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Reaction of the η^2(4e)-donor alkyne complexes $[Mo\{\eta^2(4e)\text{-}R^1C_2R^2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ ($R^1 = R^2$ = Ph or Me; R^1 = Me, R^2 = Ph) with the Grignard reagents $MgR^3(X)$ (R^3 = Me, Et, CH_2Ph, $CH_2CH{=}CH_2$ or $CH{=}CH_2$) and $CH_2(MgI)_2$*

Georg Brauers,[a] Frank J. Feher,[b] Michael Green,[a,b] John K. Hogg[b] and A. Guy Orpen[b]

[a] *School of Chemistry, University of Bath, Bath BA2 7AY, UK*
[b] *School of Chemistry, University of Bristol, Bristol BS8 1TS, UK*

Reaction of the complex $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ **1** with MgR(X) (R = Me, Et or $PhCH_2$) afforded good yields of $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}R\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$. Unexpectedly, reaction of **1** with the 1,1-di-Grignard reagent $CH_2(MgI)_2$ gave the X-ray crystallographically identified zwitterionic complex $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$, similar reactions with the but-2-yne and 1-phenylprop-2-yne complexes affording the analogous $[Mo\{\eta^2(4e)\text{-}RC_2R^2\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}\text{-}(\eta\text{-}C_5H_5)]$ (R = R^2 = Me; R = Me, R^2 = Ph). Treatment of the zwitterionic diphenylacetylene- and 1-phenylprop-2-yne-substituted complexes with $K[BHBu^s_3]$ gave the anionic η^2(3e)-vinyl complexes $K[Mo\{{=}C(R)CH(Ph)\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2(\eta\text{-}C_5H_5)]$ (R = Ph or Me). Protonation ($HBF_4{\cdot}Et_2O$) of the diphenyl-substituted η^2(3e)-vinyl complex followed by addition of carbon monoxide, trimethyl phosphite, or diphenylacetylene afforded *trans*-stilbene and the complexes $[Mo(CO)_2\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}\text{-}(\eta^2\text{-}C_5H_5)]$, $[Mo\{P(OMe)_3\}_2\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ and $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ respectively. When $CH_2{=}CHCH_2MgBr$ was added to **1** an unstable compound was formed, which on addition of $P(OMe)_3$ gave $[Mo\{\eta^3\text{-}C(Ph){=}C(Ph)CH_2CH{=}CH_2\}\text{-}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, the identity of which was confirmed by X-ray crystallography. This reaction is explained in terms of an unusual metalla-3,3-sigmatropic shift process. A similar reaction between **1** and $CH_2{=}CHMgBr$ followed by addition of $P(OMe)_3$ surprisingly gave the η^3-cyclopropenyl complex $[Mo(\eta^3\text{-}C_3Ph_2Me)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$. The complex $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}Me\{P(OMe)_3\}\text{-}(\eta\text{-}C_5H_5)]$ reacted thermally (78 °C) with an excess of PhC_2Ph to give the X-ray crystallographically identified complex $[MoH(\eta^4\text{-}C_5H_2Ph_4)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$, which on heating (100 °C) afforded the dihydride $[MoH_2(\eta^5\text{-}C_5HPh_4)(\eta\text{-}C_5H_5)]$.

We have previously reported[2-4] that reaction of the cationic complex $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ with nucleophilic reagents can result in the formation of two different types of product. Thus, with the hydride-anion donor $K[BHBu^s_3]$ the product was the η^2(3e)-vinyl complex $[Mo\{{=}C(Ph)CH(Ph)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, whereas with lithium dimethylcuprate a mixture of $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}Me\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ and the η^2(3e)-vinyl complex $[Mo\{{=}C(Ph)CMe(Ph)\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ was formed. Related reactions with other substituted alkyne complexes afforded carbyne and η^3-allyl complexes. In order to understand this chemistry more fully it was important to extend the range of nucleophilic reagents. In this paper we report a detailed study of the corresponding reactions with Grignard reagents,[5] and some of the chemistry of the resulting products.

Results and Discussion

A suspension of the violet complex $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$[6] **1** in tetrahydrofuran (thf) was treated with MgMe(I) at 0 °C changing rapidly to dark green. Column chromatography on alumina using CH_2Cl_2–hexane as eluent gave a green fraction, which after recrystallisation from hexane afforded an excellent (91%) yield of the known[3] complex $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}Me\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ **4**. Analogous reactions between **1** and MgEt(Br) or $Mg(CH_2Ph)Br$ gave moderate yields of the green crystalline complexes $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}R\{P(OMe)_3\}\text{-}(\eta\text{-}C_5H_5)]$ (R = Et **5** or $PhCH_2$ **6**) (Scheme 1). These complexes are very soluble in the common polar and non-polar solvents and are quite air sensitive. In the ^1H NMR spectrum of **6** the two diastereotopic benzyl protons show chemical shifts of δ 2.92 and 2.53, with a geminal coupling of 11.4 Hz, and a coupling to the ^{31}P nucleus of 6.6 and 6.0 Hz. In contrast, the couplings of the methylene protons in **5** are obscured, because all five protons of the ethyl group appear as a multiplet between δ 1.73 and 1.52. The contact carbon atoms of the alkyne ligand in **5** show a singlet at δ 202.8 and a doublet at δ 201.3 [*J*(PC) 10.6 Hz]. From the two different shifts it can be concluded that the alkyne is not fluxional. The singlet can be assigned to the carbon cisoid to the phosphorus, and the doublet to the transoid bonded carbon. The alkyne ligand in **6** exhibits very similar data with a singlet at δ 204.1 and a doublet at δ 201.1 [*J*(PC) 10.8 Hz]. Hence, in all these complexes, the alkyne acts as a four-electron donor.[7]

In view of these observations it was thought that reaction of complex **1** with a 1,1-di-Grignard reagent might result in replacement of one phosphite ligand to give a mono- or di-meric carbene complex. The reagent $CH_2(MgI)_2$[8] was chosen for an initial study because this is the only readily available 1,1-di-Grignard reagent. Surprisingly, addition of $CH_2(MgI)_2$ to a suspension of complex **1** in thf did not result in an immediate colour change, instead a white precipitate was formed, but on stirring overnight a green solution was obtained. Work-up by column chromatography afforded a moderate yield of a blue crystalline complex **7** (Scheme 1). Reaction of the cationic

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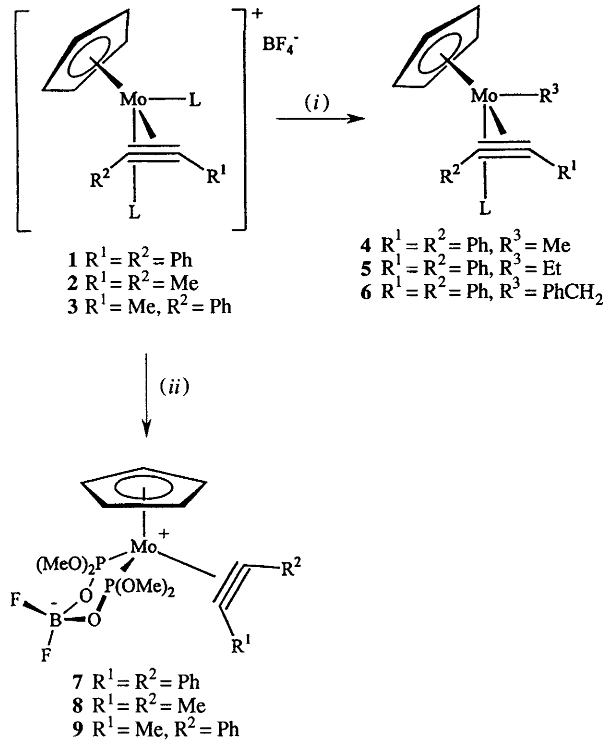
* Reactions of Co-ordinated Ligands. Part 63.[1]



1 $R^1 = R^2 = Ph$
2 $R^1 = R^2 = Me$
3 $R^1 = Me, R^2 = Ph$

4 $R^1 = R^2 = Ph, R^3 = Me$
5 $R^1 = R^2 = Ph, R^3 = Et$
6 $R^1 = R^2 = Ph, R^3 = PhCH_2$

7 $R^1 = R^2 = Ph$
8 $R^1 = R^2 = Me$
9 $R^1 = Me, R^2 = Ph$

Scheme 1 L = $P(OMe)_3$. (*i*) $MgR^3(Br)$, thf; (*ii*) $CH_2(MgI)_2$, thf

complexes **2** and **3** with $CH_2(MgI)_2$ formed the analogous blue compounds **8** and **9** in similar yield. Elemental analysis and examination of the NMR spectra of these compounds indicated that an unusual reaction had occurred resulting in the formation of the chelating ligand $(MeO)_2POBF_2OP(OMe)_2$, in which the BF_2 fragment has its origin in the BF_4^- counter anion. Interestingly, this ligand has previously been reported as being formed on reaction of the complexes $[M\{P(OH)(OMe)_2\}\{P(O)(OMe)_2\}(\eta-C_5H_5)]$ (M = Ni or Pd) with $HBF_4 \cdot Et_2O$. However, although the products $[M\{\eta^2-P(OMe)_2OBF_2OP(OMe)_2\}(\eta-C_5H_5)]$ were fully characterised by NMR spectroscopy, crystal structure determination was not reported.[9,10] A crystal structure study was therefore undertaken on complex **7**, suitable crystals being obtained by slowly cooling a solution in thf. The resulting molecular structure is shown in Fig. 1, selected bond lengths and angles being listed in Table 1.

In agreement with the NMR spectra, complex **7** contains the cationic $Mo\{\eta^2(4e)-PhC_2Ph\}(\eta-C_5H_5)$ fragment bonded to the anionic ligand $\eta^2-P(OMe)_2OBF_2OP(OMe)_2$. This ligand adopts a chair-like conformation with pseudo-axial and -equatorial environments for the P(OMe) groups. The C–C vector of the contact carbons of the co-ordinated alkyne lies parallel to one of the ligand Mo–P vectors, *i.e.* Mo–P(2), although in solution it is evident from the NMR spectra that the alkyne has a low barrier to rotation. The P–O distances in the ring system [P(1)–O(4) 1.539(2) and P(2)–O(1) 1.553(2) Å] are considerably shorter than the exocyclic P–O distance, with an average length of 1.585Å, indicating a contribution from the canonical forms **A** and **C** (Scheme 2) where the positive charge in the zwitterionic complex resides on the ring oxygens rather than on the molybdenum centre as depicted in **B**.

