Reactions of Co-ordinated Ligands. Part 41.[1] Synthesis and Reactions of Cationic Functionalised Alkyne Molybdenum Complexes; Formation of Carbyne and Vinylidene Complexes and Crystal Structure of $[Mo(C{=}CHPh)Br\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ *

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Treatment of a solution of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in CH_2Cl_2 with $AgBF_4$ in the presence of the substituted alkynes RC_2X (R = Bu^t or Ph, X = SMe or Br) gives the cations $[Mo(\eta^2\text{-}RC_2X)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$, which react with $P(OMe)_3$ to form the highly coloured monoalkyne cations $[Mo(\eta^2\text{-}RC_2X)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$. Reaction of the thiosubstituted cations with $K[BHBu^s_3]$ or $Li[CuMe_2]$ affords the η^2-vinyl complexes $[Mo\{{=}C(R)C(SMe)R'\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (R = Bu^t or Ph, R′ = H or Me), which react with $AgBF_4$ in CH_2Cl_2 to form the alkyne cations $[Mo(\eta^2\text{-}RC_2R')\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$. Treatment of the bromo-substituted cation $[Mo(\eta^2\text{-}Bu^tC_2Br)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ with $K[BHBu^s_3]$ gives the carbyne $[Mo({\equiv}CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, whereas the phenyl-substituted cation affords a mixture of $[Mo({\equiv}CCH_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and the vinylidene complex $[Mo(C{=}CHPh)Br\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, the latter being identified by single-crystal *X*-ray crystallography. The molecule has a typical $ML_4(\eta\text{-}C_5H_5)$ 'piano-stool' geometry, the Mo=C=CHPh moiety adopting an essentially linear arrangement [Mo–C(7)–C(8) 177.9(5)°] with C(7)–C(8) and Mo–C(7) bond lengths of 1.327(7) Å and 1.917(5) Å respectively. Treatment of the bromo-vinylidene complex with $K[BHBu^s_3]$ or $Li[CuPh_2]$ affords the carbynes $[Mo({\equiv}CCH_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and $[Mo({\equiv}CCPh_2)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$. Reaction of $[Mo(\eta^2\text{-}PhC_2Br)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ with $Li[CuPh_2]$ affords the η^2-vinyl complex $[Mo\{{=}C(Br)CPh_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, which reacts with $Li[CuMe_2]$ or $Li[CuPh_2]$ to give $[Mo\{{=}C(R)CPh_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (R = Me or Ph). The bromo-vinylidene complex also reacts with PEt_3 to give $[Mo(C{=}CHPh)Br\{P(OMe)_3\}(PEt_3)(\eta\text{-}C_5H_5)]$, which in turn reacts with $K[BHBu^s_3]$ to give a carbyne complex.

In earlier papers[2–4] we have developed the chemistry of cationic molybdenum complexes which have the general formula $[Mo(\eta^2\text{-}RC_2R')\{P(OMe)_3\}_2(\eta^5\text{-}C_mH_n)][BF_4]$ (m = n = 5; m = 9, n = 7) and where the alkyne functions as a four-electron donor. Our observation[5] that the η^2-vinyl complex $[Mo\{{=}C(SiMe_3)CH_2\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ obtained by the reaction of $K[BHBu^s_3]$ with $[Mo(\eta^2\text{-}Me_3SiC_2H)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$, readily rearranged to the carbyne $[Mo({\equiv}CCH_2SiMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ encouraged us to investigate the synthesis and reactions of other cationic complexes where the alkyne carries potentially reactive functional groups. One of the previously most extensively studied substituents in alkyne co-ordination chemistry is the carbomethoxy group, reactions of $C_2(CO_2Me)_2$- and PhC_2CO_2Me-substituted complexes having played an important role in the development of η-cyclopentadienyl cobalt chemistry.[6,7] Previous studies[8–10] have also focused on bis(methylthio)ethyne as a ligand leading to the characterisation of $[Cr(\eta^2\text{-}MeSC_2SMe)_2(CO)_2]$ and $[M(\eta^2\text{-}MeSC_2SMe)_3(CO)]$ (M = Mo or W). Bis(methylthio)ethyne also reacts with $[Co_2(CO)_8]$, as do other alkynes containing the functional groups CO_2H, CO_2Me, CH_2OH, $CH{=}CMe_2$, CH_2Br, CH_2NEt, and PPh_2,[11–13] to form the dinuclear complexes $[Co_2(\mu\text{-}RC_2R')(CO)_6]$ whose chemistry has not been developed. In many other reactions of alkynylphosphines cleavage of the carbon–phosphorus bond also occurs.[14] In this paper the chemistry of the cations $[Mo(\eta^2\text{-}RC_2X)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (R = Ph or Bu^t, X = Br or SMe) is explored.[15]

Results and Discussion

The addition of silver tetrafluoroborate to a solution of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and Bu^tC_2SMe or PhC_2SMe in CH_2Cl_2 results in the slow (24 h) deposition of a silver mirror and the formation of the yellow crystalline bis(alkyne)-substituted cations (**1**) and (**2**) (Scheme 1). A similar reaction using 1-bromo-3,3-dimethylbut-1-yne (Bu^tC_2Br) or 1-bromo-2-phenylethyne (PhC_2Br) afforded the bromo-substituted alkyne cations (**3**) and (**4**), again as stable yellow crystalline materials, which are formed as mixtures of two rotational isomers. Addition of an excess of trimethyl phosphite to methylene chloride solutions of (**1**)—(**4**) resulted in the displacement of carbon monoxide and one alkyne molecule leading to the formation of the monoalkyne bis(trimethyl phosphite) cations (**5**)—(**8**). These were isolated as purple to blue air-stable crystalline materials. The $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of (**5**)—(**8**) showed low-field alkyne contact carbon resonances characteristic[16] of four-electron donor alkynes. Previous *X*-ray crystallographic studies[5,17] on related bis(trimethyl phosphite)-substituted cations have shown that in the solid state the co-ordinated alkyne adopts a conformation in which the C–C bond lies parallel to one of the Mo–P vectors. In solution the corresponding but-2-yne cations[3,17] can also undergo a low-energy rotational (2π) process [(**A**) $\rightleftharpoons$ (**B**) $\rightleftharpoons$ (**C**) $\rightleftharpoons$ (**D**), Scheme 1] about an axis through the metal centre and perpendicular to the alkyne

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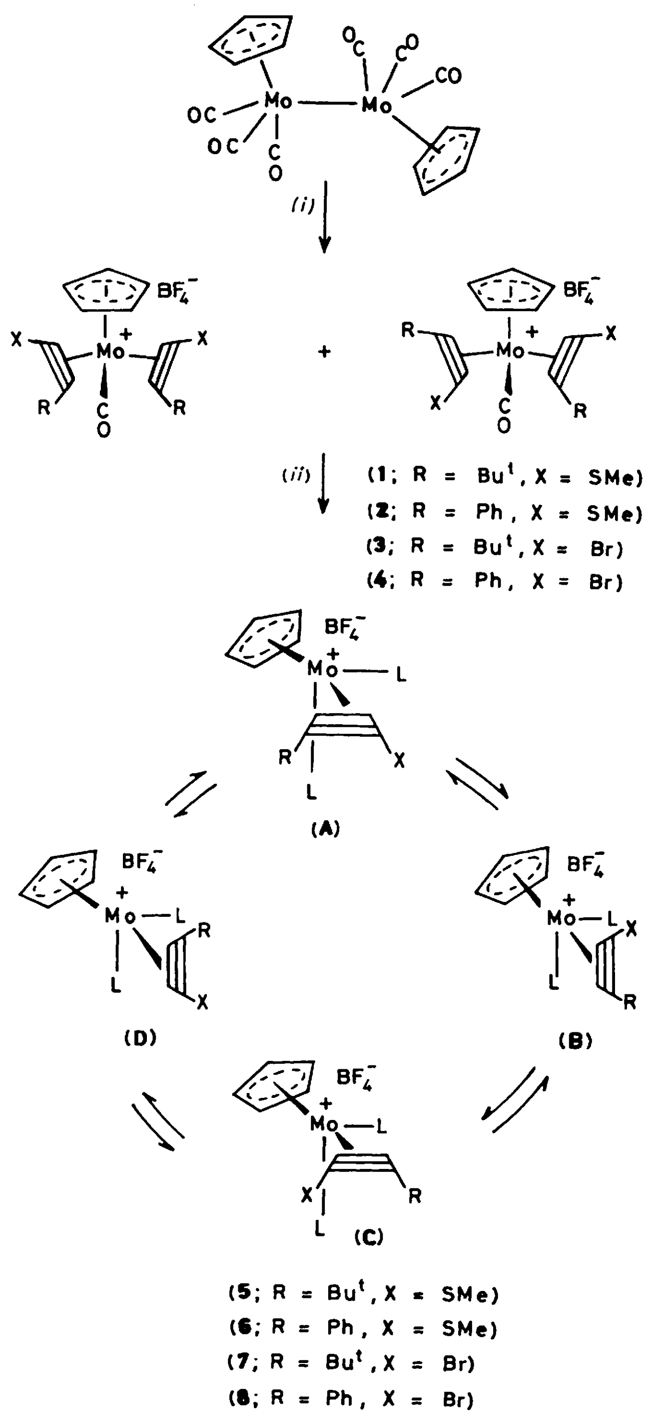
* Bromo(η-cyclopentadienyl)(phenylvinylidene)bis(trimethyl phosphite)molybdenum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Non-S.I. unit employed: cal = 4.184 J.



Scheme 1. L = $P(OMe)_3$. (*i*) +$AgBF_4$ − Ag^0, CH_2Cl_2; (*ii*) +$P(OMe)_3$

C–C bond, whereas the co-ordinated 3,3-dimethylbut-1-yne ligand in $[Mo(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ only undergoes a 'windscreen-wiper' motion [(**A**) $\rightleftharpoons$ (**D**), Scheme 1], the unsubstituted end of the alkyne remaining adjacent to a phosphite ligand.[4,17] The complexes (**5**)—(**8**) clearly have related structures. The Bu^t-substituted cations (**5**) and (**7**) undergo a windscreen-wiper motion [(**A**) $\rightleftharpoons$ (**D**)], whereas, the room-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of the phenyl-substituted cations (**6**) and (**8**) exhibit similar *J*(CP) couplings to both alkyne contact carbons implying that in these molecules complete rotation of the alkyne can occur.

