Chemistry of Phosphido-bridged Dimolybdenum Complexes. Part 5.[1] Synthesis and Protonation of a Phosphido-bridged Dimolybdenum Complex containing a Terminal Alkyne Ligand: *X*-Ray Crystal Structures of $[Mo_2(\mu-PPh_2)_2(CO)(\eta-C_2Me_2)(\eta-C_5H_5)_2]$ and $[Mo_2(\mu-CO)(\mu-PPh_2)\{\mu-Ph_2PC(Me)=CHMe\}(\eta-C_5H_5)_2][BF_4]$ †

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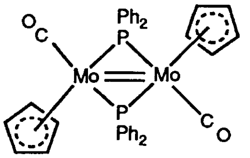
The reaction between the alkyne complex $[Mo_2(\mu-C_2Me_2)(CO)_4(\eta-C_5H_5)_2]$ and P_2Ph_4 in refluxing toluene affords a 42% yield of $[Mo_2(\mu-PPh_2)_2(CO)(\eta-C_2Me_2)(\eta-C_5H_5)_2]$. An *X*-ray diffraction study has revealed that the but-2-yne ligand is co-ordinated to only one molybdenum atom, and that the molecule contains a planar $Mo_2(\mu-PPh_2)_2$ unit with a formal Mo–Mo double bond of length 2.865(1) Å. Several other minor products are discussed in relation to the proposed mechanism of the reaction. Reaction of the terminal alkyne complex with $HBF_4 \cdot OEt_2$ causes a structural rearrangement in which the protonated but-2-yne is inserted into one of the Mo–P bonds to give a bridging $Ph_2PC(Me)=CHMe$ vinylphosphine ligand; the structure of the product has been confirmed by *X*-ray diffraction.

The organic chemistry of dimolybdenum complexes derived from $[Mo_2(CO)_6(\eta-C_5H_5)_2]$ and $[Mo_2(CO)_4(\eta-C_5H_5)_2]$ is extensive, and has been recently reviewed.[2] As part of our current effort to develop a similar range of chemistry for phosphido-bridged dimolybdenum systems [3,4] we have recently reported that the thermal reaction of $[Mo_2(CO)_6(\eta-C_5H_5)_2]$ with tetraphenyldiphosphane produces $[Mo_2(\mu-PPh_2)_2(CO)_2(\eta-C_5H_5)_2]$ (**1**), which on further photochemical decarbonylation gives $[Mo_2(\mu-CO)(\mu-PPh_2)_2(\eta-C_5H_5)_2]$ (**2**).[5] Despite their formally unsaturated nature, however, neither (**1**) nor (**2**) reacted with alkynes either thermally or under u.v. irradiation, a fact we attribute to steric hindrance by the bulky diphenylphosphido groups. To circumvent this problem we decided to explore an alternative synthetic strategy, in which the alkyne ligand is introduced into the dimolybdenum complex prior to the incorporation of the phosphido groups. In this paper we describe the reaction of P_2Ph_4 with the complex $[Mo_2(\mu-C_2Me_2)(CO)_4(\eta-C_5H_5)_2]$ (**3**), containing a transversely bound but-2-yne ligand, and the protonation of the resulting product.

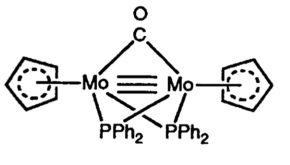
Results and Discussion

(*a*) *Synthesis of* $[Mo_2(\mu-PPh_2)_2(CO)(\eta-C_2Me_2)(\eta-C_5H_5)_2]$.—Heating $[Mo_2(\mu-C_2Me_2)(CO)_4(\eta-C_5H_5)_2]$ with 1 equivalent of P_2Ph_4 in refluxing toluene for 96 h resulted in the consumption of most of the starting material according to spot t.l.c. monitoring. Subsequent chromatographic work-up provided $[Mo_2(\mu-PPh_2)_2(CO)(\eta-C_2Me_2)(\eta-C_5H_5)_2]$ (**4**) as an air-stable, red-purple crystalline solid in 42% yield, as well as several other minor products which are described in detail below.

The i.r. spectrum of (**4**) showed a single peak at 1 826 cm^{-1}. As well as two cyclopentadienyl resonances (one split into a triplet), the ^1H n.m.r. spectrum showed phenyl and methyl protons in a ratio of 20:6, indicating the incorporation of two PPh_2 groups into the dinuclear molecule with retention of the alkyne ligand. The $^{31}P-\{^1H\}$ spectrum consisted of a single peak in the region expected for bridging phosphido ligands [δ 30.2 p.p.m. relative to $P(OMe)_3$ = 0.0 p.p.m.], and a molecular ion was observed in the mass spectrum at *m*/*z* 774 (^{96}Mo) with one carbonyl loss peak at *m*/*z* 746. Peaks corresponding to a single terminal carbonyl ligand and two inequivalent C_5H_5 rings were observed in the ^{13}C n.m.r. spectrum, with the resonance due to the internal carbons of the alkyne appearing at 155.8 p.p.m. The general similarity of the spectroscopic data to those of the oxo complex *trans*-$[Mo_2O(\mu-PPh_2)_2(CO)(\eta-C_5H_5)_2]$ (**5**)[5] indicated a similar structure with the alkyne acting as a two-electron ligand terminally bound to one molybdenum atom. No evidence was found for the existence of a *cis* isomer of (**4**).



(**1**)



(**2**)

It has previously been shown by Templeton and Ward[6] that for mononuclear molybdenum(II) alkyne complexes there is an experimental correlation between the number of electrons formally donated by an alkyne ligand and its ^{13}C n.m.r. chemical shift. The value observed for (**4**) lies to somewhat lower field than might be expected for a two-electron donor alkyne, and an alternative canonical form, (**4′**), can be envisaged in which the but-2-yne ligand is donating four electrons and the metal atoms are joined by a single bond (see Scheme 1). An *X*-ray

