3(PEt_3)]$ **2** was isolated as orange crystals in 80% yield (Found: C, 36.0; H, 8.5; N, 11.2. $C_{15}H_{42}MoN_4P_4$ requires C, 36.1; H, 8.5; N, 11.2%). IR (Nujol mull): $\nu(N_2)$ 1950vs (br) cm^{-1}. NMR (C_6D_6): ^1H (200 MHz), δ 1.69 [m, 6 H, $P(CH_2CH_3)_3$], 1.30 (pseudo-triplet, 18 H, $J_{HP_{app}}$ = 2 Hz, 2 PMe_3 *trans*), 1.28 (d, 9 H, $^2J_{HP}$ = 5 Hz, PMe_3) and 1.05 [dt, 9 H, $^3J_{HP}$ = 13, $^3J_{HH}$ = 7.5, $P(CH_2CH_3)_3$]; $^{31}P-\{^1H\}$, (81 MHz), AM_2X spin system) δ_A 27.3 (PEt_3), δ_M −1.4 (2 PMe_3), δ_X 1.2 (PMe_3), $^2J_{AM} = {}^2J_{MX}$ = 7.5 Hz, $^2J_{AX}$ = 107.5; $^{13}C-\{^1H\}$ (50 MHz), δ 22.9 [d, $P(CH_2CH_3)_3$, $^1J_{CP}$ = 14], 21.6 (pseudo-triplet, 2 PMe_3 *trans*, $J_{CP_{app}}$ = 7), 20.2 (d, PMe_3, $^1J_{CP}$ = 15 Hz) and 8.7 [$P(CH_2CH_3)_3$].

As already mentioned, the preparation of *trans*-$[Mo(N_2)_2(PMe_3)_4]$ **3**, as a cocrystallized mixture with *trans*-$[MoCl_2(PMe_3)_4]$, was reported by our group some years ago.[9] The following is a high-yield procedure for pure complex **3**: an excess of PMe_3 (1.5–2 mmol) was added to a light petroleum solution of complex **1** (0.3 g, 0.3 mmol) and the mixture stirred overnight. Volatiles were removed under vacuum and the residue was dissolved in Et_2O (30 cm^3). The solvent was partially evaporated and the resulting solution cooled at −20 °C to give orange crystals of *trans*-$[Mo(N_2)_2(PMe_3)_4]$ **3**. Yield: 85% (Found: C, 31.8; H, 8.6; N, 11.8. $C_{12}H_{36}MoN_4P_4$ requires C, 31.6; H, 7.9; N, 12.3%). IR (Nujol mull): $\nu(N_2)$ 1930vs (br) cm^{-1}. NMR (C_6D_6): ^1H (200 MHz), δ 1.27 (m); $^{31}P-\{^1H\}$ (81 MHz), δ 0.34 (s); $^{13}C-\{^1H\}$ (50 MHz), δ 21.0 (br s).

$[Mo(N_2)(PMe_3)_3(L–L)]$ (L–L = dmpm **4b**, dmpe **4c** *or* depe **4d**). Essentially the same procedure was employed for the synthesis of these monodinitrogen complexes. That leading to **4b** is described as a representative example. To a stirred solution of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (0.46 g, 1 mmol) in light petroleum (30 cm^3) was added 1 molar equivalent of dmpm (2 cm^3 of a 0.5 mol dm^{-3} solution in C_6H_6) and the mixture stirred for 30 min. The resulting solution was taken to dryness and the oily residue extracted with acetone (10 cm^3). Centrifugation, partial evaporation of the solvent and cooling at −20 °C afforded yellow crystals of the desired complex $[Mo(N_2)(PMe_3)_3(dmpm)]$ **4b**. Yield: 65%. Complexes **4c** and **4d** were isolated as yellow crystals in 70 and 75% respectively.