With the synthesis and characterisation of the cations (**5**)—(**8**) it was possible to begin to explore their reactivity towards nucleophilic reagents. Addition (−78 °C) of the hydride anion donor $K[BHBu^s_3]$ to a suspension of (**5**) or (**6**) led to a rapid colour change and chromatographic work-up afforded the orange crystalline complexes (**9**) and (**10**) (Scheme 2). Examination of their ^1H, ^{13}C, and ^{31}P n.m.r. spectra (see Experimental section) showed that these molecules are η^2-vinyl complexes[4] where the Bu^t or Ph substituent is bonded to the C_α or carbenoid carbon. Thus, 'H^-' has been formally delivered, either under kinetic or thermodynamic control, to the alkyne carbon carrying the thiomethyl substituent. A η^2-vinyl complex (**11**) was also formed on reaction of (**6**) with $Li[CuMe_2]$ in thf, the corresponding reaction with (**5**) leading to decomposition. These thiomethyl-substituted η^2-vinyl complexes reacted with silver tetrafluoroborate in CH_2Cl_2 to give a precipitate of AgSMe and the purple crystalline cationic alkyne complexes illustrated in Scheme 2. The isolobal relationship[18] CR $\overset{}{\underset{o}{\longleftrightarrow}}$ $MoL_2(\eta\text{-}C_5H_5)$ provides a rationale for these reactions where, for example, the transformation of (**9**) into $[Mo(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ by reaction with $AgBF_4$ parallels the conversion of a 3-thiomethyl-substituted cyclopropene into a cyclopropenium cation. Thus, from a synthetic standpoint this sequence of reactions allows for the replacement of an SMe substituent by either a hydrogen or more interestingly by an alkyl group. It should be noted, however, that the stereochemistry at C_β is not defined by the n.m.r. data, but it is likely[4] that the initially formed kinetically controlled product undergoes a windscreen-wiper motion to give the thermodynamically controlled product.

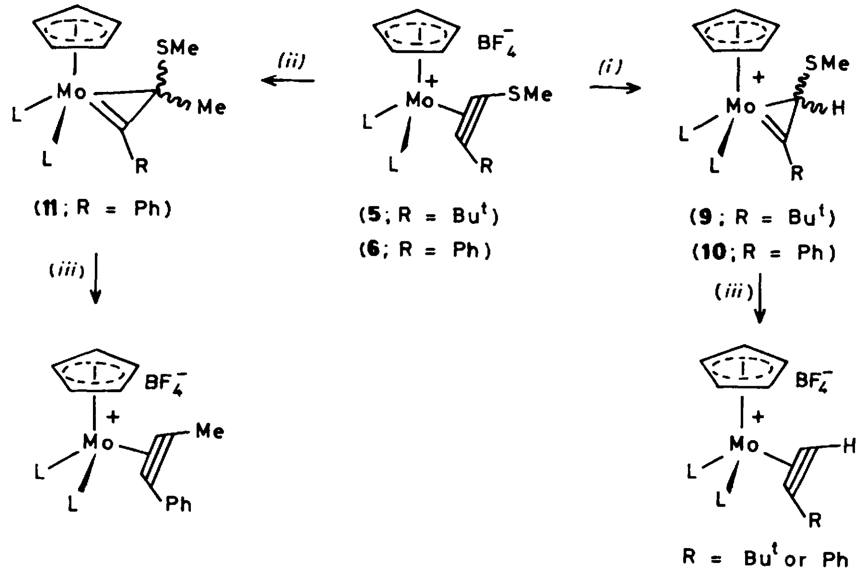
The reactions of the bromo-substituted cations (**7**) and (**8**) proved to be more interesting. Reaction of $Li[CuMe_2]$ with (**7**) led to a type of reaction which had been observed previously,[4,19] with attack at the molybdenum centre resulting in the formation of the purple crystalline $[Mo(\eta^2\text{-}Bu^tC_2Br)(Me)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (**12**). This was identified by analysis and n.m.r. spectroscopy. In contrast, treatment of (**7**) with $K[BHBu^s_3]$ gave only the yellow carbyne complex $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, which had previously[5,20] been obtained by thermolysis of the σ-vinyl species $[Mo\{\sigma\text{-}(E)\text{-}CH{=}CHBu^t\}\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)]$.[2] This formation of a carbyne complex was initially difficult to understand, however, a study[15] of the related reaction between $K[BHBu^s_3]$ and (**8**) provided valuable insights.

Column chromatography of the reaction mixture obtained from (**8**) and $K[BHBu^s_3]$ gave a low yield of a yellow crystalline material, which was identified by analysis and n.m.r. spectroscopy as the benzyl-substituted carbyne $[Mo(\equiv CCH_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**13**). Further elution of the column gave the major product (**14**), which was isolated as an orange crystalline material. Elemental analysis showed that (**14**) contained bromine, the figures being compatible with the empirical formula $[Mo(PhC_2BrH)\{P(OMe)_3\}_2(C_5H_5)]$. In addition the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum exhibited a lowfield resonance at 336.5 p.p.m. characteristic of Mo=C or Mo≡C carbon. A single-crystal *X*-ray diffraction study defined the molecular geometry shown in the Figure, selected bond lengths and angles being listed in Table 1.

The molecule is a vinylidene complex which adopts a typical $ML_4(\eta\text{-}C_5H_5)$ 'piano-stool' geometry. The vinylidene moiety Mo=C=CHPh is essentially linear [Mo–C(7)–C(8) 177.9(5)°] with a C(7)–C(8) bond of 1.327(7) Å; the Mo–C(7) bond length is 1.917(5) Å. This is intermediate between the Mo≡C triple bonds found in $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ [1.796(2) Å] and $[Mo(\equiv CCH_2Bu^t)H\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ [1.798(2) Å][5,21] and the formal Mo=C double bonds observed in the carbene complexes $[Mo\{C(OEt)Ph\}(CO)_2(SePh_3)(\eta\text{-}C_5H_5)]$ [2.062(11) Å][22] and $[Mo\{=C(CH_2Bu^t)P(O)\text{-}$

Table 1. Selected bond lengths (Å) and angles (°) for (**14**)

Mo–Br	2.651(1)	Mo–P(1)	2.462(2)	O(4a)–C(4)	1.448(12)	O(4b)–C(4)	1.396(21)
Mo–P(2)	2.463(2)	Mo–C(7)	1.917(5)	O(5)–C(5)	1.454(9)	O(6a)–C(6)	1.361(14)
Mo–C(15)	2.417(7)	Mo–C(16)	2.338(7)	O(6b)–C(6)	1.388(16)	C(7)–C(8)	1.327(7)
Mo–C(17)	2.250(7)	Mo–C(18)	2.271(8)	C(8)–H(8)	0.905(59)	C(8)–C(9)	1.465(8)
Mo–C(19)	2.386(7)	P(1)–O(1)	1.593(4)	C(9)–C(10)	1.409(7)	C(9)–C(14)	1.390(8)
P(1)–O(2)	1.604(5)	P(1)–O(3)	1.596(4)	C(10)–C(11)	1.375(9)	C(11)–C(12)	1.377(10)
P(2)–O(4a)	1.538(7)	P(2)–O(4b)	1.695(18)	C(12)–C(13)	1.377(9)	C(13)–C(14)	1.385(8)
P(2)–O(5)	1.569(5)	P(2)–O(6a)	1.650(7)	C(15)–C(16)	1.379(10)	C(15)–C(19)	1.416(11)
P(2)–O(6b)	1.578(14)	O(1)–C(1)	1.395(9)	C(16)–C(17)	1.430(10)	C(17)–C(18)	1.433(11)
O(2)–C(2)	1.424(7)	O(3)–C(3)	1.438(10)	C(18)–C(19)	1.418(9)		
Br–Mo–P(1)	82.0(1)	Br–Mo–P(2)	79.7(1)	O(1)–P(1)–O(3)	98.5(3)	O(2)–P(1)–O(3)	104.3(2)
P(1)–Mo–P(2)	142.7(1)	Br–Mo–C(7)	113.9(2)	Mo–P(2)–O(4a)	123.8(3)	Mo–P(2)–O(4b)	113.0(7)
P(1)–Mo–C(7)	79.1(2)	P(2)–Mo–C(7)	79.2(2)	Mo–P(2)–O(5)	112.6(2)	O(4a)–P(2)–O(5)	106.1(3)
Br–Mo–C(15)	90.0(2)	P(1)–Mo–C(15)	106.0(2)	O(4b)–P(2)–O(5)	87.3(6)	Mo–P(2)–O(6a)	113.8(3)
P(2)–Mo–C(15)	106.2(2)	C(7)–Mo–C(15)	156.1(2)	O(4a)–P(2)–O(6a)	100.9(4)	O(5)–P(2)–O(6a)	95.3(4)
Br–Mo–C(16)	106.1(2)	P(1)–Mo–C(16)	79.1(2)	Mo–P(2)–O(6b)	126.7(6)	O(4b)–P(2)–O(6b)	90.7(8)
P(2)–Mo–C(16)	137.3(2)	C(7)–Mo–C(16)	130.6(2)	O(5)–P(2)–O(6b)	115.6(6)	P(1)–O(1)–C(1)	123.2(4)
C(15)–Mo–C(16)	33.7(2)	Br–Mo–C(17)	142.3(2)	P(1)–O(2)–C(2)	122.8(4)	P(1)–O(3)–C(3)	120.6(4)
P(1)–Mo–C(17)	87.6(2)	P(2)–Mo–C(17)	125.7(2)	P(2)–O(4a)–C(4)	127.2(6)	P(2)–O(4b)–C(4)	119.6(11)
C(7)–Mo–C(17)	99.2(2)	C(15)–Mo–C(17)	58.4(2)	P(2)–O(5)–C(5)	122.3(4)	P(2)–O(6a)–C(6)	129.3(7)
C(16)–Mo–C(17)	36.3(2)	Br–Mo–C(18)	142.2(2)	P(2)–O(6b)–C(6)	133.3(11)	O(4a)–C(4)–O(4b)	35.6(8)
P(1)–Mo–C(18)	124.0(2)	P(2)–Mo–C(18)	89.1(2)	O(6a)–C(6)–O(6b)	49.5(8)	O(6a)–H(6c)–O(6b)	95.8(19)
C(7)–Mo–C(18)	98.9(2)	C(15)–Mo–C(18)	58.6(2)	O(6a)–H(6c)–C(6)	97.3(8)	O(6b)–H(6c)–C(6)	113.0(16)
C(16)–Mo–C(18)	60.1(3)	C(17)–Mo–C(18)	36.9(3)	Mo–C(7)–C(8)	177.9(5)	C(7)–C(8)–H(8)	119.3(33)
Br–Mo–C(19)	106.9(2)	P(1)–Mo–C(19)	136.6(2)	C(7)–C(8)–C(9)	127.2(5)	H(8)–C(8)–C(9)	113.5(32)
P(2)–Mo–C(19)	80.0(2)	C(7)–Mo–C(19)	129.4(2)	C(8)–C(9)–C(10)	120.5(5)	C(8)–C(9)–C(14)	122.3(5)
C(15)–Mo–C(19)	34.3(3)	C(16)–Mo–C(19)	57.6(3)	C(10)–C(9)–C(14)	117.1(5)	C(9)–C(10)–C(11)	120.9(6)
C(17)–Mo–C(19)	59.2(3)	C(18)–Mo–C(19)	35.3(2)	C(10)–C(11)–C(12)	120.8(6)	C(11)–C(12)–C(13)	119.3(6)
Mo–P(1)–O(1)	116.9(2)	Mo–P(1)–O(2)	121.3(2)	C(12)–C(13)–C(14)	120.4(6)	C(9)–C(14)–C(13)	121.4(5)
O(1)–P(1)–O(2)	98.2(2)	Mo–P(1)–O(3)	114.2(2)				