As mentioned in the Introduction, treatment of cationic complexes of the type $[Mo\{\eta^2(4e)-alkyne\}\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ with nucleophiles can lead to the formation of η^2-(3e)-vinyl, carbyne and η^3-allyl complexes. It was therefore of interest to examine the related reactions of **7** and **9**. Treatment of (−78 °C) a solution of **7** in toluene with a thf solution of $K[BHBu^s_3]$ resulted on warm up to room temperature in a change from blue to green. Addition of hexane afforded a green powder, which on recrystallisation from diethyl ether–hexane

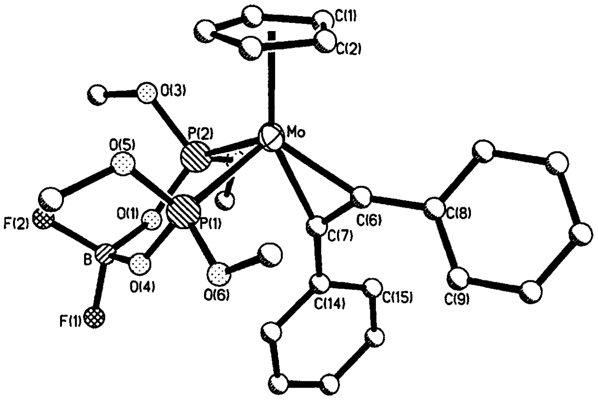
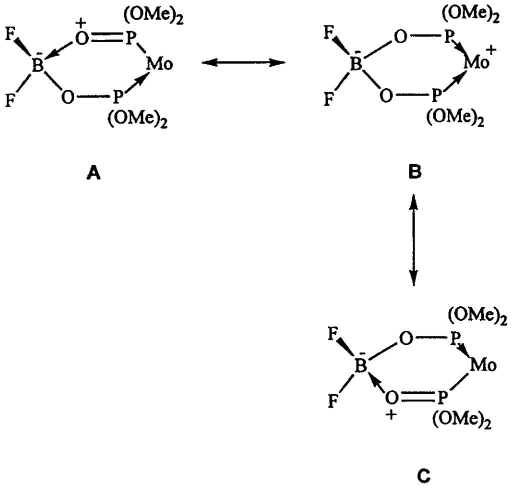


Fig. 1 Molecular structure of complex **7** showing the atom labelling scheme. All hydrogen atoms have been omitted for clarity

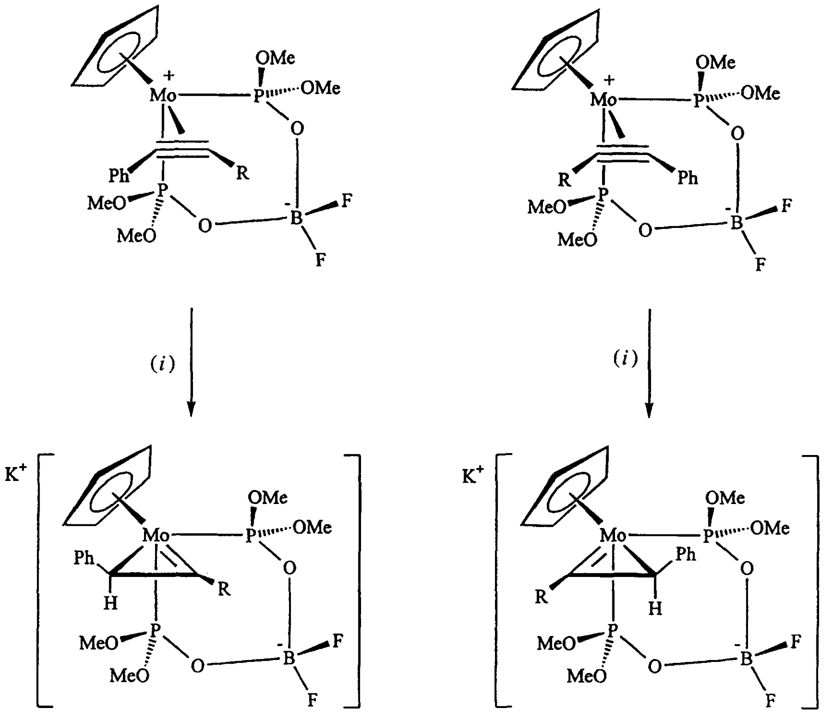


Scheme 2

Table 1 Selected bond lengths (Å) and angles (°) for complex **7**

Mo–P(2)	2.375(1)	Mo–P(1)	2.397(1)
Mo–C(7)	2.050(3)	Mo–C(6)	2.013(2)
Mo–C(1)	2.325(3)	Mo–C(2)	2.341(3)
Mo–C(3)	2.326(3)	Mo–C(4)	2.304(3)
Mo–C(5)	2.297(3)	P(2)–O(1)	1.553(2)
P(2)–O(3)	1.592(2)	P(2)–O(2)	1.587(2)
P(1)–O(4)	1.539(2)	P(1)–O(5)	1.581(3)
P(1)–O(6)	1.590(2)	O(1)–B	1.471(4)
O(4)–B	1.471(3)	O(3)–C(20)	1.421(3)
O(2)–C(21)	1.412(3)	C(7)–C(14)	1.458(4)
O(7)–C(6)	1.310(3)	O(5)–C(23)	1.443(5)
O(6)–C(22)	1.419(4)		
P(2)–Mo–P(1)	83.5(1)	P(2)–Mo–C(7)	82.0(1)
P(1)–Mo–C(7)	88.9(1)	P(2)–Mo–C(6)	118.4(1)
P(1)–Mo–C(6)	101.6(1)	C(7)–Mo–C(6)	37.6(1)
Mo–P(2)–O(1)	121.5(1)	Mo–P(2)–O(3)	109.6(1)
O(1)–P(2)–O(3)	106.0(1)	Mo–P(2)–O(2)	112.4(1)
O(1)–P(2)–O(2)	101.6(1)	O(3)–P(2)–O(2)	104.1(1)
Mo–P(1)–O(4)	119.2(1)	Mo–P(1)–O(5)	112.4(1)
O(4)–P(1)–O(5)	106.8(1)	Mo–P(1)–O(6)	115.2(1)
O(4)–P(1)–O(6)	95.8(1)	O(5)–P(1)–O(6)	105.7(1)
P(2)–O(1)–B	129.5(2)	P(1)–O(4)–B	132.2(2)
P(2)–O(3)–C(20)	121.8(2)	P(2)–O(2)–C(21)	127.6(2)
Mo–C(7)–C(14)	155.3(2)	Mo–C(7)–C(6)	69.7(2)
C(14)–C(7)–C(6)	135.0(2)	P(1)–O(5)–C(23)	120.9(3)
P(1)–O(6)–C(22)	120.7(2)	Mo–C(6)–C(7)	72.7(1)
Mo–C(6)–C(8)	148.0(2)	C(7)–C(6)–C(8)	139.3(2)
O(1)–B–F(1)	107.7(3)	O(1)–B–O(4)	111.2(2)
O(1)–B–F(2)	109.9(2)	O(4)–B–F(1)	106.8(2)
F(1)–B–F(2)	111.0(2)	O(4)–B–F(2)	110.2(3)

gave an excellent yield of a bright green crystalline complex **10**. A similar reaction between **9** and $K[BHBu^s_3]$ afforded pale



10a R = Me
11a R = Me

10b R = Me
11b R = Me

Scheme 3 (*i*) + K[$BHBu^s_3$], thf

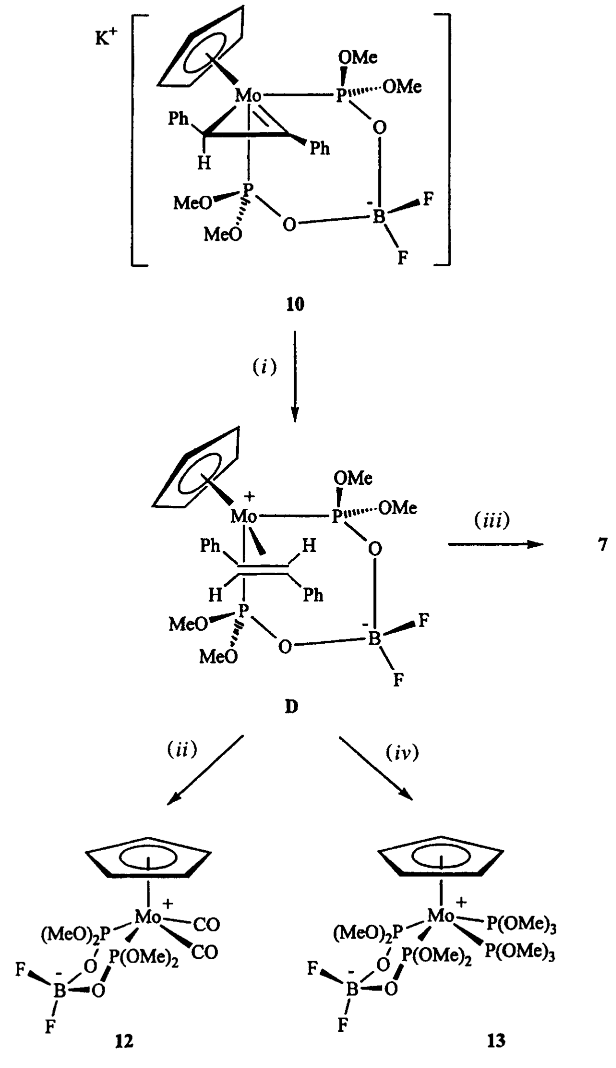
green crystals of **11**. Both these compounds proved to be extremely air sensitive and reproducible elemental analyses could not be obtained, however they could be characterised using multinuclear NMR techniques as the η^2(3e)-vinyl complexes K[Mo{=C(R)C(H)Ph}{η^2-P(OMe)$_2$OBF$_2$OP(OMe)$_2$}(η-C_5H_5)] (R = Ph **10** or Me **11**) (see Scheme 3). They are soluble in thf and CH_2Cl_2, but slowly decompose in the latter. The ^{1}H NMR spectrum of **10** showed four doublets between δ 3.44 and 3.30 for the phosphorus-bound methoxy groups, the proton on the η^2(3e)-vinyl ligand resonating as a multiplet at δ 3.42–3.35. In the spectrum of **11** these signals are indistinguishable and appear as one complex multiplet between δ 3.55 and 3.27, however the NMR spectrum also showed a singlet at δ 2.58 integrating for 3 H, which can be assigned to the Mo=CMe group. The carbon NMR spectra revealed the carbenoid character of the α-carbon of the η^2(3e)-vinyl group with resonances at δ 240.8 (**10**) and 242.3 (**11**), and the inequivalence of the phosphorus nuclei in **10** and **11** is reflected in an AB pattern in the ^{31}P-{^{1}H} spectrum.