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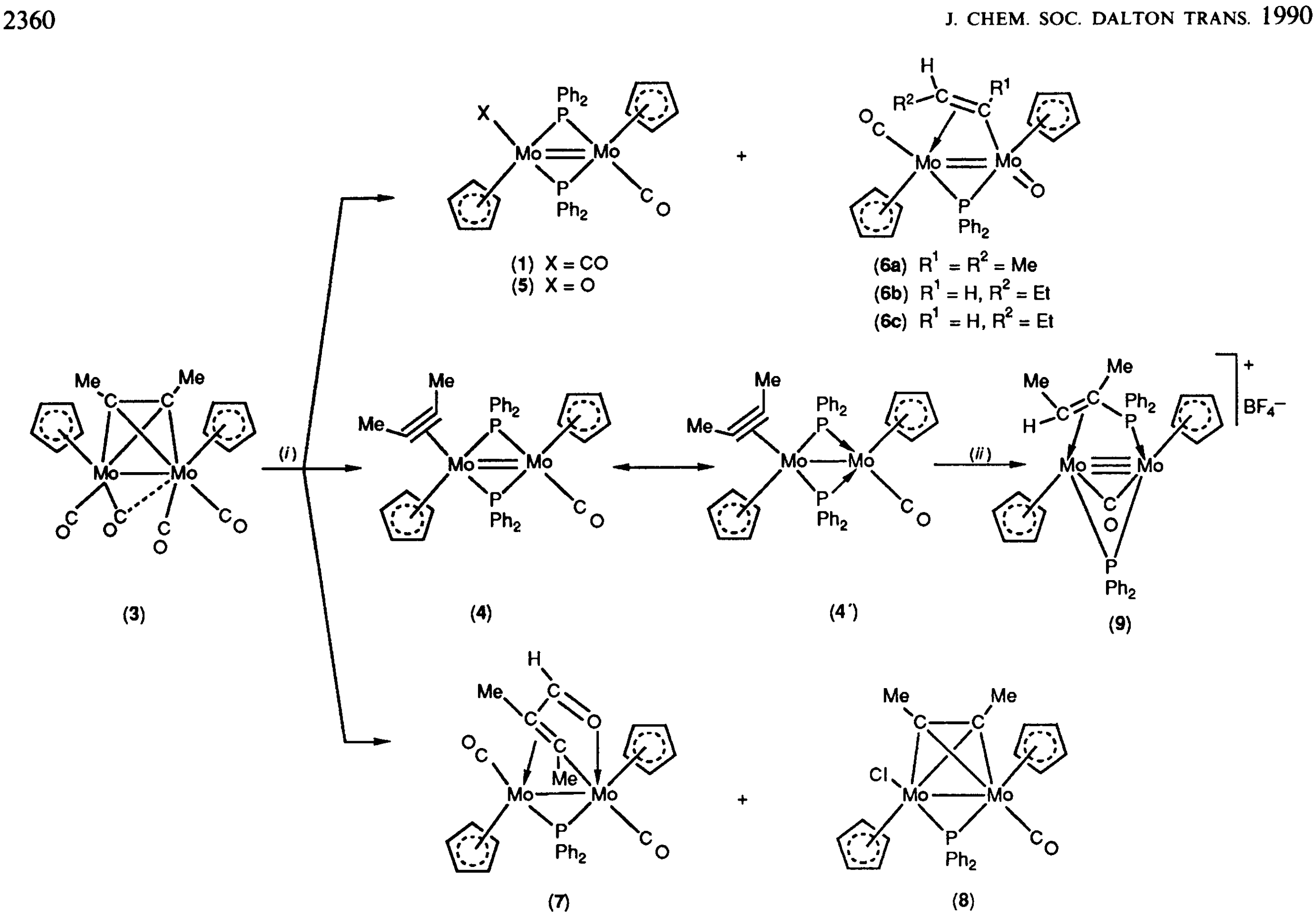
† $[1(\eta^2)$-But-2-yne]carbonyl-$2\kappa C$-bis$[1,2(\eta^5)$-cyclopentadienyl]bis(μ-diphenylphosphido)-dimolybdenum (2 *Mo–Mo*) and μ-carbonyl-bis$[1,2(\eta^5)$-cyclopentadienyl]-μ-diphenylphosphido-μ-[2-(diphenylphosphino-$2\kappa P$)but-2-ene-$1\kappa^2 C^{2,3}$]-dimolybdenum (3 *Mo–Mo*) tetrafluoroborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.



Scheme 1. Products from the reaction of $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ with tetraphenyldiphosphane. (*i*) P_2Ph_4; (*ii*) $HBF_4{\cdot}OEt_2$, − 78 °C

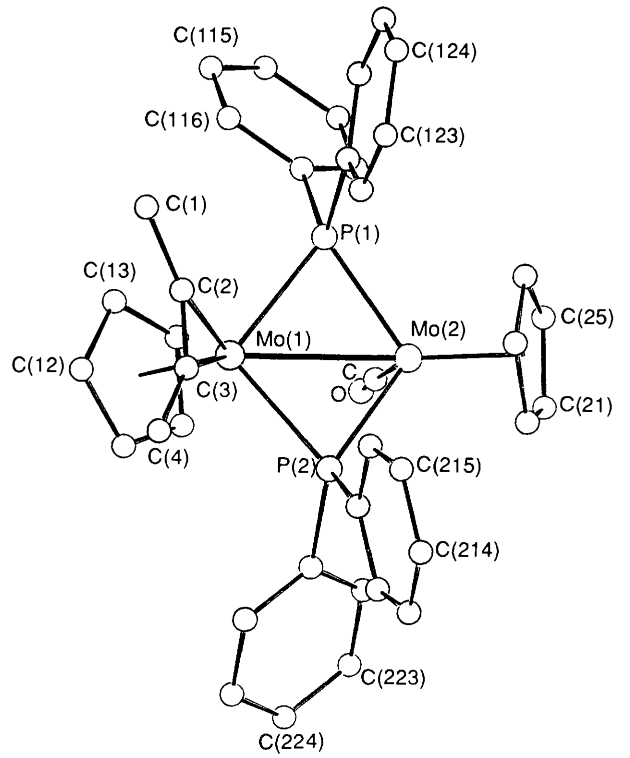


Figure 1. Molecular structure of $[Mo_2(\mu\text{-}PPh_2)_2(CO)(\eta\text{-}C_2Me_2)(\eta\text{-}C_5H_5)_2]$ (**4**) including the atom numbering scheme

diffraction study was therefore carried out on a suitable crystal of (**4**) in order to compare the structural parameters with those of other $Mo_2(\mu\text{-}PPh_2)_2$ complexes.

Figure 1 shows the molecular structure of complex (**4**) in the crystal, with selected bond lengths and angles collected in Table 1. The structure consists of discrete dinuclear molecules with no unusually short intermolecular contacts.

As deduced from the spectra, the but-2-yne ligand is solely bonded to Mo(1). This is unusual for dinuclear complexes,[7] where alkynes tend to adopt bridging modes of co-ordination. As in (**1**) and (**5**) the Mo_2P_2 unit is virtually planar (maximum deviation 0.14 Å) with the C(2)–C(3) bond of the alkyne ligand almost parallel to it. The C(2)–C(3) bond is of length 1.271(10) Å, and the two methyl groups are bent back at angles of 144.5(6) [C(1)–C(2)–C(3)] and 143.6(6)° [C(4)–C(3)–C(2)], these values being typical for non-bridging but-2-yne ligands bonded to molybdenum.[8]

The Mo(1)–Mo(2) bond length of 2.865(1) Å lies between that of 2.716(1) Å in (**1**) and that of 2.942(1) Å in (**5**),[5] and is close to that of 2.885(1) Å found in $[Mo_2O(\mu\text{-}CH{=}CHPh)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$[9] (see below), all of which may be considered as having Mo–Mo double bonds. In the first canonical form (**4**) a formal double bond is required purely on the basis of the 18-electron rule if the alkyne ligand acts as a two-electron donor. The alternative description of the bonding, (**4'**), in which the alkyne ligand acts as a four-electron donor with a formal Mo–Mo bond order of one, could account for the asymmetry observed in the phosphido bridges [Mo(1)–P(1) 2.420(2), Mo(2)–P(1) 2.346(2), Mo(1)–P(2) 2.419(2), and Mo(2)–P(2) 2.348(2) Å].

The other products obtained from the reaction of $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**3**) with P_2Ph_4 can be divided into

Table 1. Selected bond lengths (Å) and angles (°) for complexes (**4**) and (**9**) *