$[Mo(N_2)(PMe_3)_3(dmpm)]$ **4b** (Found: C, 34.5; H, 8.5; N, 5.5. $C_{14}H_{41}MoN_2P_5$ requires C, 34.4; H, 8.4; N, 5.7%): IR (Nujol mull): $\nu(N_2)$ 1950vs cm^{-1}; NMR (C_6D_6), ^1H (200 MHz); δ 3.65 (m, 2 H, PCH_2P), 1.52 (d, 9 H, $^2J_{HP}$ = 5, PMe_3), 1.33 (d, 18 H, $^2J_{HP}$ = 5, 2 PMe_3) and 1.21 (d, 12 H, $^2J_{HP}$ = 4, 2 PMe_2); $^{31}P-\{^1H\}$ (81 MHz, AA'MXX' spin system) (δ and *J* values obtained by computer simulation of the experimental spectrum), δ_A 1.5 (2 PMe_3), δ_M −3.9 (1 PMe_3), δ_X −21.6 ($Me_2PCH_2PMe_2$), $^2J_{AA'}$ = 12.4, $^2J_{AX} = {}^2J_{A'X'}$ = 97.8, $^2J_{AX'} = {}^2J_{A'X}$ = −26.3, $^2J_{XX'}$ = 12.4, $^2J_{AM} = {}^2J_{A'M}$ = 23.6, $^2J_{XM} = {}^2J_{X'M}$ = 19.5 Hz.

$[Mo(N_2)(PMe_3)_3(dmpe)]$ **4c** (Found: C, 36.0; H, 8.6. $C_{15}H_{43}MoN_2P_5$ requires C, 35.8; H, 8.5%): IR (Nujol mull). $\nu(N_2)$ 1960s cm^{-1}; NMR (C_6D_6), ^1H (200 MHz), δ 1.41 (d, 18 H, $^2J_{HP}$ = 4.5, 2 PMe_3), 1.39 (d, 9 H, $^2J_{HP}$ = 5, PMe_3), 1.22 (d, 6 H, $^2J_{HP}$ = 4, 2 PMe), and 0.98 (d, 6 H, $^2J_{HP}$ = 4, 2 PMe); $^{31}P-\{^1H\}$ (81 MHz, AA'MXX' spin system) (δ and *J* values obtained by computer simulation of the experimental spectrum), δ_A −5.0 (2 PMe_3), δ_M −7.1 (1 PMe_3), δ_X 36.4 ($Me_2PCH_2CH_2PMe_2$), $^2J_{AA'}$ = 17.2, $^2J_{AX} = {}^2J_{A'X'}$ = 101.6, $^2J_{AX'} = {}^2J_{A'X}$ = −17.7, $^2J_{XX'}$ = 0.3, $^2J_{AM} = {}^2J_{A'M}$ = 21.4, $^2J_{XM} = {}^2J_{X'M}$ = 18.3 Hz.

$[Mo(N_2)(PMe_3)_3(depe)]$ **4d** (Found: C, 40.9; H, 9.0; N, 4.9. $C_{15}H_{43}MoN_2P_5$ requires C, 40.9; H, 9.1; N, 5.0%): IR (Nujol mull) $\nu(N_2)$ 1950vs cm^{-1}; NMR (C_6D_6), ^1H (200 MHz), complex spectrum consisting of a doublet at δ 1.45, tentatively assigned to the two equivalent PMe_3 ligands with another superimposed signal, a multiplet at δ 1.1 and a number of smaller, unresolved signals between δ 2.0 and 1.0; $^{31}P-\{^1H\}$ (81 MHz, AA'MXX' spin system) (δ and *J* values obtained by computer simulation of the experimental spectrum), δ_A −6.5 (2 PMe_3), δ_M −9.5 (1 PMe_3), δ_X 54.1 ($Et_2PCH_2CH_2PEt_2$), $^2J_{AA'}$ = 14.5, $^2J_{AX} = {}^2J_{A'X'}$ = 99.1, $^2J_{AX'} = {}^2J_{A'X}$ = −16.6, $^2J_{XX'}$ = 4.6, $^2J_{AM} = {}^2J_{A'M}$ = 21.4, $^2J_{XM} = {}^2J_{X'M}$ = 19.0 Hz.