Scheme 2. L = P(OMe)$_3$. (*i*) K[BHBu$^s_3$], thf, −78 °C; (*ii*) Li[CuMe$_2$], thf, −78 °C; (*iii*) AgBF$_4$, CH$_2$Cl$_2$

(OMe)$_2$}{P(OMe)$_3$}(η-C$_5$H$_5$)] [2.006(4) Å].[23] It is, however, considerably longer than the Mo=C bond found in the dicyanovinylidene complex [Mo{C=C(CN)$_2$}Cl{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] [1.83(1) Å].[24] Calculations by Kostić and Fenske[25] suggest that the metal–carbon bond order in vinylidene complexes lies between two and three. The dihedral angle between the plane of the cylopentadienyl ring and the plane of the vinylidene atoms C(7)–C(8) and the phenyl *i*-carbon C(9) is 90.4°. Although extended-Hückel molecular orbital calculations[26] for the ML$_3$(η-C$_5$H$_5$)-type vinylidene cation [Fe(C=CH$_2$)(CO)$_2$(η-C$_5$H$_5$)]$^+$ suggest that there is a preference of the vinylidene moiety for an orientation in which the substituents on the β-carbon atom are bisected by a molecular mirror plane rather than coincident with it, the barrier to solution is computed to be only 3.6 kcal mol^{-1}, suggesting that this preference is easily overridden by steric effects. We would expect this preference to be even smaller in ML$_4$(η-C$_5$H$_5$) species. The phosphite ligands are symmetrically bound to the

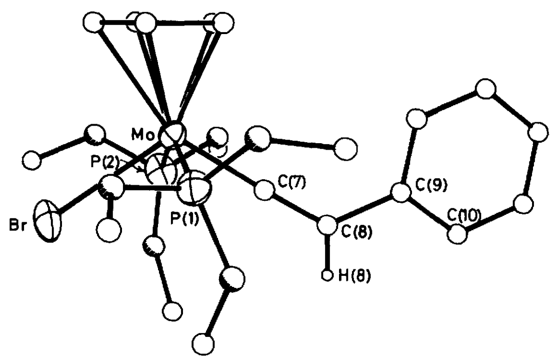
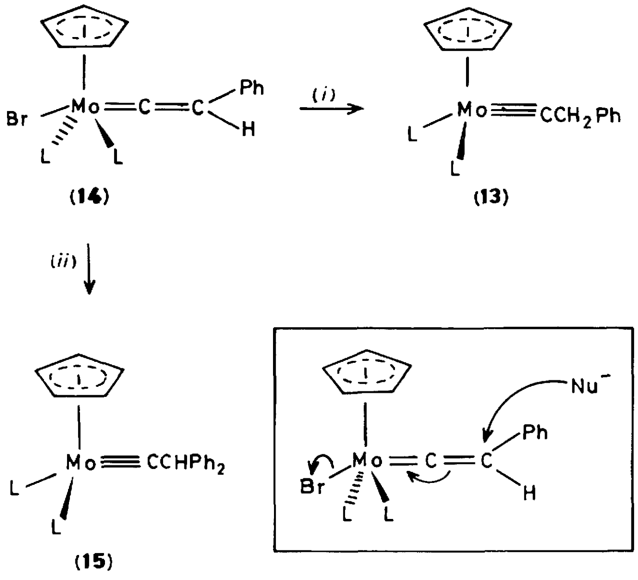


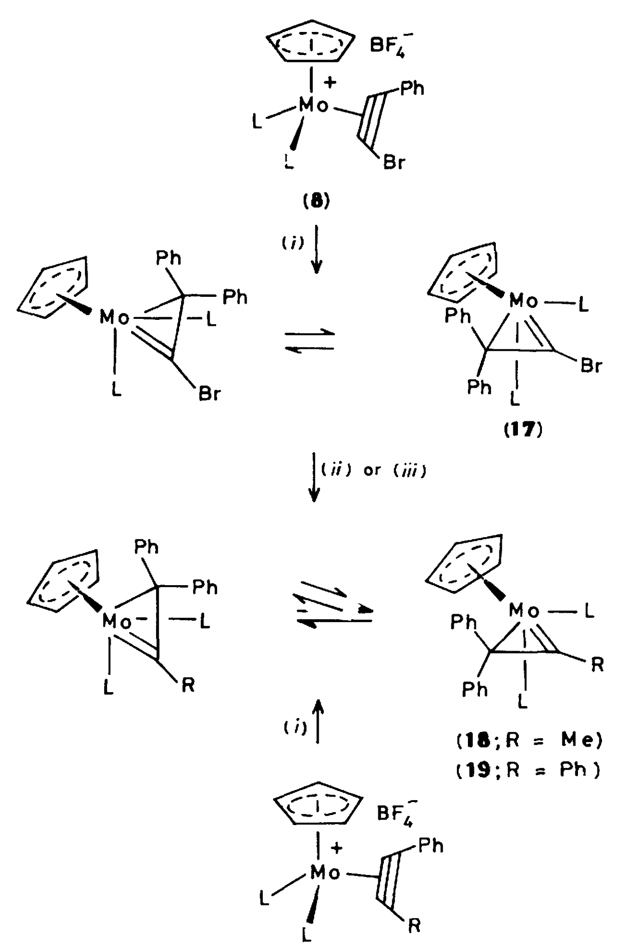
Figure. Molecular structure of [Mo(C=CHPh)Br{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] (**14**) with phenyl, cyclopentadienyl, and methyl group hydrogens omitted for clarity. Only the majority site is shown for the disordered methoxy groups attached to P(2)



Scheme 3. L = P(OMe)$_3$. (*i*) K[BHBu$^s_3$]; (*ii*) Li[CuPh$_2$]

metal, although there is no crystallographic mirror plane through the molecule. The Mo–P bond lengths are essentially equal [Mo–P(1) 2.462(2), Mo–P(2) 2.463(2) Å]. The cisoid interligand angles also show the pseudo-symmetry: Br–Mo–P(1) 82.0(1), Br–Mo–P(2) 79.7(1), C(7)–Mo–P(1) 79.1(2), and C(7)–Mo–P(2) 79.2(2)°. The transoid angles show considerable variation being 142.7(1)° between the phosphites and 113.9(2)° for Br–Mo–C(7).

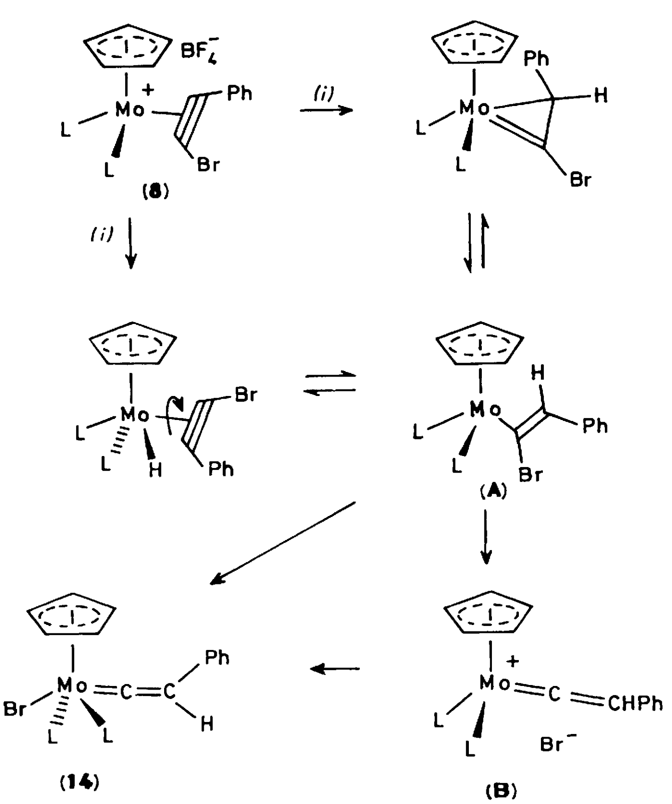
When the bromo-vinylidene complex (**14**) was reacted with K[BHBu$^s_3$] the benzyl carbyne complex (**13**) was formed in good yield. Moreover, reaction of (**14**) with Li[CuPh$_2$] gave the diphenyl-substituted carbyne (**15**) isolated as yellow crystals and identified by analysis and n.m.r. spectroscopy. Thus it appears that (**14**) can undergo an S_N2' type reaction with 'H$^-$' or 'Ph$^-$' delivered by K[BHBu$^s_3$] or Li[CuPh$_2$] respectively resulting in attack on the β-carbon of the vinylidene moiety with concomitant loss of bromide anion from the molybdenum (Scheme 3). We note, however, that Kostić and Fenske[25] have shown that nucleophilic attack on ML$_3$(η-C$_5$H$_5$)-type vinylidene complexes would be expected to take place at the α-carbon, if it proceeds under orbital control, leading to σ-vinyl complexes.