(4)		(9)	
Mo(1)–Mo(2)	2.865(1)	Mo(1)–Mo(2)	2.593(2)
Mo(1)–P(1)	2.420(2)		
Mo(1)–P(2)	2.419(2)	Mo(1)–P(2)	2.367(3)
		Mo(1)–C	2.373(12)
Mo(1)–C(2)	2.094(6)	Mo(1)–C(2)	2.249(12)
Mo(1)–C(3)	2.100(6)	Mo(1)–C(3)	2.340(12)
Mo(2)–P(1)	2.346(2)	Mo(2)–P(1)	2.428(4)
Mo(2)–P(2)	2.348(2)	Mo(2)–P(2)	2.387(3)
Mo(2)–C	1.930(6)	Mo(2)–C	1.947(12)
		P(1)–C(2)	1.810(13)
C(1)–C(2)	1.487(10)	C(1)–C(2)	1.535(20)
C(2)–C(3)	1.271(10)	C(2)–C(3)	1.416(16)
C(3)–C(4)	1.498(11)	C(3)–C(4)	1.518(18)
Range Mo(1)–Cp	2.350(7)—2.415(9)	Range Mo(1)–Cp	2.325(15)—2.376(16)
Range Mo(2)–Cp	2.341(10)—2.377(9)	Range Mo(2)–Cp	2.343(18)—2.378(17)
Mo(2)–P(1)–Mo(1)	73.9(1)	—	
—		C(2)–P(1)–Mo(2)	111.6(4)
Mo(2)–P(2)–Mo(1)	73.9(1)	Mo(2)–P(2)–Mo(1)	66.1(1)
—		P(1)–C(2)–Mo(1)	86.3(5)
C(1)–C(2)–Mo(1)	141.3(5)	C(1)–C(2)–Mo(1)	125.7(8)
—		C(1)–C(2)–P(1)	120.7(8)
C(3)–C(2)–Mo(1)	72.6(4)	C(3)–C(2)–Mo(1)	75.6(7)
—		C(3)–C(2)–P(1)	111(1)
C(3)–C(2)–C(1)	144.5(6)	C(3)–C(2)–C(1)	124(1)
C(2)–C(3)–Mo(1)	72.1(4)	C(2)–C(3)–Mo(1)	68.6(7)
C(4)–C(3)–Mo(1)	142.7(5)	C(4)–C(3)–Mo(1)	127.4(9)
C(4)–C(3)–C(2)	143.6(6)	C(4)–C(3)–C(2)	122(1)
—		Mo(2)–C–Mo(1)	73.0(4)
—		O–C–Mo(1)	129(1)
O–C–Mo(2)	175.0(5)	O–C–Mo(2)	158(1)

* Cp = Cyclopentadienyl ring carbon atoms.

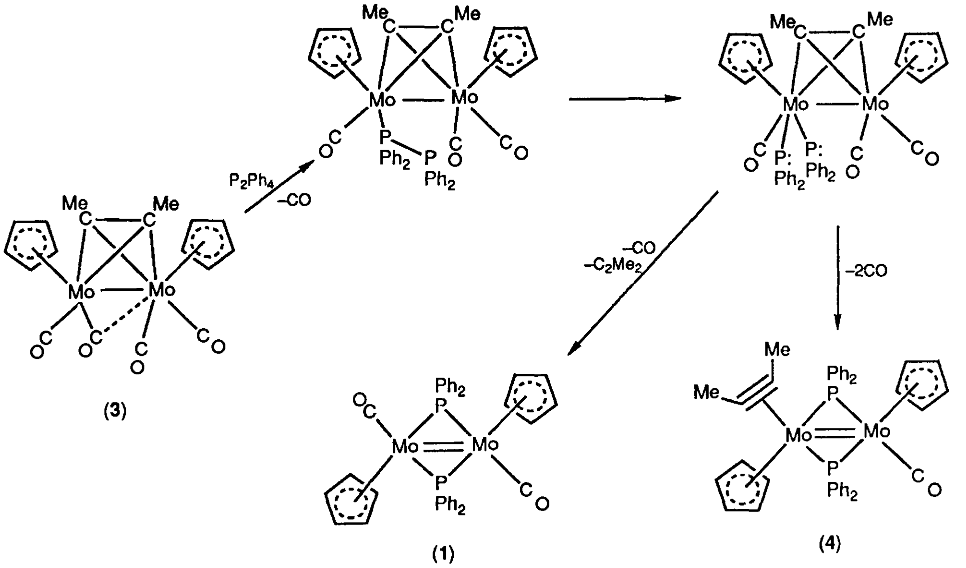
three groups in order of their subsequent elution from the chromatography column. First, the green complex $[Mo_2(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (**1**) was obtained in 7—25% yield, accompanied by a small amount of the oxo complex (**5**), which we have previously shown to be derived from (**1**) by oxidation in air [5] [complex (**4**) cannot also be a source of (**5**) since it appears to be completely air-stable].

The following zone was purple, and was shown to contain the two isomeric complexes $[Mo_2O(\mu\text{-}CMe{=}CHMe)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ (**6a**) and $[Mo_2O(\mu\text{-}CH{=}CHEt)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ (**6b**). These proved extremely difficult to separate: (**6b**) could be obtained pure but (**6a**), which is also obtained from the reaction of $[Mo_2(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ with buta-1,3-diene,[1] was characterised as a mixture. In related reactions of other dimolybdenum μ-alkyne complexes with P_2Ph_4 we have prepared a number of such complexes differing only in the substituents on the μ-vinyl ligand, all of which display similar n.m.r. spectra; in particular their ^{31}P chemical shifts all lie in the range 34—44 p.p.m. As mentioned above, one of these, $[Mo_2O(\mu\text{-}CH{=}CHPh)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$, was originally prepared and structurally characterised by Ziegler and co-workers.[9] The structures of (**6a**) and (**6b**) are probably similar, with a *trans* orientation of the cyclopentadienyl groups and with the vinyl ligand σ-bound to the molybdenum atom bearing the oxo group. However, as pointed out previously,[4] the stereochemistry of the substituents on the vinyl ligand is difficult to assign unambiguously from the spectroscopic data.

On some occasions, in addition to (**6a**) and (**6b**), a further complex of this type, (**6c**), was obtained from the reaction of (**3**) with P_2Ph_4. According to its ^{1}H n.m.r. spectrum, (**6c**), which was eluted as a separate purple band during chromatography, contains a μ-CH=CHEt ligand and we therefore assume it to be another isomer similar to (**6b**), though it is not possible to say whether this isomerism involves the *cis*/*trans* orientation of the C_5H_5 rings, the orientation of the vinyl ligand, or simply the arrangement of the substituents on the vinyl ligand.

Further elution of the chromatography column provided another red-purple zone, again containing two compounds. These could readily be separated by fractional crystallisation into the less-soluble red complex $[Mo_2\{\mu\text{-}CMe{=}C(Me)CHO\}(\mu\text{-}PPh_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ (**7**) and a purple compound which we identify as $[Mo_2(\mu\text{-}C_2Me_2)(\mu\text{-}PPh_2)Cl(CO)(\eta\text{-}C_5H_5)_2]$ (**8**).

We have previously prepared several complexes analogous to (**7**) from related reactions; again all have similar spectroscopic characteristics *e.g.* their ^{31}P n.m.r. chemical shifts lie in the range δ +5 to −5 p.p.m. Such complexes have also been prepared by Knox and co-workers[10] who found that thermolysis of the phosphine-substituted compound $[Mo_2(\mu\text{-}C_2H_2)(CO)_3(PPh_3)(\eta\text{-}C_5H_5)_2]$ led to phosphorus–carbon bond cleavage and phenyl migration to give $[Mo_2\{\mu\text{-}CH{=}CHC(Ph)O\}(\mu\text{-}PPh_2)(CO)_2(\eta\text{-}C_5H_5)_2]$. A range of alkyne complexes and phosphines was explored; if the phosphine involved was PPh_2H, P–H bond cleavage occurred preferentially, and we concluded from their results that (**7**) might alternatively be prepared from $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ and diphenylphosphine. In order to confirm this point a separate reaction of (**3**) with PPh_2H was undertaken, and (**7**) indeed proved the major product (20% yield); the vinyl complexes (**6a**) and (**6b**) (combined yield 11.5%) and (**6c**) (8%) were also formed. It is therefore likely that the presence of small quantities of diphenylphosphine remaining from the *in situ* synthesis of P_2Ph_4 (from PPh_2H and PPh_2Cl [11]) is responsible for the production of at least some proportion of these four compounds in the original reaction.