$[Mo(N_2)(PMe_3)\{N(CH_2CH_2PMe_2)_3\}]$ **4e**. To a stirred solution of *cis*-$[Mo(N_2)_2(PMe_3)_4]$ (0.46 g, 1 mmol) in light petroleum (30 cm^3) was added 1 molar equivalent of $N(CH_2CH_2PMe_2)_3$ and the mixture stirred for 3 h at 60 °C. Volatiles were removed under vacuum and the reddish oily residue extracted with acetone (10 cm^3). Partial evaporation of the solvent and cooling at −20 °C overnight produced red-orange crystals of **4e** in 70% yield (Found: C, 36.7; H, 8.2; N, 8.7. $C_{27}H_{39}MoN_3P_4$ requires C, 37.4; H, 8.1; N, 8.7%). IR (Nujol mull): $\nu(N_2)$ 1890vs cm^{-1}. NMR (C_6D_6): ^1H (200 MHz), δ 1.58 (t, 6 H, $J_{HP_{app}}$ = 2, 2 PMe *trans*), 1.48 (d, 9 H, $^2J_{HP}$ = 5, PMe_3), 1.28 (t, 6 H, $J_{HP_{app}}$ = 2, 2 PMe *trans*) and 0.98 (d, 6 H, $^2J_{HP}$ = 4, PMe_2); $^{31}P-\{^1H\}$ (81 MHz, A_2MX spin system), δ_A 23.8, δ_M 16.2, δ_X −7.1, $^2J_{AM}$ = 8.5, $^2J_{AX}$ = 16.0, $^2J_{XM}$ = 16.0 Hz.

$[Mo(\eta^4-C_4H_6)_2L_2]$ (L = PEt_3 **5a** *or* PMe_2Ph **5b**). A solution of complex **1** (0.52 g, 0.5 mmol) in light petroleum (30 cm^3) was placed in a pressure vessel and stirred under 1 atm of ethylene for 20 h. The resulting clear solution was taken to dryness and the residue extracted with light petroleum (15 cm^3). The solvent was partially removed and the solution cooled at −20 °C to give yellow crystals of $[Mo(\eta^4-C_4H_6)_2(PEt_3)_2]$ **5a** (0.33 g, 75% yield). Similar yields (*ca.* 80%) were obtained from the reaction of complex **1** with butadiene under the same conditions. This route was also employed to obtain the PMe_2Ph derivative. A diethyl ether solution of *trans*-$[Mo(C_2H_4)_2(PMe_2Ph)_4]$ was treated with butadiene to produce $[Mo(\eta^4-C_4H_6)_2(PMe_2Ph)_2]$ **5b** as yellow-orange crystals following crystallization from light petroleum–Et_2O (2:1) (yield: 65%).

$[Mo(\eta^4-C_4H_6)_2(PEt_3)_2]$ **5a** (Found: C, 54.7; H, 10.1. $C_{20}H_{42}MoP_2$ requires C, 54.5; H, 9.6%): NMR (C_6D_6), ^1H (300 MHz), δ 4.27 (m, 2 H, 2 =CH), 3.40 (m, 2 H, 2 =CH), 1.50 [m, 12 H, $P(CH_2CH_3)_3$], 1.32 (m, 2 H, 2 =CH*H*), 0.88 (m, 2 H, 2 =C*H*H), 0.88 [m, 18 H, 2 $P(CH_2CH_3)_3$], −0.74 (m, 2 H, 2 =C*H*H), and −0.92 (m, 2 H, 2 =C*H*H); $^{31}P-\{^1H\}$ (81 MHz), δ 0.34 (s); $^{13}C-\{^1H\}$ (75 MHz), δ 81.6 (2 =CH, $^1J_{CH}$ = 168), 68.4 (2 =CH, $^1J_{CH}$ = 168), 41.5 (t, 2 =CH_2, $^1J_{CH}$ = 155), 36.9 (=CH_2, $^1J_{CH}$ = 150 Hz), 20.4 [m, 2 $P(CH_2CH_3)_3$] and 8.6 [s, 2 $P(CH_2CH_3)_3$].

$[Mo(\eta^4-C_4H_6)_2(PMe_2Ph)_2]$ **5b** (Found: C, 59.9; H, 7.3. $C_{24}H_{34}MoP_2$ requires C, 60.0; H, 7.1%): NMR (C_6D_6), ^1H (500 MHz), δ 7.21, 7.09 and 7.01 (t, t, t, 4 H, 4 H, 2 H, 2 PMe_2Ph), 3.95, 3.42, 1.32, 0.70, −0.92, −1.26 (multiplets, 2 H each, 2 C_4H_6), 1.39 and 1.36 (d, $^2J_{HP}$ = 6, 6 H each, 2 PMe_2Ph); $^{31}P-\{^1H\}$ (81 MHz), δ 22.4 (s); $^{13}C-\{^1H\}$ (125 MHz), δ 81.9 and 71.1 (=CH), 44.7 (t, $^2J_{CP}$ = 9 Hz, =CH_2), 37.9 (s, =CH_2), 19.3 and 19.0 (m, diasterotopic PMe groups).