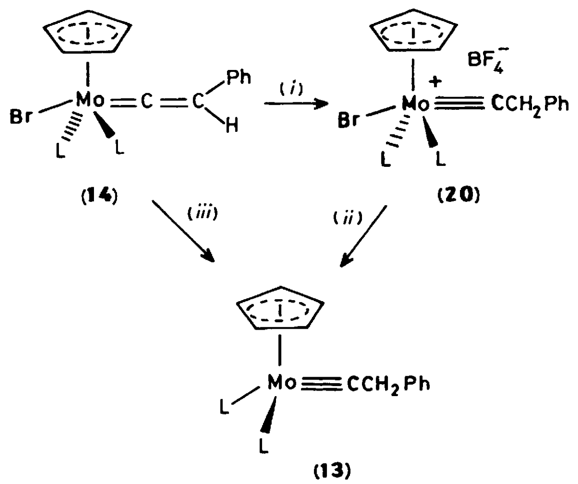
Scheme 4. L = P(OMe)$_3$. (*i*) Li[CuPh$_2$], 1.5 h; (*ii*) Li[CuMe$_2$]; (*iii*) Li[CuPh$_2$], 24 h

A related sequence of reactions is implicated in the reaction of (**8**) with Li[CuMe$_2$], which leads to the formation of the dimethylphenyl-substituted carbyne complex [Mo(≡CCMe$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] (**16**). Presumably the intermediate vinylidene complex [Mo{C=C(Me)Ph}Br{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] is formed initially, but this rapidly reacts with a further molecule of Li[CuMe$_2$] in an S_N2'-type reaction to form (**16**). If this is correct, how then is the vinylidene complex (**14**) and the postulated intermediate [Mo{C=C(Me)Ph}Br{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] formed from the alkyne cation (**8**)?

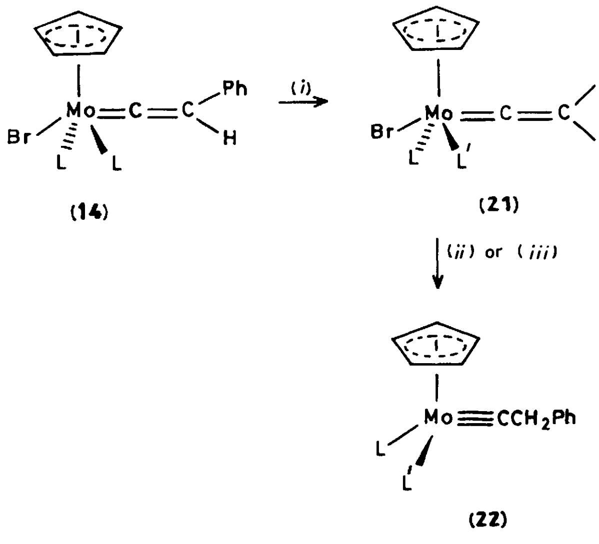
An understanding of these reactions was provided when the related reaction between (**8**) and Li[CuPh$_2$] was examined. This led to the isolation of a neutral dark green crystalline complex (**17**) (Scheme 4). Elemental analysis and n.m.r. spectroscopy showed that the molecule was an η^2-vinyl[4] complex with the illustrated structure; the ^{13}C-{^{1}H} n.m.r. spectrum exhibiting a characteristic[4] low-field triplet at 230.5 p.p.m. [*J*(CP) 25.5 Hz]. The appearance of one singlet resonance in the ^{13}P-{^{1}H} spectrum shows that the β-carbon of the η^2-vinyl complex carries both phenyl substituents, a facile windscreen-wiper motion equivalencing the ^{31}P phosphite environments. Additional evidence that the α-carbenoid carbon carries the bromine substituent was provided by the observation that reaction of (**17**) with Li[CuMe$_2$] resulted in the formation of (**18**), an η^2-vinyl complex which had previously[4] been obtained by reaction of [Mo(η^2-PhC$_2$Me){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][BF$_4$] with Li[CuPh$_2$], and which had been structurally characterised by *X*-ray crystallography. Reaction of (**17**) with Li[CuPh$_2$] afforded the analogous triphenyl-substituted η^2-vinyl species (**19**), which has also been synthesised[27] by the reaction of Li[CuPh$_2$] with [Mo(η^2-PhC$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][BF$_4$].



Scheme 5. L = P(OMe)$_3$. (*i*) K[BHBu$^s_3$]



Scheme 6. L = P(OMe)$_3$. (*i*) HBF$_4$·Et$_2$O; (*ii*) Mg–Hg; (*iii*) K[BHBu$^s_3$]



Scheme 7. L = P(OMe)$_3$, L′ = PEt$_3$. (*i*) PEt$_3$, r.t.; (*ii*) K[BHBu$^s_3$]; (*iii*) excess PEt$_3$, 55 °C

These reactions are interesting because they provide examples of formal nucleophilic attack on an η^2-vinyl complex. Examination of the frontier orbitals[4,28] presented by η^2-vinyl ligands shows that the lowest unoccupied molecular orbital is in fact located on the α-carbon implying the intermediacy of a bromo-alkene species in these reactions. Thus, depending on whether the reaction with the cuprate is a two- or a one-electron transfer process the intermediates would have the structure [Mo{η^2-CPh$_2$=C(Br)R}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] (R = Me or Ph), these species carrying either a negative charge or an odd electron. Loss of Br$^-$ or Br would then afford (**18**) or (**19**). In relation to this last step it is interesting to note that bromo-substituted η^2-bonded alkene complexes have been observed to rearrange to vinyl species.[29,30]

Thus, these observations show that η^2-vinyl complexes can be formed when they carry a bromine substituent on the α-carbon atom. This suggests a possible mechanism for the formation of the vinylidene complexes. For example, in the reaction leading to the formation of (**14**) the σ-vinyl intermediate (**A**, Scheme 5) could be accessed either by delivery of 'H$^-$' onto the molybdenum centre or to the $\pi_\perp$ orbital of the phenyl-substituted alkyne contact carbon. The bromo-vinylidene complex (**14**) could then be formed either by an intramolecular transfer of the bromine atom from the α-carbon onto the molybdenum followed by *cis–trans* isomerisation, or by direct heterolysis of the C$_\alpha$–Br bond in (**A**) affording the cationic species (**B**) which then collapses to form (**14**). It is interesting, to note, however, that all attempts to form the cation (**B**) from (**14**) failed implying that the first reaction path is followed.

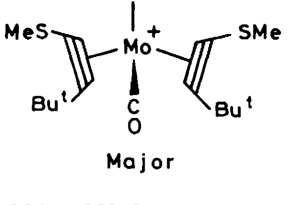
As described above, (**14**) reacts with nucleophiles to afford carbyne complexes by apparent attack on the β-carbon atom. Calculations by Kostić and Fenske[25] on ML$_3$(η-C$_5$H$_5$)-type vinylidene complexes suggest that there is a build-up of negative charge on the β-carbon atom. This suggested that it might also be possible to carry out a charge-controlled electrophilic attack on the β-carbon atom of (**14**). Addition (−78 °C) of HBF$_4$·Et$_2$O to a diethyl ether solution of (**14**) led on warm-up to the formation of a cationic complex (**20**) (Scheme 6). Analysis and examination of the ^{1}H, ^{13}C-{^{1}H}, and ^{31}P-{^{1}H} n.m.r. spectra showed that a carbyne complex with a formal oxidation state of Mo^{VI} had been formed. In agreement with the illustrated geometry the ^{13}C spectrum showed a low-field signal at 384.7 p.p.m. due to Mo≡C which appeared as a triplet [*J*(CP) 43.9 Hz], the ^{31}P spectrum exhibiting one singlet resonance. This cation is clearly isostructural with the hydridocarbyne [Mo(≡CCH$_2$Bu^t)H{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][BF$_4$], which we have previously[21] structurally characterised by *X*-ray crystallography. It is interesting that reaction of (**20**) with Mg–Hg amalgam affords the Mo^{IV} carbyne complex (13), which can also, of course, be formed by reaction with the 'H$^-$' source K[BHBu$^s_3$].

Finally, the lability of the two phosphite ligands present in (**14**) was examined. At room temperature (**14**) reacted with an excess of triethylphosphine to replace one phosphite ligand, forming the crystalline complex (**21**) in high yield. An attempt to introduce a second triethylphosphine ligand by heating (**21**) with an excess of PEt_3 at 55 °C for 7 d in a sealed tube gave only unreacted material and a low yield (10%) of a yellow crystalline carbyne complex (**22**). This carbyne was also formed in good yield on reacting (**21**) with $K[BHBu^s{}_3]$ in tetrahydrofuran (thf) (Scheme 7). Synthetically this provides a route to unsymmetrically substituted electron-rich carbyne complexes. It is likely that the formation of (**22**) by direct reaction with PEt_3 under forcing conditions involves attack by the phosphine on the bromine atom of (**21**) followed by proton abstraction by the resulting vinylidene anion $[Mo(C{=}CHPh)\{P(OMe)_3\}(PEt_3)(\eta\text{-}C_5H_5)]$ from the solvent.

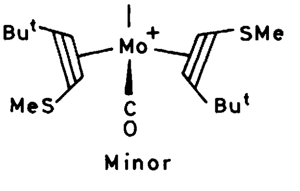
Experimental

The ^1H, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were recorded on JEOL FX90Q or FX200 spectrometers, as appropriate. Data given are for room-temperature (r.t.) measurements unless otherwise indicated, and coupling constants are in Hz (at = apparent triplet). Chemical shifts are positive to high frequency of the reference; $SiMe_4$ for ^{13}C and ^1H, and H_3PO_4 (85% external) for ^{31}P. I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Preparation of Starting Materials.—*Carbonyl*(η-*cyclopentadienyl*)*bis*(3,3-*dimethyl*-1-*methylthiobut*-1-*yne*)*molybdenum*(II) *tetrafluoroborate*, (**1**). Silver tetrafluoroborate (3.9 g, 20 mmol) was added to a stirred solution of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (4.8 g, 9.8 mmol) and Bu^tC_2SMe (5.8 g, 45.3 mmol) in CH_2Cl_2 (100 cm^3) at room temperature. After 24 h the reaction mixture was filtered through a pad of Kieselguhr, and the volume reduced *in vacuo* to 30 cm^3 and diethyl ether (30 cm^3) added to give a yellow precipitate. This was recrystallised (0 °C) from CH_2Cl_2–Et_2O to give yellow *crystals* of $[Mo(\eta^2\text{-}Bu^tC_2SMe)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**1**) (7.0 g, 67%) (Found: C, 45.2; H, 5.2; S, 11.9. $C_{20}H_{29}BF_4MoOS_2$ requires C, 45.1; H, 5.5; S, 12.0%); ν_{CO} (CH_2Cl_2) at 2 061 cm^{-1}. N.m.r.: ^1H ($CDCl_3$), major isomer, δ 5.94 (s, 5 H, C_5H_5), 2.93 (s, 6 H, SMe), 1.37 (s, 18 H, Bu^t); minor isomer, δ 6.08 (s, 5 H, C_5H_5), 3.21 (s, 3 H, SMe), 2.98 (s, 3 H, SMe), 1.66 (s, 9 H, Bu^t), 1.52 p.p.m. (s, 9 H, Bu^t). The ratio of major to minor isomers is 2.8:1. Major isomer: $^{13}C\text{-}\{^1H\}$ n.m.r. ($CDCl_3$), δ 226.4 (CO), 166.1 ($Bu^tC{\equiv}C$), 162.8 ($MeSC{\equiv}C$), 101.6 (C_5H_5), 38.3 (CMe_3), 30.9 (CMe_3), and 23.4 p.p.m. (SMe).