Scheme 2. Proposed mechanism for the reaction of complex (3) with P_2Ph_4

In a similar manner, (8) is probably formed through the presence of small amounts of residual PPh_2Cl, and we have recently shown that the reaction of PPh_2Cl with alkyne-bridged dimolybdenum[12] and ditungsten[13] complexes does give rise to similar compounds under conditions of comparatively high dilution. The relatively high value of ν(CO) for these compounds [1959 cm^{-1} for (8)] compared to the other complexes discussed provides a convenient method for their identification. Despite several attempts, however, we have so far failed to produce (8) by the direct reaction of (3) with PPh_2Cl; in each case, even with 0.5 equivalents of the chlorophosphine, the only isolated product has been the mononuclear chelate complex [MoCl(CO){*cis*-$Ph_2PC(Me)$=$C(Me)PPh_2$}(η-C_5H_5)], which contains two diphenylphosphido groups coupled to the but-2-yne ligand.[12] However we feel that this does not exclude the formation of (8) by this route in the original reaction, considering the very small amounts of PPh_2Cl which are likely to be present.

The mechanism of the reaction between complex (3) and P_2Ph_4 is uncertain, but a plausible proposal (Scheme 2) consists of initial substitution of a CO ligand of (3) by a P_2Ph_4 molecule, followed by cleavage of the P–P bond (effectively oxidative addition of the P_2Ph_4 to one molybdenum centre). Similar oxidative-cleavage processes of P–C, P–H, and P–Cl bonds have previously been postulated in reactions of dimolybdenum complexes analogous to (3) with phosphines[10] and chlorophosphines.[12] Migration of both PPh_2 groups to bridging positions could then occur with concomitant displacement of either two CO ligands to give (4) or of one CO and the alkyne ligand to give (1).

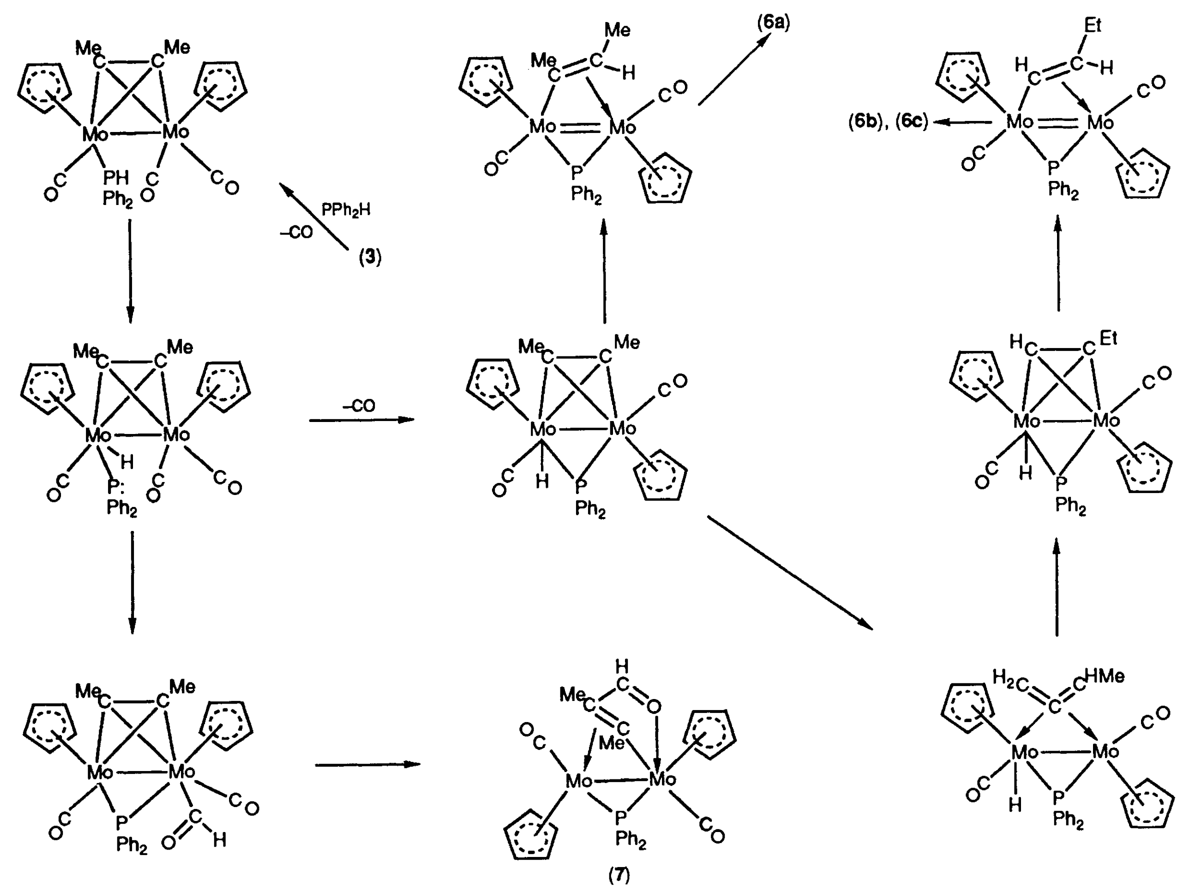
The reaction of complex (3) with PPh_2H can be rationalised in a similar manner (Scheme 3). Initial substitution is followed by oxidative addition of the P–H bond to give terminal PPh_2 and H ligands. Migration of the diphenylphosphido group to a bridging position is accompanied by migration of the hydride ligand either to a carbonyl group, as previously described by Knox and co-workers,[10] to give (7) (by subsequent migration of the resulting formyl to the alkyne) or to the alkyne, leading eventually to (6a), (6b), and (6c). Clearly a hydrogen-shift process is involved in the producton of (6b) and (6c); one possibility might involve the formation of an intermediate containing a μ-CH_2=C=CHMe allene ligand, as shown.

(*b*) *Protonation of* [Mo_2(μ-PPh_2)$_2$(CO)(η-C_2Me_2)(η-C_5H_5)$_2$].—We have previously shown that protonation of complex (1) occurs at the metal–metal bond to give [Mo_2(μ-H)(μ-PPh_2)$_2$(CO)$_2$(η-C_5H_5)$_2$][BF_4].[5] Addition of an excess of HBF_4·OEt_2 to a dichloromethane solution of (4) at −78 °C caused an immediate colour change to bright purple. We have so far been unable to isolate or characterise this initial product, but on warming a further colour change to dark green occurred, and work-up afforded a quantitative yield of [Mo_2(μ-CO)(μ-PPh_2){μ-$Ph_2PC(Me)$=CHMe}(η-C_5H_5)$_2$][BF_4] (9) (Scheme 1).

The i.r. spectrum now showed a peak at 1 798 cm^{-1}, which, taking into account the shift to higher wavenumber expected for a cationic complex, implied that the CO ligand had migrated to a bridging position. Extensive structural reorganisation was also indicated by the n.m.r. spectra; hence in the ^{31}P spectrum the two phosphorus atoms were no longer equivalent, one appearing at δ 105.1 p.p.m. and the other at −110.7 p.p.m., this latter being characteristic of a terminally bound phosphine ligand. The coupling pattern observed in the ^{1}H and ^{13}C n.m.r. spectra showed that the proton was attached to the but-2-yne ligand, and moreover that this had inserted into one of the Mo–P bonds to form a bridging vinylphosphine ligand. Hence the proton of the CHMe group appears as a doublet of doublet of quartets through coupling to the methyl protons and both phosphorus atoms, with one small *J*(HP) and one large.

Confirmation of this formulation was obtained by an *X*-ray diffraction study of complex (9). The structure of the dinuclear organometallic cation is shown in Figure 2, with relevant bond lengths and angles collected in Table 1.

