Reactions of Co-ordinated Ligands. Part 52.[1] Formation and Reactivity of Molybdenum Vinylidene Anions; Crystal Structures of $[MoI(\eta^4\text{-}CH_2{=}CHCH{=}CHCH_2Bu^t)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ and $[Mo(\eta^3\text{-}CBu^tCHCHCMe_2CO)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$‡

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Reaction of $LiBu^n$ with the carbyne complexes $[Mo(\equiv CCH_2R)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (R = Ph or Bu^t) affords the red lithium species $Li[Mo(CCHR)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ characterised in solution by ^{13}C and ^{31}P NMR spectroscopy as vinylidene complexes with the negative charge localised on the metal centre. The reactions of the potentially ambident nucleophiles with a wide range of organic electrophilic reagents have been studied. Quenching with MeI, EtBr, $SiMe_3Cl$, $EtOCH_2Cl$, MeSSMe, CH_2CH_2O, Bu^tCOCl and $CH_2{=}CHCH_2Cl$ results in attack on the β-carbon atom of the vinylidene with formation of a range of β-substituted carbyne complexes isolated as crystalline materials. In the case of the benzyl-substituted systems there was also evidence for the formation of β,β′-disubstituted carbynes. In contrast, quenching with allyl iodide leads to an unusual reaction and formation of 1,3-diene complexes, this being confirmed by a single-crystal X-ray diffraction study on $[MoI(\eta^4\text{-}CH_2{=}CHCH{=}CHCH_2Bu^t)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$. This is explained in terms of a competing allylation reaction at the molybdenum centre. Ultraviolet irradiation of $[Mo\{\equiv CCH(COBu^t)Bu^t\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ affords the η^3-allyl complex $[Mo\{\eta^3\text{-}CBu^tCHCHCMe_2CO\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ in a reaction involving an unusual C–H activation.

The base-promoted interconversion of alkynes and 1,2-dienes, *e.g.* $RC\equiv CCH_3 \rightleftharpoons RCH{=}C{=}CH_2$, involving propargyl and allenyl carbanions, is a well known reaction in organic chemistry. This suggested to us that in view of the isolobal relationship $HC \underset{o}{\longleftrightarrow} ML_2(\eta\text{-}C_5H_5)$ (M = Mo or W) it might be possible to deprotonate carbyne complexes of the type $[M(\equiv CCH_2R)L_2(\eta\text{-}C_5H_5)]$ (M = Mo or W) to form anionic species $[M(CCHR)L_2(\eta\text{-}C_5H_5)]^-$, in which the negative charge is centred either on the metal, *i.e.* a vinylidene complex, or on the β-carbon atom. Our discovery[2] that co-ordinated alkynes could be transformed into the Group 6 substituted carbyne complexes $[M(\equiv CCH_2R)\{P(OMe)_3\}_2L']$ (M = Mo or W, L′ = $\eta\text{-}C_5H_5$ or $\eta^5\text{-}C_9H_7$) provided an opportunity to examine this idea, and in an initial study[3] we observed that treatment of $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ with $LiBu^n$ in tetrahydrofuran (thf) afforded a deep red lithium species, which on being quenched with D_2O afforded $[Mo\{\equiv CCH(D)Bu^t\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and $[Mo(\equiv CCD_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$. This suggested the intermediacy of the lithium species $Li[Mo(CCHBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and $Li[Mo(CCDBu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$. It was also found[2b,4] that reaction of $[Mo\{\equiv CCH(R)SiMe_3\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ (R = H or Ph) with NaF in MeCN–water as solvent formed the methyl- and benzyl-substituted carbynes $[Mo(\equiv CCH_2R)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ (R = H or Ph), which implied that protonation of the anions $[Mo(CCHR)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]^-$ formed by desilylation occurs regioselectively on the β-carbon atom of the CCHR ligand. With the insight these experiments provided we were then led to examine the reaction of a wider range of electrophiles (E^+) with the anions $[Mo(CCHR)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^-$ (R = Ph or Bu^t) thus providing a synthetic pathway to a range of β-substituted carbyne complexes $[Mo\{\equiv CCH(E)R\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$.[5] Recently, in a related study it was shown by Templeton and co-workers[6] that $[Mo(\equiv CMe)(CO)_2\{HB(dmpz)_3\}]$ (dmpz = 3,5-dimethylpyrazol-1-yl) is deprotonated by $Na[N(SiMe_3)_2]$ to form the anion $[Mo(CCH_2)(CO)_2\{HB(dmpz)_3\}]^-$, which also reacts with RI (R = Me or Et) at the β-carbon to form the carbynes $[Mo(\equiv CCH_2R)(CO)_2\{HB(dmpz)_3\}]$. In this paper we describe full details of our studies.