Although confirming the overall structures of complexes **10** and **11**, the NMR data did not establish that the 'H^-' delivered by K[$BHBu^s_3$] occupies a pseudo-axial position, nor the orientation of the η^3(3e)-vinyl fragment. However, it is assumed that there is a stereochemical parallel between these reactions and those established[3] by X-ray crystallography for the corresponding reactions of [Mo{η^2(4e)-RC$_2$Ph}{P(OMe)$_3$}$_2$(η-C_5H_5)][BF$_4$] (R = Me or Ph), and it is on this basis that the structures of **10** and **11** are drawn, *i.e.* **10** has the structure **10a**, and **11** the structure **11b**.

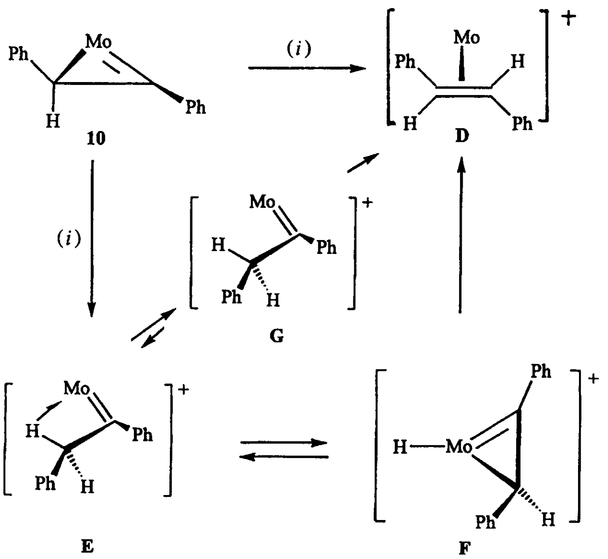
The protonation (HBF_4·Et_2O) of complex **10** was next explored. This was of interest because Templeton and co-workers[11] had shown that the η^2(3e)-vinyl group present in [W{=C(Ph)C(H)Me}(CO)$_2${HB(dmpz)$_3$}] (dmpz = 3,5-dimethylpyrazolyl) is protonated on the β-carbon to give the β-agostic stabilised cation [W{=C(Ph)CH$_2$Ph}(CO)$_2${HB(dmpz)$_3$}][BF$_4$]. Addition of HBF_4·Et_2O to a toluene solution of **10** cooled to −78 °C resulted in an immediate change from yellow to red. The reaction mixture was filtered through an alumina pad to give a red solution of an intermediate **D**. The ^{1}H NMR spectrum of **D** showed no high-field signals characteristic of a MH or M(μ-H)C system, but there were four cyclopentadienyl signals. Since a separation of these products was not feasible, carbon monoxide was bubbled through the NMR sample resulting in a change to yellow. The NMR spectrum of the reaction mixture revealed that all the products, *i.e.* isomers of **D**, from the protonation reaction react with CO to give one metal complex. When the reaction was scaled up and hexane added to the reaction mixture the bis(carbonyl-substituted) complex [Mo(CO)$_2${η^2-P(OMe)$_2$OBF$_2$OP(OMe)$_2$}(η-C_5H_5)] **12** (Scheme 4) was obtained in high (82%) yield as yellow crystals, which were characterised by elemental analysis, IR, ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectroscopy. Column chromatography of the supernatant solution gave exclusively *trans*-stilbene. A similar reaction between **11**, HBF_4·Et_2O and CO also gave **12** in high yield. Reaction of **10** with HBF_4·Et_2O followed by addition of diphenylacetylene or 2 molar equivalents of trimethyl phosphite gave the parent complex **7**, or the bright yellow crystalline complex [Mo{P(OMe)$_3$}$_2${η^2-P(OMe)$_2$OBF$_2$OP(OMe)$_2$}(η-C_5H_5)] **13**. The ^{1}H NMR spectrum of **13** showed three virtual triplets at δ 3.74, 3.70 and 3.42 with relative intensities 1 : 1 : 3. The first two resonances are assigned to the chelating ligand P(OMe)$_2$OBF$_2$OP(OMe)$_2$, and the last to the two P(OMe)$_3$ ligands. In the ^{31}P-{^{1}H} NMR spectrum the expected AA′XX′ pattern appears between δ 196.5–195.0 and 173.9–172.7. However, due to broadening of the XX′ part not all of the signals necessary to determine the underlying coupling constants could be found.

The formation of complex **7**, **12** or **13** through protonation of **10** can be explained in two ways. Protonation of **10** proceeds by charge-controlled attack of a proton delivered by [Et_2OH][BF$_4$] on the α-carbon of the η^2(3e)-vinyl ligand, generating directly the co-ordinatively unsaturated cationic *trans*-stilbene-substituted complex **D** (Scheme 5), which can then react with PhC$_2$Ph, CO or P(OMe)$_3$ to give *trans*-stilbene and **7**, **12** or **13** respectively. Alternatively, protonation occurs by attack on C_β to give **E**, a carbene complex stabilised by a C_β agostic Mo(μ-H)C interaction similar to that reported by Templeton and co-workers. This species then rearranges into **D** either by the steps **E** $\longrightarrow$ **F** $\longrightarrow$ **D**, or by **E** $\longrightarrow$ **G**, followed by migration of a benzylic hydrogen onto the cationic (carbonium ion-like) carbene carbon, *i.e.* **G** $\longrightarrow$ **D**.

An insight into these possible pathways can be derived from extended-Hückel molecular orbital (EHMO) studies[3,12] of known 18e, d^4, η^2(3e)-vinyl complexes. These show that these species have a lowest unoccupied molecular orbital (LUMO) that has a substantial ligand component arising from the M–C_α π^* interaction. In addition there is a negative charge build-up on the C_α carbon relative to the singly bonded C_β carbon (net charges in typical example by Mulliken population analysis of EHMO orbital: C_α, 0.5e; C_β, 0.15e), suggesting that, assuming charge-controlled protonation, it is the direct pathway **10** $\longrightarrow$ **D** which is preferred.



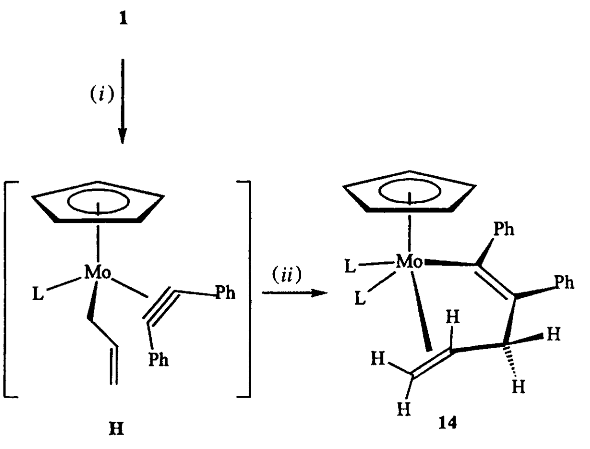
Scheme 4 (*i*) $+HBF_4 \cdot OEt_2$, $-KBF_4$; (*ii*) +CO, −*trans*-stilbene; (*iii*) $+PhC_2Ph$, −*trans*-stilbene; (*iv*) $+P(OMe)_3$, −*trans*-stilbene



Scheme 5 Ligands omitted for clarity. (*i*) $+HBF_4 \cdot OEt_2$

Returning to our study of the reactions of simple mono-Grignard reagents with the cationic complex $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, it was expected that reaction with $CH_2{=}CHCH_2MgBr$ would lead to a product analogous to the green complexes **4**–**6**. Indeed, after addition of the Grignard reagent at low temperature the mixture initially became green before considerable darkening occurred. With a view to obtaining a stable product the reaction was repeated, and after the mixture had turned green 1 equivalent of trimethyl phosphite was added. On warming to room temperature a yellow mixture was obtained. Column chromatography yielded a moderate yield of complex **14**, and examination of the NMR spectra suggested that the product had the formula $[Mo\{\eta^3\text{-}C(Ph){=}C(Ph)CH_2CH{=}CH_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (Scheme 6). Thus, the ^1H NMR spectrum showed a multiplet for the ten phenyl protons between δ 7.31 and 6.96 and a doublet for the five cyclopentadienyl protons at δ 5.03 [*J*(PH) 3.1 Hz]. Two doublets, at δ 3.29 [*J*(PH) 10.3] and 3.24 [*J*(PH) 9.5 Hz], could be assigned to the phosphite moieties. The methylene resonances appeared as a multiplet between δ 2.49 and 2.19. The signals for the $CH{=}CH_2$ group were obscured by other signals and therefore could not be assigned. The $^{31}P\text{-}\{^1H\}$ NMR spectrum displayed an AB system for two non-equivalent phosphorus nuclei with shifts of δ 194.3 and 183.3, respectively, and a coupling constant of 70.5 Hz. Owing to the thermal instability of the complex in solution a ^{13}C NMR spectrum could not be observed. Since only incomplete NMR data were obtained an X-ray diffraction study was performed on a single crystal of **14** obtained by slowly cooling a saturated solution in Et_2O–hexane. The resulting molecular structure is shown in Fig. 2, selected bond lengths and angles being listed in Table 2.