The Mo–Mo distance of 2.593(2) Å in (9) is comparable to that of 2.515(1) Å observed in (2),[5] and is thus consistent with the presence of the metal–metal triple bond required for each molybdenum atom to attain an 18-electron configuration. The bond is bridged almost symmetrically by the remaining μ-PPh_2 unit [Mo(1)–P(2) 2.367(3), Mo(2)–P(2) 2.387(3) Å] and asymmetrically by the semibridging CO ligand [Mo(1)–C 2.373(12), Mo(2)–C 1.947(12) Å]. The linking of the second phosphido group to the protonated alkyne has produced a bridging vinylphosphine ligand, $Ph_2PC(Me)$=CHMe, which is co-ordinated to Mo(2) through the phosphorus atom [Mo(2)–P(1) 2.428(4) Å] and to Mo(1) by the double bond of the vinyl group [Mo(1)–C(2) 2.249(12), Mo(1)–C(3) 2.340(12) Å]. As expected, the two methyl substituents adopt a *cis* arrangement, and the



Scheme 3. Proposed mechanism for the reaction of complex (3) with PPh_2H

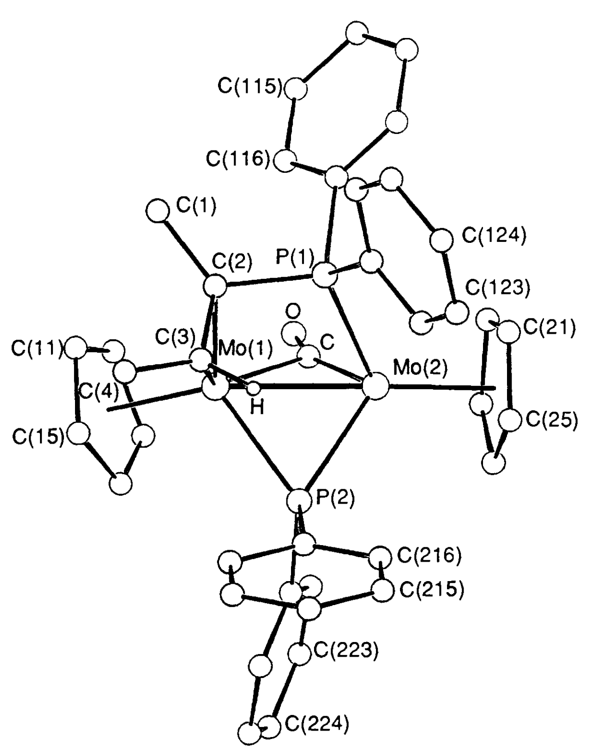


Figure 2. Molecular structure of $[Mo_2(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Ph_2PC(Me)\text{=}CHMe\}(\eta\text{-}C_5H_5)_2][BF_4]$ (9) including the atom numbering scheme

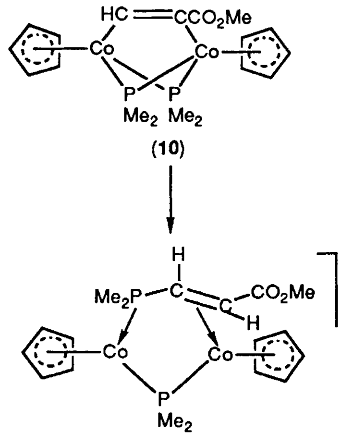
C(2)–C(3) distance of 1.416(16) Å is longer than the corresponding length of 1.271(10) Å in (4).

Comparison of the structures of complexes (4) and (9) reveals that comparatively little movement of the alkyne ligand is required to effect P–C bond formation during the protonation reaction. In terms of mechanism, if protonation occurs at the organic ligand (or at the metal centre with subsequent transfer to the organic ligand) this would produce a σ,π-bound vinyl group (*i.e.* a metallacyclopropene) which could then insert into the Mo–P bond. Insertion of alkynes into bridging phosphido groups has been observed previously by several groups, but the most closely related reaction is that reported by Werner and Zolk;[14] protonation with HPF_6 of the dicobalt complex $[Co_2(\mu\text{-}HC_2CO_2Me)(\mu\text{-}PMe_2)_2(\eta\text{-}C_5H_5)_2]$ (10), containing an alkyne bound in the two-electron 'parallel' mode, results in a similar coupling with one of the $\mu\text{-}PMe_2$ groups to give the bridging vinylphosphine complex $[Co_2(\mu\text{-}PMe_2)(\mu\text{-}Me_2PCH\text{=}CHCO_2Me)(\eta\text{-}C_5H_5)_2][PF_6]$ (11). We have also previously observed the coupling of vinyl ligands with $\mu\text{-}PPh_2$ groups to give similar ligands in dimanganese complexes.[15]

It is interesting that in the reaction of $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ with P_2Ph_4 no products are isolated in which phosphorus–carbon bond formation has taken place, yet on protonation of (4) facile coupling of the organic ligand with the phosphido group occurs at low temperature. Further studies of the factors influencing such processes are in progress.

Experimental

General techniques and instrumentation were as described in Part 1 of this Series.[3] The complex $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (3) was prepared by the literature method.[16] Examin-



(10)

(11)

ation of the ^{1}H n.m.r. spectrum of (3) showed that contamination by $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ was negligible (*ca.* 1—2%). Tetraphenyldiphosphane was prepared by the method of Küchen and Buchwald;[11] PPh_2Cl and PPh_2H were purchased from Aldrich and used without further purification. I.r. spectra were recorded in CH_2Cl_2. Unless otherwise stated, all n.m.r. spectra were recorded in $CDCl_3$, with chemical shifts in p.p.m. on the δ scale relative to $SiMe_4$ (0.0 p.p.m.) (for ^{1}H and ^{13}C) or $P(OMe)_3$ (0.0 p.p.m.) for ^{31}P (upfield shifts negative).

(*i*) *Reaction of* $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (3) *with* P_2Ph_4.—Tetraphenyldiphosphane was prepared *in situ* by refluxing a mixture of PPh_2H (1.10 cm^3, 6.32 mmol) and PPh_2Cl (1.14 cm^3, 6.35 mmol) in heptane (175 cm^3) for 3 h. The solvent was removed *in vacuo*, and $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (2.5024 g, 5.27 mmol) was added, followed by toluene (175 cm^3). The resulting solution was refluxed for 96 h, monitoring the reaction by spot t.l.c. until virtually all of the starting material had disappeared. After addition of silica (5 g) the solvent was removed and the residue loaded onto a silica chromatography column.

Elution with hexane–dichloromethane (4:1) produced a red band of the starting complex (3) contaminated with excess of phosphine (623.6 mg), followed by a further red band containing $[Mo_2(\mu\text{-}PPh_2)_2(CO)(\eta\text{-}C_2Me_2)(\eta\text{-}C_5H_5)_2]$ (4) (1.7142 g, 42%), m.p. 260—264 °C, $\nu(CO)$ 1 826 cm^{-1}. N.m.r.: ^{1}H, δ 8.48—6.30 (m, 20 H, Ph), 4.64 [t, *J*(HP) 0.8, 5 H, C_5H_5], 4.02 (s, 5 H, C_5H_5), and 2.20 (s, 6 H, Me); ^{13}C, δ 237.0 [t, *J*(CP) 8.5, CO], 155.8 (s, *C*Me), 151.5 [d, *J*(CP) 28.2, C_{ipso}], 142.5 [d, *J*(CP) 37.2 Hz, C_{ipso}], 135.6—126.1 (m, Ph), 96.1 (s, C_5H_5), 87.6 (s, C_5H_5), and 21.4 p.p.m. (s, Me) (Found: C, 60.60; H, 4.65; P, 7.60. $C_{39}H_{36}Mo_2OP_2$ requires C, 60.45; H, 4.65; P, 8.00%).