Protonation of $[Mo(\eta^4-C_4H_6)_2L_2]$ *to give* $[Mo(\eta^3-CH_3CHCHCH_2)(\eta^4-C_4H_6)L_2][BF_4]$ (L = PEt_3 **6a** *or* PMe_2Ph **6b**). Two equivalents of $HBF_4\cdot Et_2O$ (1 mol dm^{-3} solution in Et_2O) were added to a yellow stirred solution of $[Mo(\eta^4-C_4H_6)_2(PEt_3)_2]$ (0.33 g, 0.75 mmol) in Et_2O (40 cm^3). A red solid precipitated immediately. The suspension was stirred for 1 h and the solid filtered off and washed with Et_2O (3 × 30 cm^3). Acetone (10 cm^3) was introduced to dissolve the residue and

Et_2O added dropwise until cloudiness. The mixture was cooled at −20 °C to give red crystals of complex **6a** (0.2 g, 70% yield). The PMe_2Ph derivative was prepared following an identical procedure. The complex $[\overline{Mo(\eta^3\text{-}CH_3CHCHCH_2)}(\eta^4\text{-}C_4H_6)(PMe_2Ph)_2][BF_4]$ **6b** was isolated in 80% yield.

$[\overline{Mo(\eta^3\text{-}CH_3CHCHCH_2)}(\eta^4\text{-}C_4H_6)(PEt_3)_2][BF_4]$ **6a** (Found: C, 45.0; H, 8.5. $C_{20}H_{43}BF_4MoP_2$ requires C, 45.5; H, 8.2%): NMR (CD_3COCD_3), ^1H (200 MHz), δ 5.56 (m, H_a), 5.33 (m, H_b), 4.65 (m, H_c), 3.88 (m, H_d), 2.63 (m, H_e), 2.01 (m, 2 $P(CH_2CH_3)_3$, 1.18 [dt, 1 $P(CH_2CH_3)_3$, $^3J_{HP}$ = 13, $^3J_{HH}$ = 7.5], 1.12 [dt, 1 $P(CH_2CH_3)_3$, $^3J_{HP}$ = 13, $^3J_{HH}$ = 7.5], 0.22 (m, H_h), −0.12 (m, H_i), −0.47 (m, H_j), and −3.31 (t, $-CH_3$, $J_{HP_{app}}$ = 6 Hz) (H_f and H_g obscured by the phosphine absorptions); $^{31}P\text{-}\{^1H\}$ (81 MHz, AX spin system), δ_A 34.5, δ_X 21.8, $^2J_{AX}$ = 23.5 Hz; $^{13}C\text{-}\{^1H\}$ (50 MHz), δ 84.0 (=CH, $^1J_{CH}$ = 165), 80.9 (=CH, $^1J_{CH}$ = 170), 79.7 (=CH, $^1J_{CH}$ = 171), 76.3 (=CH, $^1J_{CH}$ = 169), 53.8 (t, $=CH_2$, $J_{CP_{app}}$ = 7, $^1J_{CH}$ = 155), 49.1 (dd, $=CH_2$, $^2J_{CP}$ = 9, 4.5, $^1J_{CH}$ = 154), 45.9 (dd, $=CH_2$, $^2J_{CP}$ = 9.5, 3, $^1J_{CP}$ = 158), 20.5 [d, $P(CH_2CH_3)_3$, $^1J_{CP}$ = 23], 19.8 [d, $P(CH_2CH_3)_3$, $^1J_{CP}$ = 22], 9.1 [d, $P(CH_2CH_3)_3$, $^2J_{CP}$ = 4.5], 8.6 [d, $P(CH_2CH_3)_3$, $^2J_{CP}$ = 4.5] and −3.0 (br d, CH_3, J_{CP} = 6, $^1J_{CH}$ = 122 Hz). Two-dimensional NMR experiments corroborate the proposed assignments.