Results and Discussion

To gain additional insight into the nature of the red species formed on deprotonation of the carbyne complexes $[Mo(\equiv CCH_2R)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (R = Ph or Bu^t) the reactions were conducted in an NMR tube. Examination of the $^{13}C\text{-}\{^1H\}$ (C_6D_6, thf, −30 °C) NMR spectrum of the red solution obtained on addition of butyllithium to $[Mo(\equiv CCH_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ **1** showed as expected the absence of the parent carbyne-carbon triplet [δ 292.7, *J*(CP) 29.3 Hz], this being replaced by a new triplet signal at δ 317.4 [*J*(CP) 17.7 Hz] assigned to the α-carbon of the (CCHPh) moiety present in the anionic species $Li[Mo(CCHPh)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ **2**. The corresponding $^{13}C\text{-}\{^1H\}$ NMR spectrum (−30 °C) of the red solution obtained from $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ **10** showed an analogous triplet centred at δ 322.8 [*J*(CP) 17.0 Hz] to low field of the contact carbyne carbon of the parent carbyne **10** [δ 299.9, *J*(CP) 27.0 Hz]. This again

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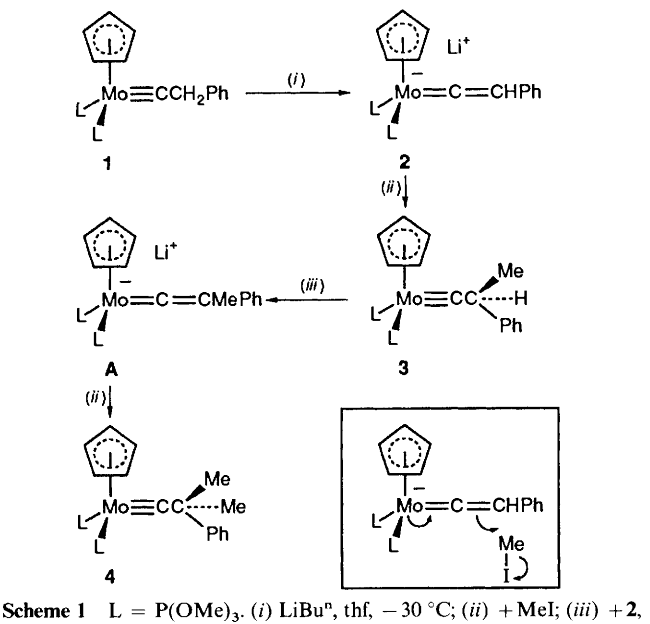
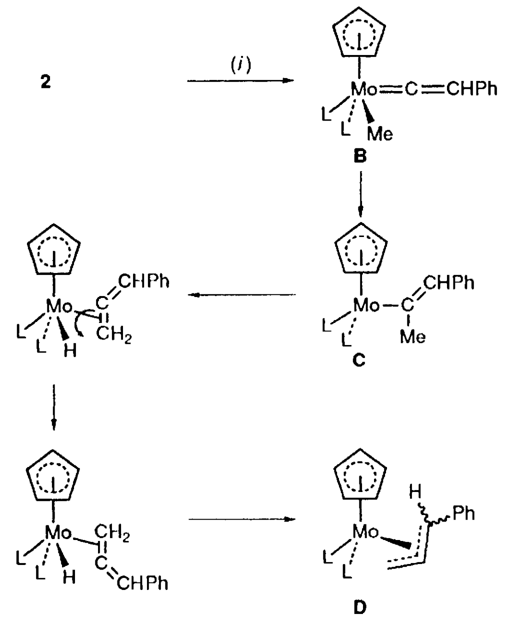
‡ (η-Cyclopentadienyl)[(1,2,3,4-η)-6,6-dimethylhepta-1,3-diene]iodo(trimethyl phosphite)molybdenum and [(1,2,3-η)-3-*tert*-butyl-5,5-dimethyl-4-oxocyclopent-2-en-1-yl)(η-cyclopentadienyl)bis(trimethyl phosphite)molybdenum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: cal = 4.184 J.



Scheme 1 L = P(OMe)$_3$. (*i*) LiBu^n, thf, −30 °C; (*ii*) +MeI; (*iii*) +2, −[Mo(≡CCH$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]