Owing to the relative insolubility of $[Mo_2(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (1), which tends to contaminate all the following bands, we adopted the following procedure to separate the remaining compounds. The eluting solvent was changed to CH_2Cl_2 and then to CH_2Cl_2–acetone (9:1) until no further bands descended. After removal of solvent from the eluate, it was washed with acetone to yield (1) (282.7 mg) as an insoluble green powder. A small amount of silica was added to the acetone washings, the solvent was removed *in vacuo*, and the residue loaded onto a second chromatography column. Elution with hexane–dichloromethane (1:1) produced small further amounts of complexes (4) (8.6 mg) and (1) (14.2 mg, total yield 7.2%), followed by a red band due to the oxo complex *trans*-$[Mo_2O(\mu\text{-}PPh_2)_2(CO)(\eta\text{-}C_5H_5)_2]$ (5) (17.2 mg, 0.4% after further purification by t.l.c. as previously described).[5]

A stronger red-purple band was eluted using hexane–CH_2Cl_2 (1:1), and shown to consist of a mixture of $[Mo_2O(\mu\text{-}CMe{=}CHMe)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ (6a) and $[Mo_2O(\mu\text{-}CH{=}CHEt)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ (6b) (combined yield 78.5 mg, 2.5%). Further purification by exhaustive t.l.c. (eluting solvent hexane–dichloromethane, first 3:7 and then 4:6) provided more mobile (6b) as a pure compound. Complex (6a) was characterised as a mixture with (6b) in *ca.* 3:1 ratio by ^{1}H n.m.r. integration.

Complex (6a). $\nu(CO)$ 1 839 cm^{-1}. N.m.r.: ^{1}H, δ 8.02—7.17 (m, 10 H, Ph), 5.09 (s, 5 H, C_5H_5), 4.73 [d, *J*(HP) 1.3, 5 H, C_5H_5], 3.19 [d, *J*(HP) 0.6, 3 H, CMe], 2.79 [q, *J*(HH) 6.3, 1 H, CH], and 1.83 [d, *J*(HH) 6.3 Hz, 3 H, CH*Me*]; ^{31}P, δ 38.4 p.p.m. (Found: C, 53.55; H, 4.65; P, 4.95. $C_{27}H_{27}Mo_2O_2P$ requires C, 53.45; H, 4.45; P, 5.10%), *m/z* 606 (M^+).

Complex (6b). M.p. 208—210 °C, $\nu(CO)$ 1 839 cm^{-1}. N.m.r.: ^{1}H, δ 9.06 [dd, *J*(HH) 9.5, *J*(HP) 1.8, 1 H, μ-CH], 8.02—7.17 (m, 10 H, Ph), 5.03 (s, 5 H, C_5H_5), 4.66 [d, *J*(HP) 1.3, 5 H, C_5H_5], 2.78 (m, 1 H, C*H*Et), 1.97 (m, 2 H, CH_2), and 1.37 [t, *J*(HH) 7.3 Hz, 3 H, CH_3]; ^{31}P, δ 34.6 p.p.m. (Found: C, 53.55; H, 4.65; P, 5.13. $C_{27}H_{27}Mo_2O_2P$ requires C, 53.45; H, 4.45; P, 5.10%), *m/z* 606 (M^+).

Elution with hexane–dichloromethane (1:4) produced a bright purple band containing $[Mo_2O(\mu\text{-}CH{=}CHEt)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ (6c) (27.7 mg, 0.9%), m.p. (92 °C, decomp.), $\nu(CO)$ 1 865 cm^{-1}. N.m.r.: ^{1}H, δ 8.48 [d, *J*(HP) 9.4, 1 H, μ-CH], 7.81—6.97 (m, 10 H, Ph), 5.35 [d, *J*(HP) 0.8, 5 H, C_5H_5], 5.00 [d, *J*(HP) 1.0, 5 H, C_5H_5], 3.21 [d of t, *J*(HH) 6.5, 9.4, 1 H, C*H*Et], 2.00 (m, 2 H, CH_2), and 1.25 [t, *J*(HH) 7.3, 3 H, CH_3]; ^{13}C, δ 235.1 [d, *J*(CP) 15, CO], 154.7 [d, *J*(CP) 2, μ-CH], 147.0 [d, *J*(CP) 26, C_{ipso}], 141.0 [d, *J*(CP) 45 Hz, C_{ipso}], 134.3—127.4 (m, Ph), 99.7 (s, C_5H_5), 88.0 (s, C_5H_5), 71.7 (s, CH), 34.9 (s, CH_2), and 17.1 p.p.m. (s, Me); ^{31}P, δ 23.9 p.p.m. (Found: C, 53.85; H, 4.76. $C_{27}H_{27}Mo_2O_2P$ requires C, 53.45; H, 4.45%), *m/z* 606 (M^+).

Further elution of the chromatography column with dichloromethane–acetone (9:1) provided another red-purple band. Fractional crystallisation from CH_2Cl_2–hexane gave small amounts of first red $[Mo_2\{\mu\text{-}CMe{=}C(Me)CHO\}(\mu\text{-}PPh_2)(CO)_2(\eta\text{-}C_5H_5)_2]$ (7) (43.3 mg, 1.3%), and then of purple $[Mo_2(\mu\text{-}C_2Me_2)(\mu\text{-}PPh_2)Cl(CO)(\eta\text{-}C_5H_5)_2]$ (8) (69.2 mg, 2.1%).

Complex (7). M.p. 237—238 °C (decomp.), $\nu(CO)$ 1 862 cm^{-1}. N.m.r.: ^{1}H, δ 8.66 (s, 1 H, CHO), 7.62—7.08 (10 H, Ph), 5.16 [d, *J*(HP) 1.5, 5 H, C_5H_5], 4.84 [d, *J*(HP) 1.0, 5 H, C_5H_5], 2.70 [d, *J*(HP) 1.4 Hz, 3 H, Me], and 1.58 (s, 3 H, Me); ^{31}P, δ 4.9 p.p.m. (Found: C, 53.85; H, 4.30; P, 4.50. $C_{29}H_{27}Mo_2O_3P$ requires C, 53.85; H, 4.20; P, 4.80%), *m/z* 618 $(M - CO)^+$.

Complex (8). $\nu(CO)$ 1 959 cm^{-1}. N.m.r.: ^{1}H, δ 8.09—6.40 (10 H, Ph), 5.36 (s, 5 H, C_5H_5), 4.83 [d, *J*(HP) 0.8 Hz, C_5H_5], 2.95 (s, 3 H, Me), and 2.81 (s, 3 H, Me); ^{31}P, δ 6.5 p.p.m. *m/z* 624 (M^+).

(*ii*) *Reaction of* $[Mo_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (3) *with* PPh_2H.—Diphenylphosphine (0.8 cm^3, 4.60 mmol) was added to a solution of complex (3) (2.2500 g, 4.61 mmol) in toluene (175 cm^3), and the mixture was refluxed for 19 h. After addition of silica (5 g) the solvent was removed and the residue subjected to chromatography. Elution with hexane–dichloromethane (6:4) gave a red zone containing unreacted (3) (0.2405 g, 10.7% recovery), followed by minor bands of $[Mo_2(\mu\text{-}PPh_2)_2(CO)_2(\eta\text{-}C_5H_5)_2]$ (1) and *trans*-$[Mo_2O(\mu\text{-}PPh_2)_2(CO)(\eta\text{-}C_5H_5)_2]$ (5).

Elution with hexane–dichloromethane (1:1) produced a purple band consisting of $[Mo_2O(\mu\text{-}CMe{=}CHMe)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ (6a) and $[Mo_2O(\mu\text{-}CH{=}CHEt)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ (6b) in approximately equal amounts by n.m.r. integration (total yield 321.8 mg, 11.5%). Further elution with CH_2Cl_2 provided the second isomer of $[Mo_2O(\mu\text{-}CH{=}CHEt)(\mu\text{-}PPh_2)(CO)(\eta\text{-}C_5H_5)_2]$ (6c) (224.4 mg, 8%) as a separate purple band.