$[\overline{Mo(\eta^3\text{-}CH_3CHCHCH_2)}(\eta^4\text{-}C_4H_6)(PMe_2Ph)_2][BF_4]$ **6b** (Found: C, 50.9; H, 6.4. $C_{24}H_{35}BF_4MoP_2$ requires C, 50.7; H, 6.2%): NMR, ^1H (CD_3COCD_3, 300 MHz); δ 7.9–7.5 (m, 10 H, 2 PMe_2Ph), 5.58 (m, H_a), 5.28 (m, H_b), 4.53 (m, H_c), 3.80 (m, H_d), 2.67 (m, H_e), 2.02 (d, PMe, $^2J_{HP}$ = 8.2), 1.92 (d, PMe, $^2J_{HP}$ = 8.2), 1.90 (obscured, H_f), 1.84 (d, PMe, $^2J_{HP}$ = 8.1), 1.80 (d, PMe, $^2J_{HP}$ = 8.0), 1.41 (m, H_g), −0.13 (m, H_h or H_i), −0.49 (m, H_i or H_h and H_j), and −3.51 (t, $-CH_3$, $J_{HP_{app}}$ = 5.9); $^{31}P\text{-}\{^1H\}$ (CD_3COCD_3, 121 MHz, AX spin system), δ_A 28.7, δ_X 12.1, $^2J_{AX}$ = 23.5 Hz; (selected) $^{13}C\text{-}\{^1H\}$ (C_6D_6, 75 MHz), δ 85.0 (=CH, $^1J_{CH}$ = 177), 83.9 (=CH, $^1J_{CH}$ = 173), 80.4 (=CH, $^1J_{CH}$ = 172), 78.8 (=CH, $^1J_{CH}$ = 175), 58.7 (t, $=CH_2$, $J_{CP_{app}}$ = 6.5, $^1J_{CH}$ = 159), 52.2 (dd, $=CH_2$, $^2J_{CP}$ = 9, 4.5, $^1J_{CH}$ = 161), 49.8 (d, $=CH_2$, $^2J_{CP}$ = 9.5, $^1J_{CH}$ = 160), 18.0 (m, 2 PMe_2Ph), and −2.1 (d, CH_3, $J_{CP_{app}}$ = 7.5, $^1J_{CH}$ = 120 Hz). Two-dimensional NMR experiments corroborate the proposed assignments.

Crystallography.—$[Mo(N_2)(PMe_3)_5]$ **4a**. A single crystal of the complex was mounted in a thin-walled glass capillary under N_2 and transferred to the goniometer. The space group was determined to be either centric *Pnma* or acentric $Pn2_1a$ from systematic absences. Successful refinement was carried out in *Pnma* despite the presence of a small amount of disorder. The data collection parameters are summarized in Table 3.

The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for Mo and P were taken from ref. 26.

Least-squares refinement with isotropic thermal parameters led to R = 0.121. Atom C(1) was found to be disordered across the mirror plane. It was refined in a general position with 50% occupancy. The space group $Pn2_1a$ was investigated, however the continued presence of disorder, high correlation parameters and higher R values precluded its choice. Thermal motion in general was high and the H atoms were not included in the refinement. The limited data set available forced a reduction in the parameters varied and only the Mo and P atoms were anisotropically refined. Unit weights were used. Calculations were carried out with SHELX.[27]

$[\overline{Mo(\eta^3\text{-}CH_3CHCHCH_2)}(\eta^4\text{-}C_4H_6)(PEt_3)_2][BF_4]$ **6a**. The fundamental crystal data are summarized in Table 3. A red crystal of prismatic shape was coated with epoxy resin and mounted in a kappa diffractometer. The cell dimensions were refined by least-squares fitting of the θ values of the 25 reflections with a range 2θ 11–26°. The intensities were corrected for Lorentz and polarization effects. The source of scattering factors was as before. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[28] was applied at the end of the isotropic refinements.

A final refinement was undertaken using a unit weighting scheme and anisotropic thermal motion for the non-hydrogen atoms with the exception of the PEt_3 carbon atoms and the BF_4 atoms, which showed thermal disorder and were refined isotropically. The hydrogen atoms were included with fixed isotropic contributions at their calculated positions, except for H(82), which was located in a Fourier-difference map and its coordinates refined.

No trend in ΔF *vs.* F_o or sin θ/λ was observed. The final difference synthesis showed no significant electron density. Most of the calculations were carried out with the X-RAY 80 system.[29]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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