The molecular structure of complex **14** shows it to belong to the class of $Mo\{P(OMe)_3\}_2L(\eta\text{-}C_5H_5)$ complexes where L is a three-electron donor ligand. In **14** the ligand is $C(Ph)C(Ph)CH_2CH{=}CH_2$ which binds to Mo through σ-vinyl [at C(11)] and η^2-alkene functions [at C(7) and C(8)]. The Mo–C σ bond is rather long [2.319(4) Å][13] presumably as a consequence of the ring constraints as reflected in the Mo–C(11)–C(10) angle of 115.0(3)° (*cf.* $[Mo(E\text{-}CH{=}CHBu^t)\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)]$, Mo–C 2.243(2) Å, Mo–C–C 128.2(1)°).[6] Other aspects of the molecular geometry are normal, including the lengths of the C–C double bond [C(10)–C(11) 1.338(5) Å] and the co-ordinated alkene C–C bond [C(7)–C(8) 1.410(7) Å]. The geometry at molybdenum may best be described as of the four-



Scheme 6 L = $P(OMe)_3$. (*i*) $+CH_2{=}CHCH_2MgBr$; (*ii*) $+P(OMe)_3$

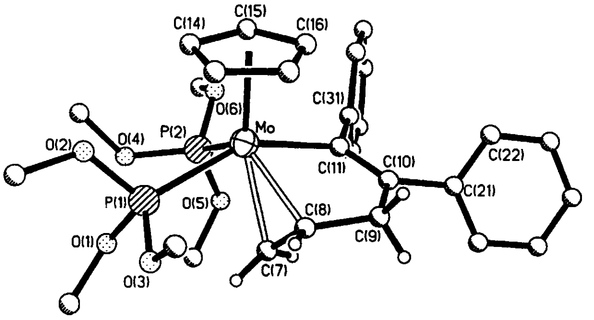


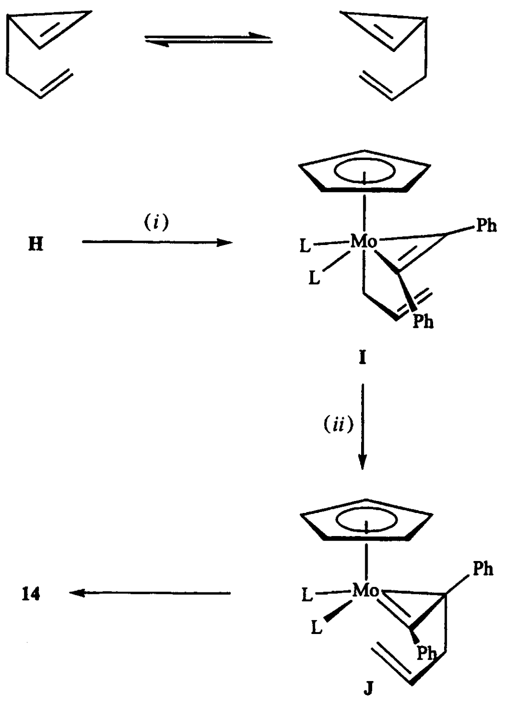
Fig. 2 Molecular structure of complex **14** showing the atom labelling scheme. All phenyl, methyl and cyclopentadienyl H atoms have been omitted for clarity

Table 2 Selected bond lengths (Å) and angles (°) for complex **14**

Mo–P(1)	2.437(2)	P(1)–O(2)	1.611(3)
Mo–P(2)	2.422(1)	P(1)–O(3)	1.629(3)
Mo–C(7)	2.286(5)	P(2)–O(4)	1.623(3)
Mo–C(8)	2.235(4)	P(2)–O(5)	1.614(3)
Mo–C(11)	2.319(4)	P(2)–O(6)	1.596(7)
Mo–C(12)	2.379(4)	C(7)–C(8)	1.410(7)
Mo–C(13)	2.320(5)	C(8)–C(9)	1.502(7)
Mo–C(14)	2.272(4)	C(9)–C(10)	1.515(7)
Mo–C(15)	2.279(4)	C(10)–C(11)	1.338(5)
Mo–C(16)	2.359(4)	C(10)–C(21)	1.503(6)
P(1)–O(1)	1.595(3)	C(11)–C(31)	1.500(6)
P(1)–Mo–P(2)	88.3(1)	P(1)–Mo–C(7)	74.6(1)
P(2)–Mo–C(7)	85.9(1)	P(1)–Mo–C(8)	85.9(1)
P(2)–Mo–C(8)	121.0(1)	C(7)–Mo–C(8)	36.3(2)
P(1)–Mo–C(11)	149.4(1)	P(2)–Mo–C(11)	83.5(1)
C(7)–Mo–C(11)	75.4(2)	C(8)–Mo–C(11)	73.4(2)
Mo–P(1)–O(1)	117.4(1)	Mo–P(1)–O(2)	113.7(1)
O(1)–P(1)–O(2)	104.4(2)	Mo–P(1)–O(3)	119.5(1)
O(1)–P(1)–O(3)	96.9(2)	O(2)–P(1)–O(3)	102.4(2)
Mo–P(2)–O(4)	124.3(1)	Mo–P(2)–O(5)	120.4(1)
O(4)–P(2)–O(5)	95.3(2)	Mo–P(2)–O(6)	110.7(1)
O(4)–P(2)–O(6)	101.3(2)	O(5)–P(2)–O(6)	101.0(2)
Mo–C(7)–C(8)	69.9(3)	Mo–C(8)–C(7)	73.8(2)
Mo–C(8)–C(9)	112.3(3)	C(7)–C(8)–C(9)	119.5(4)
C(8)–C(9)–C(10)	110.3(3)	C(9)–C(10)–C(11)	118.2(4)
C(9)–C(10)–C(21)	114.9(3)	C(11)–C(10)–C(21)	126.9(4)
Mo–C(11)–C(10)	115.0(3)	Mo–C(11)–C(31)	126.8(3)
C(10)–C(11)–C(31)	118.2(4)		

legged piano-stool type with P(1) lying transoid to σ-vinyl, P(2) to the alkene. The η^2-alkene C–C bond lies nearly parallel to Mo–P(2).

The formation of complex **14** is especially interesting, because attempts to promote the migration of the methyl, ethyl or benzyl groups present in the complexes **4**–**6** onto the co-ordinated diphenylacetylene by reaction with trimethyl phosphite were unsuccessful. It is likely that the initial product of the reaction of **1** with $CH_2{=}CHCH_2MgBr$ is, in fact, the sought-for complex $[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}(CH_2CH{=}CH_2)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (the species **H** shown in Scheme 6), however the problem is to explain why the simple addition of $P(OMe)_3$ is apparently able to promote migration of the allyl group from the metal centre onto the co-ordinated diphenylacetylene, whereas this does not happen with the corresponding Me-, Et- or $PhCH_2$-substituted systems. An explanation for this difference in reactivity is provided by the isolobal relationship between $MoL_2(\eta\text{-}C_5H_5)$ and CR.[14] Thus, as is shown in Scheme 7, addition of $P(OMe)_3$ to **H** would be expected to result in the formation of the intermediate **I**, a process facilitated by a switch (4e ⟶ 2e) in the bonding mode of the diphenylacetylene. The species **I** is, of course, isolobal with a 3-allyl-substituted cyclopropene, and as is well known[15] such molecules can undergo a facile degenerate 3,3-sigmatropic shift. Therefore, the rearrangement **I** ⟶ **J** is merely a metalla-version of the organic 3,3-shift process, and would be expected to occur readily. Since it is known[7] that η^2(3e)-vinyl species, *i.e.* complex **J**, can 'ring-open' to give η^1(1e)-vinyl ligands, such a process can then lead to the isolated product **14**.



Scheme 7 L = $P(OMe)_3$. (*i*) + $P(OMe)_3$, (*ii*) 3,3-sigmatropic shift

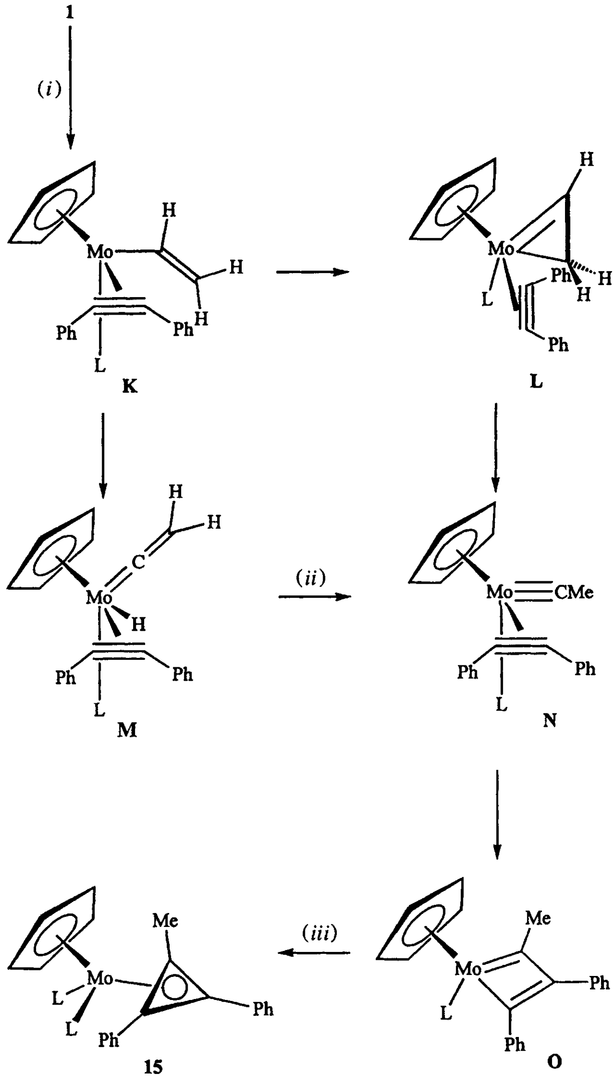
Attention was next turned to a study of the reaction of complex **1** with the vinyl Grignard reagent $CH_2{=}CHMgBr$, but as in the case of the allyl system, simple addition of the Grignard at 0 °C followed by warm up led to decomposition. However, addition of $P(OMe)_3$ before warm up resulted in the formation of a stable yellow crystalline complex **15**, which was isolated by column chromatography. Elemental analysis indicated that the new complex had the molecular formula $[Mo(C_3Ph_2Me)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, and, interestingly, examination of the ^1H, $^{13}C\text{-}\{^1H\}$ and $^{31}P\text{-}\{^1H\}$ NMR spectra showed that **15** is an η^3-cyclopropenyl complex.[16] The cyclopropenyl *C*Ph and *C*Me ^{13}C resonances both appeared as triplets [*J*(CP) 12.4 and 3.3 Hz respectively] and the $^{31}P\text{-}\{^1H\}$ NMR spectrum showed only one resonance indicating a low barrier to rotation about an axis through the metal and perpendicular to the C_3 plane. A similar effect has been previously observed with the related dicarbonyl complex $[Mo(\eta^3\text{-}C_3Ph_3)(CO)_2(\eta\text{-}C_5H_5)]$,[16] and has been attributed to the almost cylindrical symmetry[17] of the frontier orbitals presented by the $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragment; clearly this explanation can be extended to explain the spectra of **15**.