The major product, $[Mo_2\{\mu\text{-}CMe{=}C(Me)CHO\}(\mu\text{-}PPh_2)\text{-}$

Table 2. Fractional atomic co-ordinates

	(4)			(9)		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
Mo(1)	0.239 25(4)	−0.066 26(5)	−0.137 21(2)	0.275 63(9)	−0.143 97(6)	0.063 50(5)
Mo(2)	0.200 67(4)	−0.329 90(5)	−0.151 44(2)	0.119 77(8)	−0.238 39(6)	0.102 61(5)
P(1)	0.355 03(12)	−0.225 54(15)	−0.161 92(6)	0.215 1(3)	−0.309 7(2)	0.024 5(1)
P(2)	0.105 18(13)	−0.190 50(15)	−0.106 56(7)	0.284 1(3)	−0.174 7(2)	0.175 0(2)
C(1)	0.477 8(6)	0.030 6(7)	−0.072 4(3)	0.364 7(12)	−0.244 5(9)	−0.060 6(6)
C(2)	0.366 1(5)	−0.007 9(6)	−0.078 5(2)	0.340 6(10)	−0.250 1(7)	0.008 7(6)
C(3)	0.284 3(5)	−0.001 3(6)	−0.057 3(3)	0.429 9(10)	−0.241 1(8)	0.066 0(7)
C(4)	0.241 6(7)	0.050 7(8)	−0.010 2(3)	0.558 6(11)	−0.222 2(9)	0.064 1(8)
C	0.131 6(5)	−0.275 0(6)	−0.222 3(3)	0.065 1(10)	−0.142 2(8)	0.046 5(6)
O	0.089 3(4)	−0.251 0(5)	−0.266 4(2)	−0.002 8(7)	−0.096 8(6)	0.014 1(5)
C(11)	0.124 6(7)	0.108 7(8)	−0.162 6(3)	0.366 8(13)	−0.056 5(10)	−0.004 0(8)
C(12)	0.230 6(7)	0.156 2(9)	−0.155 9(4)	0.246 7(13)	−0.024 3(10)	−0.006 2(8)
C(13)	0.282 9(7)	0.096 2(8)	−0.195 1(3)	0.236 1(13)	0.000 4(10)	0.059 9(8)
C(14)	0.208 4(6)	0.010 6(7)	−0.226 8(3)	0.351 6(13)	−0.013 2(10)	0.101 7(8)
C(15)	0.112 2(6)	0.019 0(7)	−0.206 5(3)	0.433 4(13)	−0.046 8(10)	0.064 5(8)
C(21)	0.112 9(8)	−0.522 7(9)	−0.161 9(4)	0.009 9(14)	−0.365 4(11)	0.103 5(8)
C(22)	0.135 6(7)	−0.495 5(8)	−0.104 9(4)	−0.072 3(14)	−0.296 6(11)	0.073 1(8)
C(23)	0.247 6(7)	−0.492 5(8)	−0.086 7(4)	−0.072 4(14)	−0.233 4(11)	0.125 9(8)
C(24)	0.296 0(8)	−0.518 4(9)	−0.134 7(4)	0.009 4(14)	−0.261 6(11)	0.183 4(8)
C(25)	0.211 1(8)	−0.537 1(10)	−0.181 2(4)	0.059 8(14)	−0.341 1(11)	0.170 4(8)
C(111)	0.399 0(3)	−0.203 2(4)	−0.227 1(1)	0.107 0(6)	−0.319 0(5)	−0.053 2(3)
C(112)	0.362 2(3)	−0.238 0(4)	−0.270 5(1)	0.056 0(6)	−0.397 0(5)	−0.073 5(3)
C(113)	0.393 6(3)	−0.264 8(4)	−0.320 3(1)	−0.029 2(6)	−0.402 9(5)	−0.131 4(3)
C(114)	0.461 7(3)	−0.166 9(4)	−0.326 7(1)	−0.063 4(6)	−0.330 9(5)	−0.168 9(3)
C(115)	0.498 5(3)	−0.087 2(4)	−0.283 3(1)	−0.012 5(6)	−0.252 9(5)	−0.148 5(3)
C(116)	0.467 1(3)	−0.105 4(4)	−0.233 5(1)	0.072 7(6)	−0.247 0(5)	−0.090 7(3)
C(121)	0.478 4(3)	−0.275 1(4)	−0.117 4(1)	0.277 3(6)	−0.414 1(4)	0.045 2(4)
C(122)	0.475 7(3)	−0.290 4(4)	−0.062 4(1)	0.291 3(6)	−0.444 3(4)	0.108 9(4)
C(123)	0.563 2(3)	−0.377 6(4)	−0.027 5(1)	0.339 3(6)	−0.524 3(4)	0.124 8(4)
C(124)	0.653 3(3)	−0.369 5(4)	−0.047 5(1)	0.373 5(6)	−0.574 2(4)	0.076 9(4)
C(125)	0.656 0(3)	−0.354 3(4)	−0.102 5(1)	0.359 5(6)	−0.544 1(4)	0.013 2(4)
C(126)	0.568 5(3)	−0.307 0(4)	−0.137 5(1)	0.311 5(6)	−0.464 1(4)	−0.002 7(4)
C(211)	0.102 9(3)	−0.229 0(4)	−0.034 6(1)	0.407 1(6)	−0.229 9(5)	0.226 1(4)
C(212)	0.009 6(3)	−0.243 6(4)	−0.015 0(1)	0.523 1(6)	−0.202 6(5)	0.227 7(4)
C(213)	0.011 8(3)	−0.287 5(4)	0.037 6(1)	0.618 8(6)	−0.244 8(5)	0.266 3(4)
C(214)	0.107 3(3)	−0.316 8(4)	0.070 6(1)	0.598 6(6)	−0.314 4(5)	0.303 4(4)
C(215)	0.200 7(3)	−0.302 2(4)	0.051 0(1)	0.482 7(6)	−0.341 7(5)	0.301 9(4)
C(216)	0.198 5(3)	−0.258 3(4)	−0.001 6(1)	0.386 9(6)	−0.299 5(5)	0.263 2(4)
C(221)	−0.032 1(2)	−0.146 1(4)	−0.131 2(2)	0.256 8(7)	−0.087 6(4)	0.228 1(4)
C(222)	−0.094 7(2)	−0.218 6(4)	−0.170 7(2)	0.147 6(7)	−0.046 0(4)	0.213 8(4)
C(223)	−0.199 0(2)	−0.185 1(4)	−0.189 3(2)	0.127 7(7)	0.024 2(4)	0.250 4(4)
C(224)	−0.240 7(2)	−0.079 1(4)	−0.168 5(2)	0.217 2(7)	0.052 7(4)	0.301 4(4)
C(225)	−0.178 1(2)	−0.006 6(4)	−0.129 0(2)	0.326 5(7)	0.011 1(4)	0.315 7(4)
C(226)	−0.073 8(2)	−0.040 0(4)	−0.110 3(2)	0.346 3(7)	−0.059 1(4)	0.279 1(4)
C(11a)	0.100 4(13)	0.063 1(21)	−0.184 9(9)	0.425 7(23)	−0.050 8(21)	0.039 0(17)
C(12a)	0.174 6(13)	0.144 3(21)	−0.153 6(9)	0.323 3(23)	−0.045 4(21)	−0.012 1(17)
C(13a)	0.269 9(13)	0.135 3(21)	−0.173 7(9)	0.228 6(23)	−0.012 7(21)	0.014 6(17)
C(14a)	0.254 6(13)	0.048 6(21)	−0.217 4(9)	0.272 4(23)	0.002 0(21)	0.082 1(17)
C(15a)	0.149 8(13)	0.004 0(21)	−0.224 3(9)	0.394 3(23)	−0.021 5(21)	0.097 2(17)
C(21a)	0.146 8(7)	−0.535 3(10)	−0.183 1(3)	0.050 3(21)	−0.361 4(13)	0.150 6(13)
C(22a)	0.102 7(7)	−0.511 0(10)	−0.136 3(3)	−0.026 5(21)	−0.344 7(13)	0.089 6(13)
C(23a)	0.186 3(7)	−0.496 5(10)	−0.091 5(3)	−0.082 9(21)	−0.265 8(13)	0.094 3(13)
C(24a)	0.282 1(7)	−0.512 0(10)	−0.110 7(3)	−0.040 9(21)	−0.233 8(13)	0.158 2(13)
C(25a)	0.257 7(7)	−0.535 9(10)	−0.167 3(3)	0.041 4(21)	−0.292 9(13)	0.193 0(13)
H(3)				0.427(10)	−0.284(10)	0.106(10)
B				0.229 3(18)	0.492 9(12)	0.312 0(9)
F(1)				0.209 1(10)	0.503 7(7)	0.248 8(5)
F(2)				0.337 1(11)	0.478 4(11)	0.338 1(7)
F(3)				0.160 2(13)	0.440 8(9)	0.330 4(7)
F(4)				0.210 7(15)	0.567 6(8)	0.336 1(6)