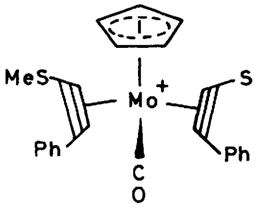


Major



Minor

Carbonyl(η-*cyclopentadienyl*)*bis*(1-*methylthio*-2-*phenylethyne*)*molybdenum*(II) *tetrafluoroborate*, (**2**). Similarly, reaction of $AgBF_4$(3.55 g, 18.2 mmol), $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (4.4 g, 9.0 mmol), and PhC_2SMe (7.5 g, 50.6 mmol) in CH_2Cl_2 afforded yellow *crystals* of $[Mo(\eta^2\text{-}PhC_2SMe)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (8.45 g, 82%) (Found: 49.8; H, 3.7; S, 11.7. $C_{24}H_{21}BF_4MoOS_2$ requires C, 50.4; H, 3.7; S, 11.2%); ν_{CO} (CH_2Cl_2) at 2 082 cm^{-1}. N.m.r.: ^1H ($CDCl_3$), major isomer, δ 7.78—6.95 (m, 10 H, Ph), 6.14 (s, 5 H, C_5H_5), 2.77 (s, 6 H, SMe); minor isomer, δ 7.78—6.95 (m, 10 H, Ph), 6.00 (s, 5 H, C_5H_5), 2.73 (s, 3 H, SMe), 2.66 (s, 3 H, SMe). The ratio of major to minor isomers is 1.7:1. Major isomer $^{13}C\text{-}\{^1H\}$ n.m.r. ($CDCl_3$), δ 214.4 (CO), 171.2 ($PhC{\equiv}C$), 152.6 ($MeSC{\equiv}C$), 133.0, 129.9, 129.0, 128.3 (Ph), 102.4 (C_5H_5), and 22.1 p.p.m. (SMe).



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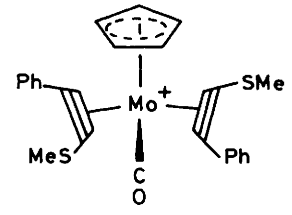
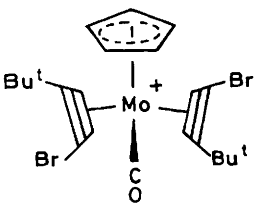
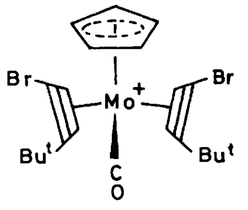


Minor

Bis(1-*bromo*-3,3-*dimethylbut*-1-*yne*)*carbonyl*(η-*cyclopentadienyl*)*molybdenum*(II) *tetrafluoroborate*, (**3**). In a similar manner, reaction of $AgBF_4$ (1.6 g, 8.22 mmol), $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (2.0 g, 4.08 mmol), and Bu^tC_2Br (4.0 g, 24.8 mmol) in CH_2Cl_2 (50 cm^3) afforded yellow *crystals* of $[Mo(\eta^2\text{-}Bu^tC_2Br)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**3**) (2.35 g, 96%) (Found: C, 36.1; H, 3.9; Br, 26.6. $C_{18}H_{23}BBr_2F_4MoO$ requires C, 36.2; H, 3.9; Br, 26.7%); ν_{CO} (CH_2Cl_2) at 2 091 cm^{-1}. N.m.r.: ^1H ($CDCl_3$), major isomer, δ 6.23 (s, 5 H, C_5H_5), 1.47 (s, 9 H, Bu^t), 1.37 (s, 9 H, Bu^t); minor isomer, δ 6.05 (s, 5 H, C_5H_5), 1.36 (s, 18 H, Bu^t). The ratio of major to minor isomers is 1.4:1. Major isomer $^{13}C\text{-}\{^1H\}$ n.m.r. ($CDCl_3$), δ 212.3 (CO), 165.2, 156.7 ($Bu^tC{\equiv}C$), 146.6, 142.8 ($BrC{\equiv}C$), 104.0 (C_5H_5), 42.6, 38.4 (CMe_3), 29.3, 29.2 p.p.m. (CMe_3).



Major



Minor

Bis(1-*bromo*-2-*phenylethyne*)*carbonyl*(η-*cyclopentadienyl*)-*molybdenum*(II) *tetrafluoroborate*, (**4**). Similarly, reaction of $AgBF_4$ (4.0 g, 20.6 mmol), $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (5.0 g, 10.2 mmol), and PhC_2Br (11.0 g, 65.6 mmol) in CH_2Cl_2 (100 cm^3) afforded on recrystallisation from CH_2Cl_2–Et_2O yellow *crystals* of $[Mo(\eta^2\text{-}PhC_2Br)_2(CO)(\eta\text{-}C_5H_5)][BF_4]$ (**4**) (9.45 g, 74%) (Found: C, 41.1; H, 2.4. $C_{22}H_{15}BBr_2F_4MoO$ requires C, 41.4; H, 2.4%); ν_{CO} (CH_2Cl_2) at 2 108 cm^{-1}. N.m.r.: ^1H (CD_2Cl_2), δ 8.25—8.13 (m, 2 H, Ph), 7.78—7.30 (m, 8 H, Ph), 6.23 (s, 5 H, C_5H_5): $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 210.7 (CO), 181.2, 177.7 ($PhC{\equiv}C$), 167.4, 165.1 ($BrC{\equiv}C$), 134.9—129.1 p.p.m. (Ph).

Preparation of Monoalkynebis(*trimethyl phosphite*) *Cations*.—(η-*Cyclopentadienyl*)(3,3-*dimethyl*-1-*methylthiobut*-1-*yne*)*bis*-(*trimethyl phosphite*)*molybdenum*(II) *tetrafluoroborate*, (**5**). A slight excess of trimethyl phosphite (2.0 cm^3, 17 mmol) was added slowly to a solution of (**1**) (4.4 g, 8.3 mmol) in CH_2Cl_2 (40 cm^3) resulting in immediate evolution of CO and a colour change from yellow to purple. The reaction mixture was stirred for a further 30 min and filtered through a Kieselguhr pad. The volume of the solvent was reduced (20 cm^3) *in vacuo*, and diethyl ether added to give purple *crystals* of $[Mo(\eta^2\text{-}Bu^tC_2SMe)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**5**) (4.7 g, 91%) (Found: C, 34.2; H, 6.6; S, 5.9. $C_{18}H_{35}BF_4MoO_6P_2S$ requires C, 34.6; H, 5.7; S, 5.2%). N.m.r.: ^1H ($CDCl_3$), δ 5.64 (s, 5 H, C_5H_5), 3.58 [at, 18 H, POMe, $|J(HP) + J(HP')|$ 11], 2.86 (s, 3 H, SMe), 1.36 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$ ($CDCl_3$), δ 244.8 [t, $Bu^tC{\equiv}C$, J(CP) 6.6], 210.1 [t, $MeSC{\equiv}C$, J(CP) 19.0], 94.3 (C_5H_5), 53.5 (POMe), 44.5 (CMe_3), 30.0 (CMe_3), 20.7 (SMe); $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ 177.9 p.p.m. (POMe).

(η-*Cyclopentadienyl*)(1-*methylthio*-2-*phenylethyne*)*bis*(*trimethyl phosphite*)*molybdenum*(II) *tetrafluoroborate*, (**6**). Similarly, addition of $P(OMe)_3$ (3.35 cm^3, 28.4 mmol) to (**2**) (8.0 g, 14.0 mmol) afforded purple *crystals* of $[Mo(\eta^2\text{-}PhC_2SMe)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**6**) (Found: C, 37.1; H, 4.8; S, 5.1. $C_{20}H_{31}BF_4MoO_6P_2S$ requires C, 37.3; H, 4.9; S, 5.0%). N.m.r.: ^1H ($CDCl_3$), δ 7.60—7.18 (m, 5 H, Ph), 5.55 (s, 5 H, C_5H_5), 3.59 [at, 18 H, POMe, |*J*(HP) + *J*(HP′)| 11.4], 2.61 (s, 3 H, SMe); $^{13}C\text{-}\{^1H\}$ ($CDCl_3$), δ 223.6 [t, Ph*C*≡C, *J*(CP) 15.1], 218.4 [t, MeS*C*≡C, *J*(CP) 13.8], 141.6 (*i*-C, Ph), 128.4, 128.1, 126.1 (Ph), 95.2 (C_5H_5), 53.5 (POMe), 20.8 (SMe); $^{31}P\text{-}\{^1H)$, δ 176.4 p.p.m. (POMe).

(1-*Bromo*-3,3-*dimethylbut*-1-*yne*)(η-*cyclopentadienyl*)*bis*(*trimethyl phosphite*)*molybdenum*(II) *tetrafluoroborate*, (**7**). Reaction of (**3**) (4.0 g, 6.7 mmol) with $P(OMe)_3$ (1.6 cm^3, 13.6 mmol) afforded purple *crystals* of $[Mo(\eta^2\text{-}Bu^tC_2Br)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**7**) (4.3 g, 85%) (Found: C, 31.0; H, 4.9; Br, 11.8. $C_{17}H_{32}BBrF_4MoO_6P_2$ requires C, 31.1; H, 4.9; Br, 12.2%). N.m.r.: ^1H ($CDCl_3$), δ 5.70 [t, 5 H, C_5H_5, *J*(HP) 1.3], 3.65 [at, 18 H, POMe, |*J*(HP) + *J*(HP′)| 11.4], 1.38 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$ ($CDCl_3$), δ 246.1 [t, Bu^t*C*≡C, *J*(CP) 6.6], 198.3 [t, Br*C*≡C, *J*(CP) 27.2], 95.2 (s, C_5H_5), 53.8 [d, POMe, *J*(CP) 4.9], 43.7 (s, *C*Me_3), 29.3 (s, C*Me*$_3$); $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ 173.2 p.p.m. (s, POMe).