Since the formation of η^3-cyclopropenyl complexes, and their relationship with metallacyclobutadienes, has attracted considerable attention,[16] it is interesting to consider how **15** is formed. It is likely that reaction of **1** with $CH_2{=}CHMgBr$ leads initially to formation of the σ-vinyl complex **K** (Scheme 8). There are then two possible reaction pathways open to this complex. The first (**K** ⟶ **L**) requires a change in the bonding mode of the vinyl ligand from σ(1e) to η^2(3e), providing access to a η^2-vinyl system, in a step which requires a concomitant switch in the bonding mode of the diphenylacetylene [η^2(4e) ⟶ η^2(2e)]. The resulting η^2-vinyl can then undergo a precedented intramolecular 1,2-migration (C_α to C_β) of the hydrogen to form the carbyne-substituted complex **N**. The intermediate **N** can in principle also be formed *via* a different process. This is suggested by observations which show that a hydrogen atom attached to the α-carbon of a σ-vinyl group can be activated. Thus, treatment of [RhCl(CH=CHR)(PPr$^i_3$)(η-C$_5$H$_5$)] with NEt$_3$ or [OsCl(CH=CHR)(PPr$^i_3$)(η^6-C$_6$H$_6$)] with LiBu^t results in apparent elimination reactions and formation of the vinylidene complexes [Rh(=C=CHR)(PPr$^i_3$)(η-C$_5$H$_5$)] and [Os(=C=CHR)(PPr$^i_3$)(η^6-C$_6$H$_6$)] respectively.[18,19] We have shown[4] that when the σ-vinyl complexes [M(CH=CH-Bu^t){P(OMe)$_3$}$_3$L′] (M = Mo or W, L′ = η-C$_5$H$_5$ or η^5-C$_9$H$_7$) are heated in solution the carbyne complexes [M(≡CCH$_2$-Bu^t){P(OMe)$_3$}$_2$L′] are formed. In a related reaction treatment of [TaCl$_2$(η-C$_5$Me$_5$)$_2$] with CH$_2$=CHMgBr has been shown[20] to give [TaH(=C=CH$_2$)(η-C$_5$Me$_5$)$_2$]. It is likely that in this reaction the tantalum(IV) dihalide is first reduced by the Grignard reagent to give [TaCl(η-C$_5$Me$_5$)$_2$], and this is then converted into [Ta(CH=CH$_2$)(η-C$_5$Me$_5$)$_2$]; an α-hydrogen migration reaction from the sp^2-hybridised C$_\alpha$ carbon of the vinyl fragment onto the tantalum completes the reaction. In the light of these observations it is therefore reasonable to postulate that **K** (Scheme 8) rearranges *via* an α-H migration (C$_\alpha$ ⟶ Mo) directly into **M** assisted by a switch [η^2(4e) ⟶ η^2(2e)] in the bonding mode of the diphenylacetylene ligand. Trimethyl phosphite-mediated transfer, *i.e.* deprotonation followed by reprotonation,[21] of the hydrogen bonded to the molybdenum centre in **M** to the β-carbon of the vinylidene ligand then provides the second pathway to the intermediate **N**, which can transform into the isolated product **15** by a well established process.

The idea that a switch [η^2(4e) ⟶ η^2(2e)] in the bonding mode of diphenylacetylene could provide the vacant co-ordination site needed to initiate the transfer of a C$_\alpha$ vinylic hydrogen to a molybdenum centre led us to consider whether it might be possible to promote an α-H elimination reaction with the methyl-substituted complex [Mo{η^2(4e)-PhC$_2$Ph}Me-{P(OMe)$_3$}(η-C$_5$H$_5$)] **4**. With this in mind a solution of **4** and an excess of diphenylacetylene in benzene was heated *in vacuo* at 78 °C in a sealed tube, it being postulated that the alkyne would capture an intermediate carbene complex. After 12 h the reaction mixture had changed from green to yellow and work-up by column chromatography and recrystallisation afforded a good yield (83%) of an orange-yellow crystalline complex **16**. Elemental analysis and examination of the ^{1}H NMR spectrum suggested that the complex had the partial molecular formula [MoH{C$_5$H$_2$Ph$_4$}{P(OMe)$_3$}(η-C$_5$H$_5$)], indicating that the methyl group bonded to the metal in the starting material **4** had undergone a major transformation. This was confirmed by a single-crystal X-ray diffraction study, the resulting molecular structure being shown in Fig. 3 and selected bond lengths and angles in Table 3.

The molecular structure of complex **16** has a gross geometry similar to that of familiar bent sandwich ML$_2$(η-C$_5$H$_5$)$_2$ species, albeit here the molybdenum is ligated by η^5-C$_5$H$_5$ and η^4-tetraphenylcyclopentadiene ligands as well as a hydride and trimethyl phosphite ligands. The centroid–molybdenum–centroid angle is 30°. The η^4-cyclopentadiene ligand adopts an envelope conformation with a hydrogen being in the *endo* conformation, which lies *anti* to the P(OMe)$_3$ ligand, presumably to limit steric interference between the ligands.

Thus, in the formation of complex **16** the σ-bonded methyl group present in **4** apparently loses two hydrogen atoms and the resulting CH fragment is incorporated into the C$_5$ ring. It is suggested that the first step in this process involves an α-hydrogen-elimination reaction, in which the required vacant co-ordination site is provided by a switch [η^2(4e) ⟶ η^2(2e)] in the bonding mode of the PhC$_2$Ph ligand. The alternative way of generating this site by trimethyl phosphite dissociation does not compete since phosphite dissociation, as measured by exchange with P(OCD$_3$)$_3$, occurs only slowly (100 °C, C$_6$D$_6$, $t_{\frac{1}{2}} \approx 6$ d). The resulting *cis*-alkyne/carbene complex **P** (Scheme 9) can then in principle undergo ‘in-plane’ or ‘perpendicular’ coupling to form either a planar metallacyclobutene **Q** or an η^3-vinylcarbene **R**. There are, of course, known examples of stable alkyne/carbene-, metallacyclobutene- and η^3-vinylcarbene-substituted complexes, and it is interesting that MO calculations on the interrelationship of the possible intermediates in the Dötz reaction, the species [Cr(=CH$_2$)(η^2-HC$_2$H)(CO)$_4$], [Cr(CH$_2$CH=CH)(CO)$_4$] and [Cr(η^3-CHCH=CH$_2$)(CO)$_4$], have shown that in the case of these d^6 systems the preferred pathway is to form an η^3-vinylcarbene directly by perpendicular coupling of the alkyne and carbene ligands. It was also found that a chromacyclobutene is less stable than the corresponding



Scheme 8 L = P(OMe)$_3$. (*i*) CH$_2$=CHMgBr; (*ii*) +P(OMe)$_3$, −HP(OMe)$_3$$^+$; (*iii*) +P(OMe)$_3$

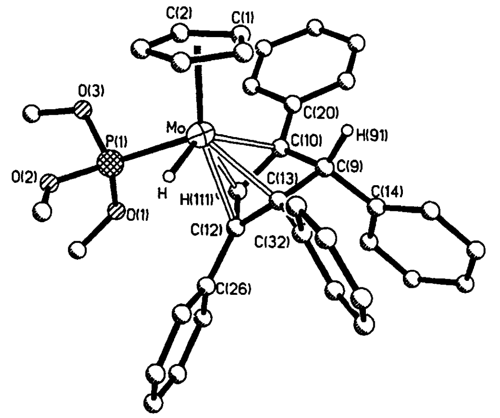


Fig. 3 Molecular structure of complex **16** showing the atom labelling scheme. All phenyl, methyl and cyclopentadienyl hydrogen atoms have been omitted for clarity

Table 3 Selected bond lengths (Å) and angles (°) for complex **16**

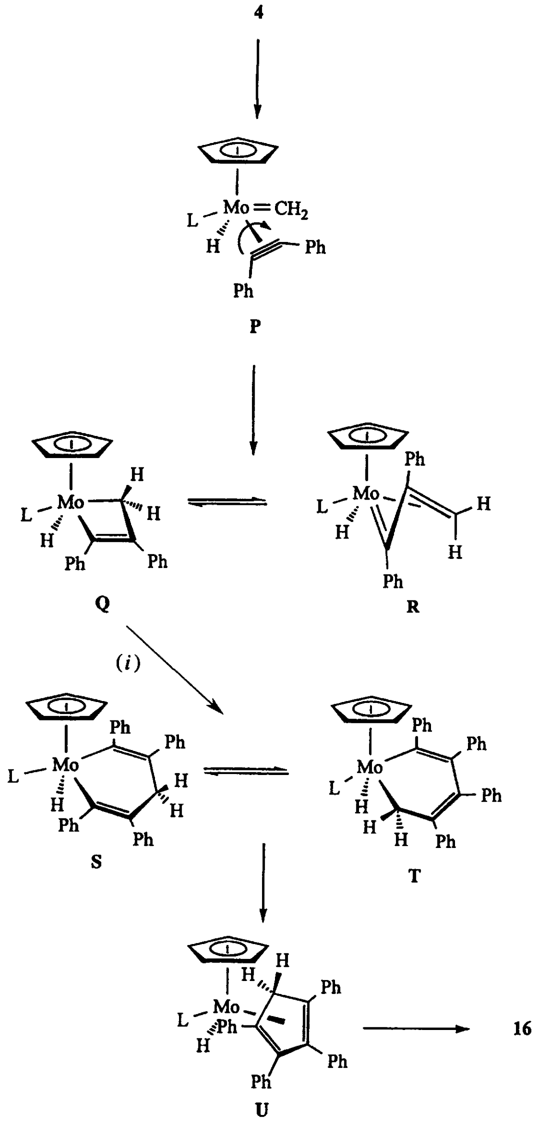
Mo–P	2.366(1)	O(1)–C(6)	1.381(8)
Mo–C(1)	2.316(5)	O(2)–C(7)	1.396(8)
Mo–C(2)	2.289(4)	O(3)–C(8)	1.419(7)
Mo–C(3)	2.284(5)	C(1)–C(2)	1.403(6)
Mo–C(4)	2.317(6)	C(1)–C(5)	1.394(7)
Mo–C(5)	2.342(5)	C(2)–C(3)	1.418(7)
Mo–C(10)	2.377(3)	C(3)–C(4)	1.419(8)
Mo–C(11)	2.275(4)	C(4)–C(5)	1.382(6)
Mo–C(12)	2.248(4)	C(9)–C(10)	1.512(5)
Mo–C(13)	2.240(3)	C(9)–C(13)	1.535(5)
Mo–H	1.589(35)	C(9)–C(14)	1.535(5)
P–O(1)	1.581(4)	C(10)–C(11)	1.401(5)
P–O(2)	1.583(4)	C(11)–C(12)	1.426(5)
P–O(3)	1.604(4)	C(12)–C(13)	1.456(5)
P–Mo–H	78.6(13)	C(10)–C(9)–C(13)	96.3(3)
C(10)–C(9)–C(14)	117.1(3)	C(13)–C(9)–C(14)	113.5(3)
C(10)–C(9)–H(91)	116(2)	C(13)–C(9)–H(91)	110(2)
C(14)–C(9)–H(91)	104(2)	Mo–C(10)–C(9)	91.7(2)
Mo–C(10)–C(11)	68.5(2)	C(9)–C(10)–C(11)	108.3(3)
Mo–C(10)–C(20)	122.3(2)	C(9)–C(10)–C(20)	123.5(3)
C(11)–C(10)–C(20)	125.0(4)	Mo–C(11)–C(10)	76.5(2)
Mo–C(11)–C(12)	70.6(2)	C(10)–C(11)–C(12)	109.3(3)
Mo–C(11)–H(111)	125(2)	C(10)–C(11)–H(111)	119(2)
C(12)–C(11)–H(111)	131(2)	Mo–C(12)–C(11)	72.7(2)
Mo–C(12)–C(13)	70.8(2)	C(11)–C(12)–C(13)	105.1(3)
Mo–C(12)–C(26)	130.2(2)	C(11)–C(12)–C(26)	126.1(4)
C(13)–C(12)–C(26)	127.7(3)	Mo–C(13)–C(9)	96.5(2)
Mo–C(13)–C(12)	71.4(2)	C(9)–C(13)–C(12)	106.7(3)
Mo–C(13)–C(32)	130.7(2)	C(9)–C(13)–C(32)	118.2(3)
C(12)–C(13)–C(32)	123.1(3)		