$(CO)_2(\eta\text{-}C_5H_5)_2]$ (**7**), was then eluted as a bright red band using dichloromethane–acetone (9:1) (yield 603.8 mg, 20.3%).

(*iii*) *Protonation of* $[Mo_2(\mu\text{-}PPh_2)_2(CO)(\eta\text{-}C_2Me_2)(\eta\text{-}C_5H_5)_2]$ (**4**).—Complex (**4**) (341.5 mg, 0.44 mmol) was dissolved in dichloromethane (15 cm^3) and the solution was cooled to −78 °C (2-propanol–solid CO_2 bath). An excess of $HBF_4 \cdot OEt_2$ (0.5 cm^3) was added, causing an immediate colour change to bright purple. On warming to room temperature a further change occurred, to give a dark green solution. The CH_2Cl_2 was removed *in vacuo*, and the salt $[Mo_2(\mu\text{-}CO)(\mu\text{-}PPh_2)\{\mu\text{-}Ph_2PC(Me){=}CHMe\}(\eta\text{-}C_5H_5)_2][BF_4]$ (**9**) was isolated in essentially quantitative yield by washing with diethyl ether: m.p. 230—233 °C, $\nu(CO)$ 1 798 cm^{-1}. N.m.r.: ^1H (CD_2Cl_2), δ 7.74—7.00 (m, 20 H, Ph), 5.50 [d, *J*(HP) 1.2, 5 H, C_5H_5], 5.29 (s, 5 H, C_5H_5), 3.31 [ddq, *J*(HP) 27.5 and 9.3, *J*(HH) 6.4, 1 H, C*H*Me], 2.16 [d, *J*(HP) 9.4, 3 H, CMe], and 1.64 [dd, *J*(HH) 6.4, *J*(HP) 0.6 Hz, CH*Me*]; ^{13}C, δ 268.9 [dd, *J*(CP) 10.4 and 6.6, CO], 149.2 [d, *J*(CP) 38.3, C_{ipso}], 135.2 [d, *J*(CP) 43.0, C_{ipso}], 134.0—128.9 (m, Ph), 126.0 [d, *J*(CP) 33.2, C_{ipso}], 99.4 (s, C_5H_5), 95.6 (s, C_5H_5), 66.0 [d, *J*(CP) 16.2, *C*HMe], 49.6 [d, *J*(CP) 30.1, *C*Me], 20.2 (s, CH*Me*), and 19.5 p.p.m. [d, *J*(CP) 12.8 Hz, C*Me*]; ^{31}P, δ 105.1 (s, μ-PPh_2) and -110.7 p.p.m. (s, PPh_2) (Found: C, 54.50; H, 4.55; P, 6.40. $C_{39}H_{37}BF_4Mo_2OP_2$ requires C, 54.30; H, 4.30; P, 7.20%). Fast atom bombardment mass spectrum: *m/z* 775 (M^+ for cation).

(*iv*) *Crystal Structure Determinations.—Crystal data for complex* (**4**). $C_{39}H_{36}Mo_2OP_2$, $M = 774.50$, monoclinic, space group $P2_1/c$, $a = 12.965(3)$, $b = 10.659(2)$, $c = 25.072(5)$ Å, $\beta = 100.44(2)°$, $Z = 4$, $U = 3\,407.44$ Å^3, $\mu(Mo\text{-}K_\alpha) = 7.66$ cm^{-1}, $D_c = 1.51$ g cm^{-3}, $F(000) = 1\,568$. A red-purple crystal of size 0.40 × 0.27 × 0.32 mm, grown by diffusion of hexane into a dichloromethane solution, was used in the data collection.

Crystal data for complex (**9**). $C_{39}H_{37}BF_4Mo_2OP_2$, $M = 862.27$, monoclinic, space group $P2_1/c$, $a = 11.494(2)$, $b = 15.836(3)$, $c = 20.944(4)$ Å, $\beta = 101.93(2)°$, $Z = 4$, $U = 3\,729.86$ Å^3, $\mu(Mo\text{-}K_\alpha) = 7.17$ cm^{-1}, $D_c = 1.54$ g cm^{-3}, $F(000) = 1\,736$. A green crystal of size 0.16 × 0.20 × 0.32 mm, grown from dichloromethane–diethyl ether solution, was used in the data collection.

Data collection. Data for both structures were collected in the range θ 3—25°, with a scan width of 0.90° for complex (**4**) and 0.74° for (**9**), using the technique described previously.[17] For both structures Lorentz and polarisation corrections were applied. The total number of independent reflections was 4 389 for (**4**) and 3 145 for (**9**). Equivalent reflections were merged to give 4 168 data for (**4**) and 2 959 for (**9**), with $I/\sigma(I) > 3.0$.

Structure solution and refinement.[18] The co-ordinates of the metal atoms in the structures of complexes (**4**) and (**9**) were deduced from Patterson syntheses, and the remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. The hydrogen atom attached to C(3) in compound (**9**) was located in a Fourier-difference synthesis calculated using data with $\sin\theta < 0.35$. This was included in the structure-factor calculations with a thermal parameter of 0.08 Å^2 but its parameters were not refined. The remaining hydrogen atoms in both structures were included in geometrically idealised positions and were constrained to ride on the relevant carbon atoms with fixed isotropic thermal parameters of 0.08 Å^2. The phenyl groups in both structures were refined as rigid hexagons. Regions of high electron density around each of the cyclopentadienyl ligands in both structures indicated that these ligands were disordered. Refinement with fixed thermal parameters of 0.05 Å^2 led to a fractional occupancy of 0.80 for the major component of atoms C(11)—C(15) in (**4**) and to 0.70 for the equivalent atoms in compound (**9**). Similarly for the second cyclopentadienyl ligands, C(21)—C(25), fractional values of 0.60 and 0.65 were found for (**4**) and (**9**) respectively. There also appears to be rotational disorder of the BF_4^- anion in (**9**), shown by regions of extended electron density in the vicinity of the fluorine atoms, which could not be resolved and therefore resulted in high anisotropic thermal parameters for these atoms.

Full-matrix refinement was carried out for both structures, with anisotropic thermal parameters assigned for all non-hydrogen atoms (except the carbon atoms of the phenyl and cyclopentadienyl rings) in the final stages of refinement. For both complexes (**4**) and (**9**) weights of $w = 1/\sigma^2 F_o$ were assigned to individual reflections. Refinement converged at R 0.0449 and R' 0.0470 for (**4**) and at R 0.0558 and R' 0.0554 for (**9**).[17] The fractional atomic co-ordinates for (**4**) and (**9**) are collected in Table 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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