(1-*Bromo*-2-*phenylethyne*)(η-*cyclopentadienyl*)*bis*(*trimethyl phosphite*)*molybdenum*(II) *tetrafluoroborate*, (**8**). Treatment of (**4**) (1.30 g, 2.09 mmol) with $P(OMe)_3$ (0.5 cm^3, 4.25 mmol) afforded steel-blue *crystals* of (**8**) $[Mo(\eta^2\text{-}PhC_2Br)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (1.25 g, 88%) (Found: C, 33.9; H, 4.3; Br, 11.3. $C_{19}H_{28}BBrF_4MoO_6P_2$ requires C, 33.7; H, 4.2; Br, 11.8%). N.m.r.: ^1H ($CDCl_3$), δ 7.96—7.90 (m, 2 H, Ph), 7.64—7.55 (m, 3 H, Ph), 5.69 [t, 5 H, C_5H_5, *J*(HP) 1.3], 3.65 [at, 18 H, POMe, |*J*(HP) + *J*(HP′)| 11.4]; $^{13}C\text{-}\{^1H\}$ ($CDCl_3$), δ 226.0 [t, Ph*C*≡C, *J*(CP) 13.1], 200.2 [t, Br*C*≡C, *J*(CP) 19.8], 135.2, 132.6, 129.6, 129.4 (Ph), 96.0 (C_5H_5), 53.9 (POMe); $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ 172.9 p.p.m. (s, POMe).

Reaction of (**5**) *with Potassium Selectride.*—A solution of potassium selectride (Aldrich), $K[BHBu^s{}_3]$ (1.30 mmol), in thf (20 cm^3) was added dropwise to a cooled (−78 °C) suspension of (**5**) (0.80 g, 1.28 mmol). The reaction mixture was allowed to warm to room temperature, and after 1.5 h the solvent was removed *in vacuo*. The residue was extracted with hexane and chromatographed on an alumina-packed column. Elution with hexane–diethyl ether (4:1) gave an orange band, which was collected and crystallised (−78 °C) from hexane to afford dark orange *crystals* of (**9**) (0.21 g, 31%) (Found: C, 40.0; H, 7.0; S, 5.9. $C_{18}H_{36}MoO_6P_2S$ requires C, 40.2; H, 6.7; S, 6.0%). N.m.r.: ^1H (C_6D_6), δ 5.23 (s, 5 H, C_5H_5), 3.42 [at, 9 H, POMe, |*J*(HP) + *J*(HP′)| 10.1], 3.22 [at, 9 H, POMe, |*J*(HP) + *J*(HP′)| 10.5], 3.05 [t, 1 H, MoCH, |*J*(HP) + *J*(HP′)| 17.5], 2.78 (s, 3 H, SMe), 1.18 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$ (C_6H_6), δ 265.6 [t, Mo=C, |*J*(CP) + *J*(CP′)| 37.4], 89.1 (C_5H_5), 51.2 (POMe), 40.8 [t, MoC, |*J*(CP) + *J*(CP′)| 19.8], 35.8 (*C*Me_3), 32.2 (C*Me*$_3$), 20.9 (SMe); $^{31}P\text{-}\{^1H\}$ (C_6D_6), δ 199.3 p.p.m. (s, POMe).

Reaction of (**6**) *with Potassium Selectride.*—Similarly, reaction of (**6**) (1.20 g, 1.86 mmol) with $K[BHBu^s{}_3]$ (1.90 mmol) gave dark orange *crystals* of (**10**) (0.45 g, 43%) (Found: C, 43.1; H, 6.1; S, 5.6. $C_{20}H_{32}MoO_6P_2S$ requires C, 43.0; H, 5.8; S, 5.7%). N.m.r.: ^1H (C_6D_6) δ 7.57—6.89 (m, 5 H, Ph), 4.75 [t, 5 H, C_5H_5, |*J*(HP) + *J*(HP′)| 2.4], 3.53 [at, 9 H, POMe, |*J*(HP) + *J*(HP′)| 11.2], 3.47 [t, 1 H, MoCH, *J*(HP) 6.4], 3.38 [at, 9 H, POMe, |*J*(HP) + *J*(HP′)| 11.2], 2.45 (s, 3 H, SMe); $^{13}C\text{-}\{^1H\}$ (C_6D_6), δ 239.4 [t, Mo≡C, |*J*(CP) + *J*(CP′)| 48.4], 158.2 (*i*-C, Ph), 127.9, 124.9, 121.4 (Ph), 89.8 (C_5H_5), 51.5, 50.8 (POMe), 23.4 (MoC), 22.3 (SMe); $^{31}P\text{-}\{^1H\}$ (C_6D_6), δ 204.4 p.p.m. (s, POMe).

Reaction of (**6**) *with Lithium Dimethylcuprate.*—A solution of $Li[CuMe_2]$ (2 mmol) in thf (10 cm^3) was added dropwise with cooling (−78 °C) to a stirred solution of (**6**) (1.20 g, 1.86 mmol) in thf (10 cm^3). The reaction mixture was allowed to warm to room temperature the solvent removed *in vacuo*, and the residue chromatographed on alumina. Elution with hexane–diethyl ether (4:1) afforded an orange band, which on crystallisation (−78 °C) from hexane gave dark orange *crystals* of (**11**) (0.65 g, 61%) (Found: C, 44.1; H, 6.0; S, 5.6. $C_{21}H_{34}MoO_6P_2S$ requires C, 43.8; H, 6.3; S, 5.6%). N.m.r.: ^1H (C_6D_6), δ 7.86—6.80 (m, 5 H, Ph), 4.59 [t, 5 H, C_5H_5, |*J*(HP) + *J*(HP′)| 2.2], 3.55 [d, 9 H, POMe, |*J*(HP) + *J*(HP′)| 10.9], 3.41 [d, 9 H, POMe, |*J*(HP) + *J*(HP′)| 10.9], 2.39 (s, 3 H, SMe), 2.24 (s, 3 H, Me); $^{13}C\text{-}\{^1H\}$ (C_6D_6), δ 240.3 [dd, Mo=C, *J*(CP) 35.2, *J*(CP′) 13.2], 162.9 (*i*-C, Ph), 127.1, 125.0, 120.7 (Ph), 90.6 (C_5H_5), 51.6 [d, POMe, *J*(CP) 4.4], 33.2 (SMe), 28.5 (MoC), 20.4 (Me); $^{31}P\text{-}\{^1H\}$ (C_6D_6), δ 207.3 [d, POMe, *J*(PP′) 59.8] and 203.3 p.p.m. [d, POMe, *J*(PP′) 59.8].

Reaction of (**7**) *with Lithium Dimethylcuprate.*—Similarly reaction of (**7**) (1.10 g, 1.67 mmol) with $Li[CuMe_2]$ (1.7 mmol) afforded on chromatography [elution with hexane–diethyl ether (9:1)] a purple band, which was collected and recrystallised (−78 °C) from hexane to give purple *crystals* of (**12**) (0.47 g, 61%) (Found: C, 38.6; H, 7.8. $C_{15}H_{26}BrMoO_3P$ requires C, 39.1; H, 7.9%). N.m.r.: ^1H (C_6D_6), δ 5.02 (s, 5 H, C_5H_5), 3.34 [d, 9 H, POMe, *J*(HP) 10.9], 3.00 [d, 3 H, Me, *J*(HP) 2.2], 1.37 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$ (C_6D_6), δ 215.1 (C≡*C*Bu^t), 194.5 [d, Br*C*≡C, *J*(CP) 39.6], 90.6 (C_5H_5), 51.5 (POMe), 33.4 (*C*Me_3), 30.8 (C*Me*$_3$), −13.3 [d, $MoCH_3$, *J*(CP) 15.4]; $^{31}P\text{-}\{^1H\}$ (C_6D_6), δ 201.0 p.p.m. (s, POMe).

Reactions of Silver Tetrafluoroborate.—(*a*) *With complex* (**9**). A solution of $AgBF_4$ (0.17 g, 0.87 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise to a solution of (**9**) (0.45 g, 0.84 mmol) in CH_2Cl_2 (5 cm^3). The reaction mixture was stirred at room temperature for 2 h during which time the colour changed from orange to purple. Filtration through Celite, reduction of the volume of the solvent, and addition of diethyl ether gave purple *crystals* of $[Mo(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (0.31 g, 64%) identical (n.m.r.) with an authentic sample. N.m.r.: $^{13}C\text{-}\{^1H\}$ ($CDCl_3$), δ 244.9 [t, Mo≡C, *J*(CP) 9.1], 201.7 [t, H*C*≡C, *J*(CP) 23.9], 94.6 (C_5H_5), 53.5 [d, POMe, *J*(CP) 3.3], 42.6 (*C*Me_3), 31.3 p.p.m. (C*Me*$_3$).

(*b*) *With complex* (**10**). Similarly, reaction of (**10**) (0.28 g, 0.50 mmol) with $AgBF_4$ (0.10 g, 0.51 mmol) in CH_2Cl_2 (10 cm^3) gave blue *crystals* of $[Mo(\eta^2\text{-}PhC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (0.17 g, 57%) identical (n.m.r.) with an authentic sample.

(*c*) *With complex* (**11**). In a similar way reaction of (**11**) (0.37 g, 0.65 mmol) with $AgBF_4$ (0.13 g, 0.67 mmol) in CH_2Cl_2 (10 cm^3) gave purple *crystals* of $[Mo(\eta^2\text{-}PhC_2Me)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (0.27 g, 68%) identical (n.m.r.) with an authentic sample.