η^3-vinylcarbene into which it can convert by a reversible folding process.[22] In the case of the d^4 system depicted in Scheme 9, less is known about the energetics of the alkyne–carbene coupling process, however the molybdacyclobutene **Q** could be intercepted by co-ordination of PhC_2Ph, thus providing access to the molybdacyclohexadienes **S** and **T**. These can then undergo a reductive elimination reaction to form the tetraphenylcyclopentadiene-substituted complex **U** before converting under thermodynamic control into the isolated product **16** by a series of reversible β-hydride addition–elimination reactions.

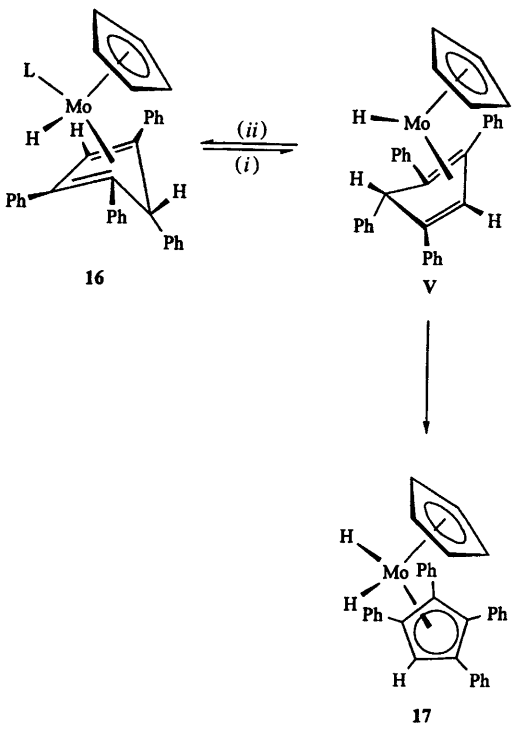
Finally, it was found that when a solution of complex **16** in C_6D_6 was heated in a sealed tube at 100 °C for 3 weeks a new compound **17** was formed (85% yield), which was characterised by elemental analysis and ^1H NMR spectroscopy as the illustrated (Scheme 10) dihydride. When the reaction was followed by recording the ^1H NMR spectrum of a solution of **16** in C_6D_6 contained in an NMR tube it was observed that it followed first-order kinetics ($t_{\frac{1}{2}}$ = 5.7 d), the rearrangement being slowed down by the addition of $P(OMe)_3$. This indicates that the rearrangement reaction involves dissociative loss of phosphite to give **V**, followed by rapid transfer of the allylic *endo*-hydrogen onto the molybdenum centre.

Experimental

The ^1H, ^{13}C-{^1H} and ^{31}P-{^1H} NMR spectra were recorded on JEOL FX200, FX270 and FX400 spectrometers. Data are given for room-temperature measurements unless otherwise stated. Chemical shifts are positive to high frequency of the reference $SiMe_4$ for ^{13}C and ^1H, $BF_3{\cdot}OEt_2$ (external) for B, CCl_3F (external) for ^{19}F and H_3PO_4 (85% external) for ^{31}P. Infrared spectra were recorded on a Nicolet 510P FT-IR spectrometer. All reactions were carried out in Schlenk tubes under atmospheres of dry oxygen-free nitrogen, using freshly distilled and degassed solvents. Column chromatography was performed using BDH alumina, Brockman activity III as the solid support. The cationic complexes [Mo{η^2(4e)-PhC_2Ph}-



Scheme 9 L = $P(OMe)_3$. (*i*) +PhC_2Ph



Scheme 10 L = $P(OMe)_3$. (*i*) −L; (*ii*) +L

$\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ **1**, $[Mo\{\eta^2(4e)\text{-}MeC_2Me\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ **2** and $[Mo\{\eta^2(4e)\text{-}MeC_2Ph\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ **3** were prepared by the published methods.[6]

Preparations

$[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}Me\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ 4. A solution of MgMe(I) (0.7 cm^3, 1 mol dm^{-3} solution in Et_2O) was added at 0 °C to a stirred suspension of complex **1** (0.24 g, 0.35 mmol) in tetrahydrofuran (10 cm^3). The colour changed immediately to dark green. After stirring for 5 min the mixture was filtered through alumina and the solvent removed *in vacuo*. The residue was dissolved in toluene and chromatographed on alumina (10 cm). Elution with toluene–hexane (1:1) gave a green band, which was collected and recrystallised (−20 °C) from pentane to give dark green *crystals* of **4** (0.18 g, 91%) (Found: C, 57.5; H, 5.7. $C_{23}H_{27}MoO_3P$ requires C, 57.7; H, 5.6%). NMR(C_6D_6): ^1H, δ 7.8–7.3 (m, 10 H, Ph), 4.97 (s, 5 H, C_5H_5), 3.23 [d, 9 H, POMe, *J*(HP) 10.8] and 0.57 [d, 3 H, MoMe, *J*(HP) 6.0 Hz]; $^{31}P\text{-}\{^1H\}$ δ 191.4.

$[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}Et\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ 5. A similar reaction between complex **1** (0.24 g, 0.35 mmol) and MgEt(Br) (0.7 cm^3, 1 mol dm^{-3} solution in Et_2O) in tetrahydrofuran (10 cm^3) gave on column chromatography and recrystallisation (−20 °C) dark green *crystals* of **5** (0.12 g, 68%) (Found: C, 58.3; H, 6.0. $C_{24}H_{29}MoO_3P$ requires C, 58.5; H, 6.0%). NMR (C_6D_6): ^1H, δ 7.91–7.09 (m, 10 H, Ph), 5.08 (s, 5 H, C_5H_5), 3.26 [d, 9 H, POMe, *J*(PH) 10.8] and 1.73–1.52 (m, 5 H, MoEt); $^{13}C\text{-}\{^1H\}$, δ 202.8 (C≡C), 201.3 [d, C≡C, *J*(PC) 10.6], 139.5–125.5 (Ph), 90.9 (C_5H_5), 51.9 [d, POMe, *J*(PC) 5.5], 27.3 [d, $MoCH_2CH_3$, *J*(PC) 5.5] and 9.6 [d, $MoCH_2CH_3$, *J*(PC) 13.6 Hz]; $^{31}P\text{-}\{^1H\}$, δ 191.7.

$[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}(CH_2Ph)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ 6. Similarly, reaction of $PhCH_2MgBr$ (2 cm^3, 0.6 mol dm^{-3} in tetrahydrofuran) and complex **1** (0.40 g, 0.6 mmol) afforded after recrystallisation (−20 °C) from hexane dark green *crystals* of **6** (0.19 g, 59%) (Found: C, 62.8; H, 5.8. $C_{29}H_{31}MoO_3P$ requires C, 62.8; H, 5.6%). NMR(C_6D_6): ^1H, δ 7.81–6.92 (m, 15 H, Ph), 4.95 (s, 5 H, C_5H_5), 3.26 [d, 9 H, POMe, *J*(PH) 10.8], 2.92 [dd, 1 H, MoCHH, *J*(HH) 11.4, *J*(PH) 6.6] and 2.53 [dd, 1 H, MoCHH, *J*(HH) 11.4, *J*(PH) 6.0]; $^{13}C\text{-}\{^1H\}$, δ 204.1 (C≡C), 201.1 [d, C≡C, *J*(PC) 10.8], 160.1–121.6 (Ph), 92.4 (C_5H_5), 51.7 [d, POMe, *J*(PC) 5.4] and 21.8 [d, $MoCH_2$, *J*(PC) 13.6 Hz]; $^{31}P\text{-}\{^1H\}$, δ 190.3.