Reaction of (**7**) *with Potassium Selectride.*—A solution of $K[BHBu^s{}_3]$ (0.8 mmol) in thf (10 cm^3) was added dropwise to a stirred cooled (−78 °C) solution of (**7**) (0.50 g, 0.76 mmol) in thf (15 cm^3). After 2 h at room temperature the solvent was removed *in vacuo* and the residue chromatographed. Elution with hexane gave a single yellow band, which was collected and recrystallised (−78 °C) from hexane to give yellow crystals of the carbyne complex $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (0.14 g, 37%) characterised by n.m.r.[20]

Reaction of (**8**) *with Potassium Selectride.*—A solution of $K[BHBu^s{}_3]$ (2.1 mmol) was added dropwise to a cooled (−78 °C) suspension of (**8**) (1.40 g, 2.1 mmol) in thf (20 cm^3). The reaction mixture was allowed to warm and stirred at room temperature for 1.5 h during which time its colour changed from dark blue to orange. After removal of volatile materials *in vacuo* the residue was extracted with hexane–diethyl ether (2:1) and chromatographed on alumina. Elution with hexane–diethyl ether (3:2) gave a yellow band which was collected and crystallised (−78 °C) from hexane to give yellow *crystals* of $[\mathrm{Mo}(\equiv\mathrm{CCH_2Ph})\{\mathrm{P(OMe)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})]$ **(13)** (0.06 g, 6%) (Found: C, 44.5; H, 5.7. $\mathrm{C_{19}H_{30}MoO_6P_2}$ requires C, 44.5; H, 5.9%). N.m.r.: ^{1}H ($\mathrm{C_6D_6}$), δ 7.35—7.04 (m, 5 H, Ph), 5.21 [t, 5 H, $\mathrm{C_5H_5}$, *J*(HP) 0.7], 3.55 [t, 2 H, $\mathrm{CH_2}$, *J*(HP) 1.0], 3.45 [at, 18 H, POMe, \|*J*(HP) + *J*(HP′)\| 11.7]; ^{13}C-{^{1}H} ($\mathrm{C_6D_6}$), δ 292.7 [t, Mo≡C, *J*(CP) 29.3], 139.2 (*i*-C, Ph), 131.8, 126.0, 124.6 (Ph), 89.2 ($\mathrm{C_5H_5}$), 55.3 (Mo≡C*C*), 50.9 (POMe); ^{31}P-{^{1}H} ($\mathrm{C_6D_6}$), δ 213.3 p.p.m. (s, POMe).

Further elution with diethyl ether gave an orange band, which was collected and recrystallised (−30 °C) from thf–hexane to afford brown *crystals* of **(14)** (0.48 g, 39%) (Found: C, 38.6; H, 5.1; Br, 13.0. $\mathrm{C_{19}H_{29}BrMoO_6P_2}$ requires C, 38.6; H, 5.0; Br, 13.5%). N.m.r.: ^{1}H ($\mathrm{C_6D_6}$), δ 7.42—6.89 (m, 5 H, Ph), 5.18 [t, 5 H, $\mathrm{C_5H_5}$, *J*(HP) 1.2], 3.64 [at, 18 H, POMe, \|*J*(HP) + *J*(HP′)\| 11.5], 3.34 [t, 1 H, C=C*H*Ph, *J*(HP) 5.7]; ^{13}C-{^{1}H} ($\mathrm{C_6D_6}$), δ 336.5 [t, Mo=C, *J*(CP) 48.8], 142.4 [t, Mo=C–*C*, *J*(CP) 7.3], 130.2, 128.5, 124.2, 122.8 (Ph), 92.1 ($\mathrm{C_5H_5}$), 54.0 (POMe); ^{31}P-{^{1}H} ($\mathrm{C_6D_6}$), δ 154.9 p.p.m. (s, POMe).

Reactions of **(14)**.—(*a*) *With* $\mathrm{K[BHBu^s{}_3]}$.—A solution of $\mathrm{K[BHBu^s{}_3]}$ (0.5 mmol) in thf was added dropwise with stirring (room temperature) to a solution of **(14)** (0.20 g, 0.34 mmol) in thf (20 cm^3). After 2 h the volatile material was removed *in vacuo*, the residue extracted with hexane, and the extract chromatographed on alumina. Elution with hexane–diethyl ether (1:1) gave a yellow band, which was recrystallised (−78 °C) from hexane to afford yellow *crystals* of $[\mathrm{Mo}(\equiv\mathrm{CCH_2Ph})\{\mathrm{P(OMe)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})]$ **(13)** (0.09 g, 52%).

(*b*) *With* $\mathrm{Li[CuPh_2]}$. A solution of $\mathrm{Li[CuPh_2]}$ (0.55 mmol) was added dropwise to a solution of **(14)** (0.31 g, 0.52 mmol) in thf (25 cm^3). After 24 h at room temperature, the solvent was removed *in vacuo*, the residue extracted with diethyl ether, and the extract chromatographed on alumina. Elution with hexane–diethyl ether (3:2) gave a yellow band, which on recrystallisation (−78 °C) from hexane–diethyl ether gave yellow *crystals* of $[\mathrm{Mo}(\equiv\mathrm{CCHPh_2})\{\mathrm{P(OMe)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})]$ **(15)** (0.06 g, 20%) (Found: C, 51.2; H, 5.7. $\mathrm{C_{25}H_{34}MoO_6P_2}$ requires C, 51.0; H, 5.8%). N.m.r.: ^{1}H ($\mathrm{C_6D_6}$), δ 7.54–6.56 (m, 10 H, Ph), 5.08 (s, 5 H, $\mathrm{C_5H_5}$), 3.94 [t, 1 H, $\mathrm{CHPh_2}$, *J*(HP) 4.1], 3.35 [at, 18 H, POMe, \|*J*(HP) + *J*(HP′)\| 11.4]; ^{31}P-{^{1}H} ($\mathrm{C_6D_6}$), δ 195.9 p.p.m. (s, POMe).

Reaction of **(8)** *with Lithium Dimethylcuprate*.—Addition of $\mathrm{Li[CuMe_2]}$ (1.6 mmol) to **(8)** (1.0 g, 1.5 mmol) in thf (25 cm^3) followed by chromatography on alumina and elution with hexane–diethyl ether (3:2) gave a yellow band which was collected and recrystallised (−78 °C) from hexane to give yellow *crystals* of $[\mathrm{Mo}(\equiv\mathrm{CCMe_2Ph})\{\mathrm{P(OMe)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})]$ **(16)** (0.35 g, 43%) (Found: C, 46.2; H, 6.7. $\mathrm{C_{21}H_{34}MoO_6P_2}$ requires C, 46.7; H, 6.5%). N.m.r.: ^{1}H ($\mathrm{C_6D_6}$), δ 7.65—7.03 (m, 5 H, Ph), 5.19 [t, 5 H, $\mathrm{C_5H_5}$, *J*(HP) 0.9], 3.41 [at, 18 H, POMe, \|*J*(HP) + *J*(HP′)\| 11.4], 1.54 (s, 6 H, Me); ^{13}C-{^{1}H} ($\mathrm{C_6D_6}$), δ 311.3 [t, Mo≡C, *J*(CP) 36.1], 139.2, 131.6, 126.5, 123.0 (Ph), 89.0 ($\mathrm{C_5H_5}$), 71.8 (Mo≡C*C*), 50.9 (POMe), 29.5 (Me); ^{31}P-{^{1}H} ($\mathrm{C_6D_6}$), δ 213.7 p.p.m. (s, POMe).

Reaction of **(8)** *with Lithium Diphenylcuprate*.—A similar reaction (1.5 h) between **(8)** (10.8 g, 1.5 mmol) and $\mathrm{Li[CuPh_2]}$ (1.5 mmol) in thf (25 cm^3) at room temperature gave, on chromatography (hexane–diethyl ether) and crystallisation (−78 °C) from hexane dark green *crystals* of **(17)** (0.32 g, 32.0) (Found: C, 44.8; H, 5.1; Br, 11.6. $\mathrm{C_{25}H_{33}BrMoO_6P_2}$ requires C, 45.0; H, 5.0; Br, 12.0%). N.m.r.: ^{1}H ($\mathrm{C_6D_6}$), δ 7.53—6.88 (m, 10 H, Ph), 5.03 (s, 5 H, $\mathrm{C_5H_5}$), 3.14 [at, 18 H, POMe, \|*J*(HP) + *J*(HP′)\| 10.5]; ^{13}C-{^{1}H} ($\mathrm{C_6D_6}$), δ 230.5 [t, Mo=C, *J*(CP) 25.5], 141.6, 141.3 (*i*-C, Ph), 131.6, 122.0 (Ph), 93.2 ($\mathrm{C_5H_5}$), 51.6 (POMe), 40.0 (Mo-C); ^{31}P-{^{1}H} ($\mathrm{C_6D_6}$), δ 195.5 p.p.m. (s, POMe).

Reaction of **(17)** *with Lithium Diphenylcuprate*.—A solution of **(17)** (0.15 g, 0.22 mmol) and $\mathrm{Li[CuPh_2]}$ (0.25 mmol) in thf (15 cm^3) was stirred at room temperature for 24 h. The solvent was removed *in vacuo* and the residue chromatographed on alumina. Elution with hexane–diethyl ether gave a dark green band, which on crystallisation (−30 °C) from hexane gave dark green *crystals* of **(19)** (0.08 g, 55%) (Found: C, 57.0; H, 5.5. $\mathrm{C_{31}H_{38}MoO_6P_2}$ requires C, 57.3; H, 5.5%). N.m.r.: ^{1}H ($\mathrm{C_6D_6}$), δ 8.1—7.0 (m, 15 H, Ph), 5.05 [t, 5 H, $\mathrm{C_5H_5}$, *J*(HP) 1.2], 3.13 [at, 18 H, POMe, \|*J*(HP) + *J*(HP′)\| 10.8]; ^{13}C-{^{1}H} ($\mathrm{C_6D_6}$), δ 230.0 [t, Mo=C, *J*(CP) 23.8], 131.6, 130.9, 130.4, 130.2, 129.6, 122.2 (Ph), 93.4 ($\mathrm{C_5H_5}$), 51.6 (POMe); ^{31}P-{^{1}H} ($\mathrm{C_6D_6}$), δ 195.6 p.p.m. (s, POMe).

Reaction of **(16)** *with Lithium Dimethylcuprate*.—A similar reaction (24 h room temperature) of **(16)** (0.14 g, 0.21 mmol) with $\mathrm{Li[CuMe_2]}$ (0.25 mmol) afforded red crystals of the η^2-vinyl complex $[\overline{\mathrm{Mo}\{=\mathrm{C(Me)C}}\mathrm{Ph_2}\}\{\mathrm{P(OMe)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})]$[18] (0.09 g, 65%), identical (n.m.r.) with an authentic sample.

Reactions of **(14)**.—(*a*) *With tetrafluoroboric acid.* $\mathrm{HBF_4{\cdot}Et_2O}$ (0.04 cm^3, 0.046 g, 0.28 mmol) was added dropwise to a cooled (−78 °C) solution of **(14)** (0.15 g, 0.25 mmol) in diethyl ether (5 cm^3). As the reaction mixture was allowed to warm its orange colouration gradually faded with the formation of an oily precipitate. When the solution became colourless the precipitate was washed with diethyl ether and dried *in vacuo*. Recrystallisation (0 °C) from methylene chloride–diethyl ether afforded pale yellow *crystals* of **(20)** (0.13 g, 77%) (Found: C, 33.2; H, 4.0; Br, 11.6. $\mathrm{C_{19}H_{30}BBrF_4MoO_6P_2}$ requires C, 33.6; H, 4.4; Br, 11.8%). N.m.r.: ^{1}H ($\mathrm{CDCl_3}$), δ 7.44—7.13 (m, 5 H, Ph), 5.69 [t, 5 H, $\mathrm{C_5H_5}$, *J*(HP) 1.6], 4.34 [t, 2 H, $\mathrm{CH_2}$, *J*(HP) 7.9], 3.90 [t, 18 H, POMe, \|*J*(HP) + *J*(HP′)\| 11.4]; ^{13}C-{^{1}H} ($\mathrm{CDCl_3}$), δ 384.7 [t, Mo≡C, *J*(CP) 43.9], 132.9, 129.5, 128.9, 127.5 (Ph), 100.5 ($\mathrm{C_5H_5}$), 61.2 (Mo≡C*C*), 26.0 [d, POMe, *J*(CP) 4.9]; ^{31}P-{^{1}H} ($\mathrm{CDCl_3}$), δ 130.9 p.p.m. (s, POMe).

(*b*) *With triethylphosphine.* A solution of **(14)** (0.20 g, 0.34 mmol) and $\mathrm{PEt_3}$ (0.2 cm^3, 0.16 g, 1.36 mmol) in diethyl ether (10 cm^3) was stirred at room temperature for 16 h. The volatile material was removed *in vacuo* and the residue chromatographed on an alumina-packed column. Elution with diethyl ether gave a brown band, which was collected and recrystallised (0 °C) from hexane–diethyl ether to give brown *crystals* of **(21)** (0.18 g, 91%) (Found: C, 45.2; H, 6.2. $\mathrm{C_{22}H_{35}BrMoO_3P_2}$ requires C, 45.1; H, 6.0%). N.m.r.: ^{1}H ($\mathrm{C_6D_6}$), δ 7.31—6.73 (m, 5 H, Ph), 5.05 [t, 5 H, $\mathrm{C_5H_5}$, *J*(HP) 1.75], 3.66 [d, 9 H, POMe, *J*(HP) 10.5], 3.33 [t, 1 H, C=C*H*Ph, *J*(HP) 10.2], 1.92 [dq, 6 H, $\mathrm{CH_2}$, *J*(HH′) 7.4, *J*(HP) 9.6], 0.92 [dt, 9 H, Me, *J*(HH′) 7.4, *J*(HP) 13.6]; ^{13}C-{^{1}H} ($\mathrm{C_6D_6}$), δ 325.6 [t, Mo=C, *J*(CP) 45.4], 143.0 [t, Mo=C=*C*, *J*(CP) 23.0], 130.0—122.4 (Ph), 91.0 ($\mathrm{C_5H_5}$), 54.1 [d, POMe, *J*(CP) 4.9], 18.5 [d, $\mathrm{CH_2}$, *J*(CP) 24.4], 9.1 (Me); ^{31}P-{^{1}H} ($\mathrm{C_6D_6}$), δ 160.5 [d, POMe, *J*(PP′) 8.30] and 19.7 p.p.m. [d, PEt, *J*(PP′) 83.0].

Reaction of **(21)** *with* $\mathrm{K[BHBu^s{}_3]}$.—The reaction of **(21)** (0.15 g, 0.26 mmol) with $\mathrm{K[BHBu^s{}_3]}$ (0.30 mmol) in thf (10 cm^3) at room temperature (2 h) gave, on chromatography and crystallisation (−78 °C) from hexane, yellow *crystals* of $[\mathrm{Mo}(\equiv\mathrm{CCH_2Ph})\{\mathrm{P(OMe)_3}\}(\mathrm{PEt_3})(\eta\text{-}\mathrm{C_5H_5})]$ **(22)** (0.06 g, 46%) (Found: C, 51.8; H, 7.4. $\mathrm{C_{22}H_{36}MoO_3P_2}$ requires C, 52.2; H, 7.2%). N.m.r.: ^{1}H ($\mathrm{C_6D_6}$), δ 7.46—6.91 (m, 5 H, Ph), 5.10 (s, 5 H, $\mathrm{C_5H_5}$), 3.45 [t, 2 H, $\mathrm{CH_2}$, *J*(HP) 4.4], 3.42 [d, 9 H, POMe, *J*(HP) 11.4], 1.49 [q, 6 H, $\mathrm{PC}\mathit{H}_2\mathrm{CH_3}$, *J*(HH) 7.3], 1.04 [dt, 9 H, $\mathrm{CH_2C}\mathit{H}_3$, *J*(HH)

Table 2. Atomic co-ordinates ($\times$ 10^4) for (**14**)

Atom	x	y	z
Mo	2 034(1)	2 043(1)	3 391(1)
Br	245(1)	681(1)	3 053(1)
P(1)	334(2)	2 541(1)	4 206(1)
P(2)	3 651(2)	804(1)	3 237(1)
O(1)	366(5)	3 583(3)	4 451(3)
O(2)	329(4)	2 117(3)	5 082(3)
O(3)	−1 258(4)	2 480(3)	3 745(3)
O(4a)[a]	3 703(8)	−105(4)	3 687(5)
O(4b)[b]	4 163(18)	196(14)	4 098(11)
O(5)	5 207(4)	1 131(3)	3 339(3)
O(6a)[a]	3 519(8)	454(5)	2 294(4)
O(6b)[b]	3 280(17)	−94(10)	2 734(8)
C(1)	1 280(8)	3 937(5)	5 122(5)
C(2)	423(8)	1 170(4)	5 238(4)
C(3)	−2 376(8)	2 660(6)	4 167(6)
C(4)	3 173(7)	−297(5)	4 415(4)
C(5)	6 339(8)	521(6)	3 252(5)
C(6)	2 811(14)	−269(8)	1 915(6)
C(7)	3 158(5)	1 998(3)	4 462(3)
C(8)	3 970(6)	1 988(4)	5 194(4)
C(9)	5 044(6)	2 651(4)	5 533(3)
C(10)	5 966(7)	2 480(4)	6 273(4)
C(11)	7 010(7)	3 083(5)	6 581(4)
C(12)	7 162(7)	3 879(4)	6 183(4)
C(13)	6 240(7)	4 077(4)	5 474(4)
C(14)	5 201(6)	3 467(4)	5 150(4)
C(15)	1 215(8)	2 651(4)	2 049(4)
C(16)	999(8)	3 271(5)	2 624(4)
C(17)	2 326(8)	3 511(4)	3 107(4)
C(18)	3 372(8)	3 002(4)	2 812(4)
C(19)	2 668(8)	2 481(5)	2 147(4)

[a] Occupancy 0.796(13). [b] Occupancy 0.204(13).

7.3, J(HP) 14.4]; ^{13}C-{^{1}H} (C_6D_6), δ 294.1 [t, Mo≡C, |J(CP) + J(CP′)| 56.8], 129.1—125.8 (Ph), 88.0 (C_5H_5), 55.2 (CH_2), 50.9 (POMe), 24.8 [d, PCH_2, J(CP) 22], 8.5 (Me); ^{31}P-{^{1}H} (C_6D_6), δ 212.2 [d, POMe, J(PP′) 40.3], 50.4 p.p.m. [d, PEt, J(PP′) 40.3].

Crystal Structure Analysis of [Mo(C=CHPh)Br{P(OMe)$_3$}$_2$(η-C_5H_5)] (**14**).—*Crystal data.* $C_{19}H_{29}BrMoO_6P_2$, $M = 519.0$, monoclinic, space group $P2_1/c$ (no. 14), $a = 9.749(7)$, $b = 14.773(9)$, $c = 16.834(9)$ Å, $\beta = 101.34(5)°$, $U = 2\,377(3)$ Å^3, $Z = 4$, $D_c = 1.65$ g cm^{-3}, $F(000) = 1\,192$, μ(Mo-K_α) = 23.7 cm^{-1}, $T = 295$ K, graphite-monochromated Mo-K_α X-radiation, $\bar{\lambda} = 0.710\,69$ Å.

All diffraction measurements were made on a red-brown crystal of irregular shape (dimensions *ca.* 0.6 × 0.4 × 0.3 mm) mounted in a thin-walled glass capillary, under N_2, on a Nicolet $R3m$ diffractometer. Of 4 157 intensity data, measured by Wyckoff ω-scans in a unique quadrant of reciprocal space for $4 < 2\theta < 50°$, 3 686 were unique observations. Of these 3 078 with $I > 2\sigma(I)$ were used. An absorption correction was applied, based on a six-parameter fit to 158 azimuthal scan data, giving transmission coefficients between 0.65 and 0.83. Structure solution and refinement was by Patterson, Fourier, and blocked-cascade full-matrix least-squares methods. Data were assigned weights $w = [\sigma_c^2(F_o) + gF^2]^{-1}$, where $g = 0.0007$ was chosen to minimise the variation of $w(|F_o| - |F_c|)^2$ with $|F_o|$. Two of the methoxy groups attached to P(2) showed associated two-fold disorder and the oxygens of these groups were refined in two pairs of sites at occupancies 0.796(13) (labelled a) and 0.204(13) (labelled b) respectively. The P–O and O–C bond lengths in these groups were constrained to be *ca.* 1.60 and 1.43 Å respectively. All non-hydrogen atoms, other than the low-occupancy oxygens were assigned anisotropic displacement parameters. The low-occupancy oxygens and H(8) were refined with isotropic displacement parameters, all other hydrogen atoms having fixed U_{iso}. The methyl, phenyl, and cyclopentadienyl hydrogens were constrained to idealised geometries (C–H 0.96 Å) and H(8) refined without constraints. Refinement of the 293 least-squares parameters converged to final residuals $R = 0.046$, $R' = 0.047$, $S = 1.43$.* A final difference electron density synthesis showed no features > 1.5 and < -1.0 e Å^{-3}, the largest of these being *ca.* 1 Å from molybdenum. Final atomic co-ordinates for the non-hydrogen atoms are given in Table 2. All calculations were carried out using the SHELXTL package[31] on a Nicolet $R3m$/E system. Complex neutral-atom scattering factors were taken from ref. 32.

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* R = $\Sigma||F_o| - |F_o||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_o||/\Sigma w^{\frac{1}{2}}|F_o|$, $S = [\Sigma w(|F_o| - |F_o|)^2/(N_o - N_v)]^{\frac{1}{2}}$; N_o = no. of observations, N_v = no. of variables.

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