$[Mo\{\eta^2(4e)\text{-}PhC_2Ph\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ 7. A solution of $CH_2(MgI)_2$ (0.36 mmol) in toluene–diethyl ether (1:1, 10 cm^3) was added dropwise to a cooled (0 °C) stirred suspension of complex **1** (0.43 g, 0.64 mmol) in tetrahydrofuran (20 cm^3). Immediately a white precipitate was formed. After stirring overnight at room temperature a green solution was obtained. This was filtered through alumina and the solvent removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (1.0 cm^3) and chromatographed on an alumina column. Elution with CH_2Cl_2–Et_2O (3:1) gave a blue fraction, which was collected. Recrystallisation (−20 °C) from CH_2Cl_2–pentane (1:2) gave blue *crystals* of **7** (0.18 g, 45%) (Found: C, 45.7; H, 4.3. $C_{23}H_{27}BF_2MoO_6P_2$ requires C, 45.6; H, 4.5%). NMR(C_6D_6): ^1H, δ 7.63–7.09 (m, 10 H, Ph), 5.31 [t, 5 H, C_5H_5, *J*(PH) 1.3], 3.54 [vt, 6 H, POMe, *N*(PH) 11.0] and 2.93 [vt, 6 H, POMe, *N*(PH) 12.2 Hz] [where *N*(AX) = *J*(AX) + *J*(AX′)]; $^{13}C\text{-}\{^1H\}$, δ 214.4 (C≡C), 142.1–128.5 (Ph), 95.8 (C_5H_5), 52.6 (POMe) and 52.1 (POMe); $^{11}B\text{-}\{^1H\}$, δ 1.95; ^{19}F, δ −135.93 to −135.54 (m) and −140.96 to −140.71 (m); $^{31}P\text{-}\{^1H\}$, δ 158.0.

$[Mo\{\eta^2(4e)\text{-}MeC_2Me\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ 8. A similar reaction between complex **2** (0.64 g, 1.16 mmol) and $CH_2(MgI)_2$ (0.58 mmol) in tetrahydrofuran (20 cm^3) afforded blue *crystals* of **8** (0.33 g, 58%) (Found: C, 32.5; H, 4.8. $C_{13}H_{23}BF_2MoO_6P_2$ requires C, 32.4; H, 4.8%). NMR (CD_2Cl_2): ^1H, δ 5.52 [t, 5 H, C_5H_5, *J*(PH) 1.1], 3.56 [vt, 6 H, POMe, *N*(PH) 11.0], 2.96 [vt, 6 H, POMe, *N*(PH) 13.0] and 2.87 [t, 6 H, MeC≡C, *J*(HP) 1.0 Hz]; $^{13}C\text{-}\{^1H\}$, δ 206.5 (C≡C), 95.1 (C_5H_5), 50.8 (POMe), 50.6 (POMe) and 21.0 (Me); $^{11}B\text{-}\{^1H\}$, δ −2.95; ^{19}F, δ −137.50 to −137.78 (m) and −142.08 to −142.32 (m); $^{31}P\text{-}\{^1H\}$, δ 166.4.

$[Mo\{\eta^2(4e)\text{-}MeC_2Ph\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ 9. Similarly, reaction of complex **3** (2.5 g, 4.1 mmol) and $CH_2(MgI)_2$ (2.04 mmol) afforded blue *crystals* of **9** (1.18 g, 53%) (Found: C, 39.4; H, 4.6. $C_{18}H_{25}BF_2MoO_6P_2$ requires C, 39.7; H, 4.6%). NMR(CD_2Cl_2): ^1H, δ 7.56–7.42 (m, 5 H, Ph), 5.63 [t, 5 H, C_5H_5, *J*(PH) 1.2], 3.60 [vt, 6 H, POMe, *N*(PH) 11.0], 3.17 [t, 3 H, MeC≡, *J*(PH) 1.2] and 2.98 [vt, 6 H, POMe, *N*(PH) 13.0]; $^{13}C\text{-}\{^1H\}$, δ 212.4, 208.9 (C≡C), 138.9–128.6 (PH), 95.0 (C_5H_5), 51.5 (POMe), 50.9 (POMe) and 21.5 (MeC≡); $^{11}B\text{-}\{^1H\}$, δ −2.90; ^{19}F, δ −137.56 to −137.84 (m) and −142.19 to −142.41 (m); $^{31}P\text{-}\{^1H\}$, δ 164.5.

Reactions of $K[BHBu^s_3]$. (*a*) *With complex* **7**. A solution of complex **7** (0.16 g, 0.26 mmol) in toluene (10 cm^3) was cooled to −78 °C and 1 equivalent of $K[BHBu^s_3]$ (0.264 cm^3, 1 mol dm^{-3} in tetrahydrofuran) was added with stirring. The reaction mixture was allowed to warm to room temperature, and the solvent reduced to 1 cm^3 *in vacuo*. Addition of hexane (10 cm^3) afforded a green powder, which was recrystallised (0 °C) from Et_2O–hexane to give bright green *crystals* of $K[Mo\{=C(Ph)C(H)Ph\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ **10** (0.15 g, 90%). NMR(CD_2Cl_2): ^1H, δ 7.35–6.68 (m, 10 H, Ph), 5.11 (s, 5 H, C_5H_5), 3.44 [d, 3 H, POMe, *J*(PH) 10.5], 3.42–3.35 [m, 1 H, CH(Ph)], 3.40 [d, 3 H, POMe, *J*(PH) 9.9], 3.30 [d, 3 H, POMe, *J*(PH) 13.2] and 3.09 [d, 3 H, POMe, *J*(PH) 12.8]; $^{13}C\text{-}\{^1H\}$, δ 240.8 (Mo=C), 157.9–121.1 (Ph), 91.0 (C_5H_5), 50.3, 49.5, 49.1, 49.0 (POMe) and 31.0 [d, MoCH(Ph), *J*(PC) 10.8]; $^{11}B\text{-}\{^1H\}$, δ −3.0; $^{31}P\text{-}\{^1H\}$, δ 192.6 [d, *J*(AB) 80.5 Hz] and 190.0 (d).

(*b*) *With complex* **9**. Similarly reaction between complex **9** (0.30 g, 0.55 mmol) and $K[BHBu^s_3]$ (0.55 cm^3, 1 mol dm^{-3} in tetrahydrofuran) in tetrahydrofuran (20 cm^3) gave pale green *crystals* of $K[Mo\{=C(Me)C(H)Ph\}\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ **11** (0.25 g, 85%). NMR(CD_2Cl_2): ^1H, δ 7.01–6.56 (m, 5 H, Ph), 4.78 (s, 5 H, C_5H_5), 3.55–3.27 [m, 13 H, MoCH(Ph), POMe] and 2.58 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$ ([$^2H_8$]thf), δ 242.3 [dd, Mo=C, *J*(PC) 20.2, *J*(P′C) 33.3], 162.9 (*ipso*-C of Ph), 128.3–120.2 (Ph), 91.1 (C_5H_5), 50.4 (POMe), 50.0 (POMe), 49.4 [t, MoCH(Ph), *J*(PC) = *J*(P′C) 8.1] and 30.5 [d, Mo=C(Me), *J*(PC) 16.3]; $^{31}P\text{-}\{^1H\}$, δ 196.5 [d, *J*(AB) 72.1 Hz] and 194.5(d).

$[Mo(CO)_2\{\eta^2\text{-}P(OMe)_2OBF_2OP(OMe)_2\}(\eta\text{-}C_5H_5)]$ 12. A solution of complex **10** (0.11 g, 0.16 mmol) in toluene (10 cm^3) was cooled to −78 °C, and 1 equivalent of $HBF_4\cdot Et_2O$ (0.023 cm^3, 0.162 mmol) added. The reaction mixture was allowed to warm to room temperature and filtered through alumina (5 cm). A stream of carbon monoxide was bubbled through the filtrate, causing a change from red to yellow. The solvent was reduced *in vacuo* to 0.5 cm^3. Addition of hexane afforded a yellow powder, which was recrystallised (0 °C) from Et_2O–hexane to give yellow *crystals* of **12** (0.064 g, 82%) (Found: C, 27.4; H, 3.6. $C_{11}H_{17}BF_2MoO_8P_2$ requires C, 27.3; H, 3.6%), IR(CH_2Cl_2): ν(CO) 1992.7 and 1923.3 cm^{-1}. NMR(C_6D_6): ^1H, δ 5.00 (s, 5 H, C_5H_5), 3.48 [vt, 6 H, POMe, *N*(PH) 6.1] and 3.46 [vt, 6 H, POMe, *N*(PH) 5.7 Hz]; $^{13}C\text{-}\{^1H\}$, δ 237.5 (CO), 92.8 (C_5H_5) and 53.2 (POMe); $^{31}P\text{-}\{^1H\}$, δ 153.4.

The supernatant liquid from the crystallisation was reduced to 0.5 cm^3 *in vacuo*, and chromatographed on an alumina column. Elution with hexane gave one fraction, which was

Table 4 Details of crystal structure determinations for complexes **7**, **14** and **16***

	7	**14**	**16**
Empirical formula	$C_{23}H_{27}BF_2MoO_6P_2$	$C_{28}H_{38}MoO_6P_2$	$C_{37}H_{37}MoO_3P$
M	606.2	628.5	656.6
Crystal habit	Blue block	Irregular yellow block	Orange block
Crystal size/mm	0.5 × 0.4 × 0.4	0.3 × 0.4 × 0.5	0.5 × 0.4 × 0.4
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$(no.2)	$P2_1/n$ (no. 14)	$P2_1/n$(no. 14)
a/Å	9.688(4)	15.103(6)	15.209(12)
b/Å	10.788(6)	10.681(3)	10.204(4)
c/Å	12.961(6)	18.437(7)	20.831(13)
α/°	98.13(4)		
β/°	96.17(3)	100.90(3)	104.87(5)
γ/°	102.52(4)		
U/Å^3	1295(1)	2921(2)	3104(3)
Z	2	4	4
D_c/Mg m^{-3}	1.53	1.43	1.41
μ/mm^{-1}	0.66	0.60	0.50
F(000)	616	1304	1360
Scan type	ω–2θ	Wyckoff, ω	ω–2θ
Scan range/ω°	$1.0 + \Delta_{\alpha1\alpha2}$	0.6	$1.0+\Delta_{\alpha1\alpha2}$
Scan speed/° min^{-1} in ω	1.25–14.65	1.5–14.65	1.25–14.65
Check reflections	(4, −3, 7); (7, −1, 1); (1, 2, 8)	(−2, −4, −2); (2, −2, 5); (5, −1, 5)	(6, 0, 0); (0, 4, 0); (0, 0, 4)
% Variation in above	2	3	2
hkl Ranges	0–12, −13 to 13, −16 to 16	0–18, 0 to 13, −22 to 22	0–18, 0–13, −25 to 25
No. reflections collected	5121	5881	3993
No. independent reflections	4613	5135	3484
R_{int}	0.015	0.011	0.016
N_{obs}	4036	3832	4854
Observation criterion, $I > n\sigma(I)$	3	2	2.5
No. azimuthal scan data	—	350	—
Minimum, maximum transmission	—	0.106, 0.137	—
Least-square variables	322	367	409
g	0.0005	0.0006	0.0005
R, R'	0.0273, 0.0375	0.0400, 0.0468	0.0346, 0.0466
Goodness of fit, S	1.29	1.28	1.62
E_{max}, E_{min}/e Å^{-3}	0.43, −0.33	0.37, −0.47	0.52, −0.15

* $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)$; $S = [\Sigma w\Delta^2/(N_{obs} - N_{var})]$; $\Delta = F_o - F_c$.

identified as *trans*-stilbene by comparison of its NMR spectra (^1H, ^{13}C) with those of a pure sample.

[Mo{P(OMe)$_3$}$_2${η^2-P(OMe)$_2$OBF$_2$OP(OMe)$_2$}(η-C$_5$H$_5$)] 13. The adduct HBF$_4$·Et$_2$O (0.112 cm^3, 0.80 mmol) and P(OMe)$_3$ (0.23 cm^3, 2.00 mmol) were added to a stirred (−78 °C) solution of complex **10** (0.46 g, 0.70 mmol) in tetrahydrofuran (20 cm^3). The reaction mixture was allowed to warm to room temperature, and the solvent reduced to 2 cm^3 *in vacuo*. Hexane (5 cm^3) was added, and the yellow solution was cooled to −20 °C overnight affording a yellow solid, which was recrystallised from tetrahydrofuran–hexane to give yellow *crystals* of **13** (0.33 g, 69%) (Found: C, 26.4; H, 5.2. $C_{15}H_{35}BF_2MoO_{12}P_4$ requires C, 26.6; H, 5.2%). NMR(C_6D_6): ^1H, δ 5.28 (s, 5 H, C_5H_5), 3.74 [vt, 6 H, POMe, *N*(PH) 10.6], 3.70 [vt, 6 H, POMe, *N*(PH) 10.6] and 3.42 [vt, 18 H, POMe, *N*(PH) 5.4]; ^{13}C-{^1H}, δ 92.7 (C_5H_5), 52.5 [vt, POMe, *N*(PC) 4], 52.2 [vt, POMe, *N*(PC) 4.8] and 51.9 [vt, POMe, *N*(PC) 5.5 Hz]; ^{31}P-{^1H}, δ 195.8 (A part of AA′XX′ system) and 173.3 (br, X part of AA′XX′ system).

[Mo{η^3-C(Ph)=C(Ph)CH$_2$CH=CH$_2$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] 14. To a suspension of complex **1** (0.23 g, 0.34 mmol) in tetrahydrofuran (10 cm^3) was added (0 °C) a solution of CH$_2$=CHCH$_2$MgBr (0.68 cm^3, 1 mol dm^{-3} in Et$_2$O). After stirring for 5 min at room temperature P(OMe)$_3$ (0.06 cm^3, 0.5 mmol) was added and the solution filtered through alumina. The solvent was removed *in vacuo*, the residue dissolved in Et$_2$O and chromatographed on alumina (10 cm). Elution with Et$_2$O–hexane (1:1) gave a yellow band, which on recrystallisation (−20 °C) from Et$_2$O–hexane gave yellow *crystals* of **14** (0.26 g, 42%). NMR(C_6D_6): ^1H, δ 7.31–6.96 (m, 10 H, Ph), 5.03 [d, 5 H, C_5H_5), *J*(PH) 3.1], 4.33–4.22 [m, 1 H, =C(H)], 3.29 [d, 9 H, POMe, *J*(PH) 10.3], 3.24 [d, 9 H, POMe, *J*(PH) 9.5] and 2.49–2.19 (m, 2 H, CH$_2$); the signals for the CH=CH$_2$ protons were obscured by other signals; ^{31}P-{^1H}, δ 194.3 [d, *J*(AB) 70.5 Hz] and 183.3 (d).

[Mo(η^3-C$_3$Ph$_2$Me){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] 15. Similarly reaction (0 °C) of complex **1** (0.23 g, 0.34 mmol) with CH$_2$=CHMgBr (0.70 cm^3, 1 mol dm^{-3} in tetrahydrofuran), followed by addition at room temperature of P(OMe)$_3$ (0.06 cm^3, 0.5 mmol) gave on column chromatography on alumina and elution with Et$_2$O–hexane (1:1) a bright yellow band, which on collection and recrystallisation (−30°) from Et$_2$O–hexane afforded bright yellow *crystals* of **15** (0.19 g, 71%) (Found: C, 52.7; H, 5.2. $C_{27}H_{36}MoO_6P_2$ requires C, 52.8; H, 5.2%). NMR(C_6D_6): ^1H, δ 7.5–6.8 (m, 10 H, Ph), 4.62 [t, 5 H, C_5H_5, *J*(HP) 1.4], 3.24 [t, 18 H, POMe, *N*(PH) 10.5] and 2.36 (s, 3 H, Me); ^{13}C-{^1H}, 144.5 (Ph), 129.9 [d, Ph, *J*(PC) 158.4], 128.0 [d, Ph, *J*(PC) 149.6], 124.0 (Ph), 123.6 [d, Ph, *J*(PC) 159.5], 85.6 [d, C_5H_5, *J*(PC) 176.0], 50.95 [qd, POMe, *J*(CP) 143.3, 3.3], 33.4 [t, CPh, *J*(CP) 12.4], 19.0 [t, CMe, *J*(CP) 3.3] and 11.8 [q, CMe, *J*(CP) 128.0 Hz]; ^{31}P-{^1H}, δ 196.1.

Thermolysis of 4. Complex **4** (0.67 g, 1.4 mmol) together with diphenylacetylene (2.5 g, 14 mmol) was placed in a sealable Pyrex tube. The tube was evacuated under high vacuum, benzene (25 cm^3) condensed (liquid N$_2$) in and the tube was sealed. It was heated at 78 °C for 12 h, the contents changing from green to yellow. The tube was opened and the volatile material removed *in vacuo*. The residue was dissolved in toluene (4 cm^3) and chromatographed on an alumina column (25 × 15 cm). Elution with Et$_2$O–hexane (1:2) afforded a yellow band, which on recrystallisation (0 °C) from tetrahydrofuran–hexane gave orange-yellow *crystals* of [MoH(η^4-$C_5H_2Ph_4$){P(OMe)$_3$}(η-C_5H_5)] **16** (0.51 g, 83%) (Found: C, 67.5; H, 5.7. $C_{37}H_{37}MoO_3P$ requires C, 67.7; H, 5.6%). NMR(CD_2Cl_2): ^1H, δ 7.30–6.71 (m, 20 H, Ph), 6.61 [dd, 1 H, CH=C, *J*(HP) 9.4, *J*(HH) 1.2], 4.58 [d, 5 H, C_5H_5, *J*(HP) 1.3], 4.54 (br s, 1 H, C*H*Ph), 3.28 [d, 9 H, POMe, *J*(HP) 11.1] and −7.15 [d, 1 H, MoH, *J*(HP) 38.9 Hz].

[MoH$_2$(η^5-C_5HPh_4)(η-C_5H_5)] 17. A sample of complex **16** (0.10 g, 0.3 mmol) was placed in a sealable Pyrex tube, evacuated and C_6D_6 (5 cm^3) condensed into the tube before sealing. The tube and contents were heated at 100 °C for 3 weeks. The volatile material was removed *in vacuo* and the residue chromatographed on alumina. Elution with toluene gave a yellow band, which on recrystallisation (−50 °C) from toluene gave yellow *crystals* of **17** (0.09 g, 85%) (Found: C, 76.9; H, 5.3. $C_{34}H_{28}Mo$ requires C, 76.7; H, 5.3%). NMR(C_6D_6): ^1H, δ 7.67–6.75 (m, 20 H, Ph), 5.29 (s, 1 H, C_5HPh_4), 4.26 (s, 5 H, C_5H_5) and −6.53 (s, 2 H, MoH).

Crystallography

Many of the details of the structure analyses carried out on **7**, **14** and **16** are listed in Table 4. X-Ray diffraction measurements were made using Siemens four-circle P3m diffractometers on single crystals mounted in thin-walled glass capillaries under nitrogen at room temperature (291 K). Graphite-monochromatised Mo-Kα radiation (λ = 0.710 73 Å) was used as the X-ray source. Cell dimensions for each analysis were determined from 40 (for **14**) or 25 (for **7** and **16**) centred reflections and the reciprocal lattice symmetry and cell axis lengths were checked by partial-rotation photographs about the unit-cell axis.

For each structure analysis intensity data were collected for unique sections of reciprocal space with $4 \leqslant 2\theta \leqslant 50°$ at variable scan speeds, those speeds being used on a pre-scan. Reflections in the range $40 \leqslant 2\theta \leqslant 50°$ with pre-scan intensity below a low threshold for **16** were not recorded. Corrections were applied for Lorentz-polarisation effects, long-term intensity fluctuations (on the basis of the intensities of three check reflections repeatedly measured during data collection), and, for **14** only, X-ray absorption on the basis of azimuthal scan data. The structures were solved by heavy-atom (Patterson and Fourier-difference) methods, and refined by least-squares against *F*. Reflection weights were $w = 1/[\sigma_c^2(F_o) + gF_o^2]$ where $\sigma_c^2(F_o)$ is the variance in F_o arising from counting statistics and *g* (see Table 4) was chosen to give minimum variation in the average value of *S* as a function of F_o. All phenyl, methyl and cyclopentadienyl hydrogen atoms were constrained to ideal geometries (C–H 0.96 Å). The hydride and cyclopentadiene ligand hydrogens in **16** and the pentadienyl ligand hydrogens in **14** were refined without positional constraints. All hydrogen atoms were assigned isotropic displacement parameters.

Final difference syntheses showed no chemically significant features, the largest maxima being close to the metal atoms. Refinements converged (mean shift/e.s.d. $\ll$ 0.1) smoothly to the residuals given in Table 4. All structure-analysis calculations were made with programs written by Sheldrick[23] as implemented on Siemens structure-determination systems. Complex neutral-atom scattering factors were taken from ref. 24.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/130.

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