Scheme 2 L = P(OMe)$_3$. (*i*) +MeI

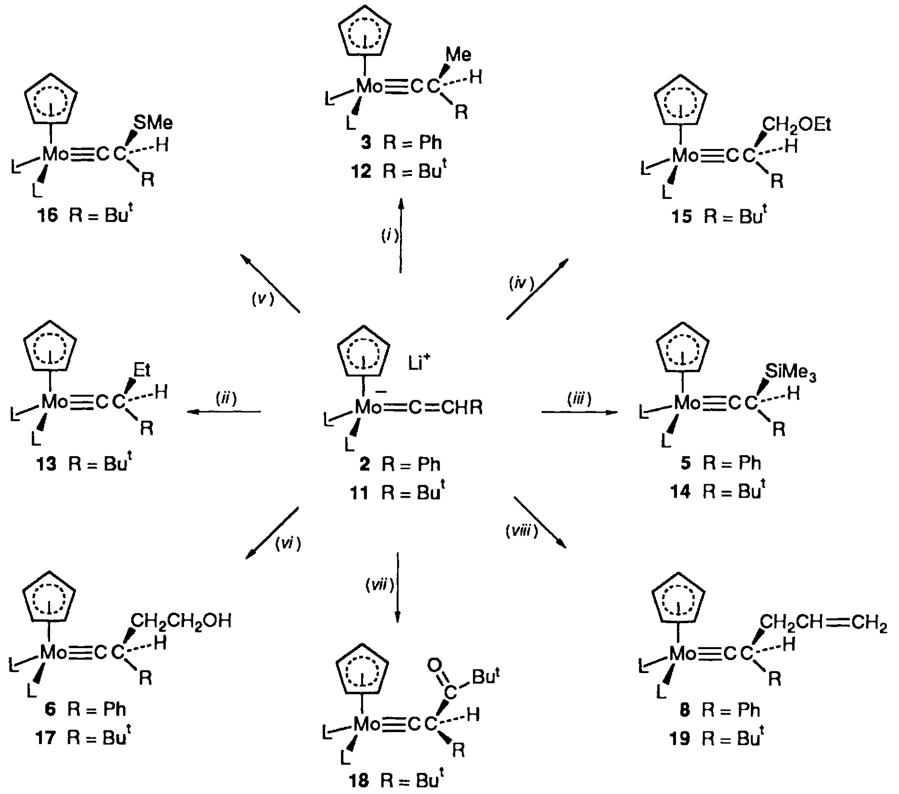
can be assigned to the (CCHBu^t) contact carbon of Li[Mo(CCHBu^t){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **11**. Comparison of these low-field chemical shifts with those observed[7] for neutral molybdenum vinylidene complexes suggests that a vinylidene bonding mode is adopted in solution for both **2** and **11**, in which the negative charge is localised on the molybdenum rather than on the β-carbon, *i.e.* [Mo(C=CHR){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]$^-$. This suggestion is further supported by the observation that the ^{13}C NMR spectra of **2** and **11** also exhibited signals at δ 122.5 [*J*(CH) 144.0] and 121.8 [*J*(CH) 142.0 Hz] respectively, which fall within the range δ 130–100 observed[7] for the β-carbons of vinylidene ligands. The *J*(CH) coupling constants are also typical of an sp^2-hybridised carbon. With regard to the question of the orientation of the vinylidene ligand relative to the molecular mirror plane, extended-Hückel molecular orbital calculations[8] for the ML$_3$(η-C$_5$H$_5$)-type vinylidene cation [Fe(C=CH$_2$)(CO)$_2$(η-C$_5$H$_5$)]$^+$, which is isoelectronic with **2**, suggest a vey low (3.6 kcal mol^{-1}) barrier to rotation; it was not therefore unexpected to observe that the ^{31}P-{^{1}H} NMR spectrum of **2** shows only one resonance at −30 °C. Thus it is not possible to assign a ground-state conformation for the vinylidene moiety.

Following our earlier observation[3] that quenching a solution of compound **2** with D$_2$O afforded the β-deuteriated carbynes [Mo{≡CCH(D)Bu^t}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] and [Mo(≡CCD$_2$Bu^t){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] it was clearly important to examine the reactivity of the vinylidene anions **2** and **11** towards a range of electrophilic reagents. When an excess of methyl iodide was added to a thf solution of Li[Mo(CCHPh){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **2** there was a rapid change in colour from bright red to yellow. Work-up afforded two yellow crystalline air-stable products, which were easily separated by column chromatography. These were identified by elemental analysis and NMR spectroscopy (see Experimental section) as the monomethyl-substituted complex [Mo{≡CCH(Me)Ph}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **3** and the previously[7] synthesised dimethyl-substituted carbyne [Mo(≡CCMe$_2$Ph){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **4**. The formation of these two compounds can be understood in terms of the initial reaction of the vinylidene anion **2** with methyl iodide to form **3** *via* electrophilic attack on the β-carbon atom (Scheme 1). If electrophilic attack had alternatively occurred at the molybdenum centre then as is shown in Scheme 2 the initial product would be expected to be the methyl-substituted vinylidene **B**. There is no obvious way in which this compound could rearrange into the carbyne **3**, and as is illustrated the most likely product[9] following attack at the molybdenum centre would be the η^3-allylic complex **D** formed by migration of the methyl group from the molybdenum to the α-carbon of the vinylidene ligand, and subsequent rearrangement of the resulting 16-electron vinyl species **C**. Therefore, the dimethyl-substituted carbyne complex **4** is presumably formed by competitive deprotonation of **3** by the anion [Mo(CCHPh){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)], a process which would be expected to be assisted by the benzylic nature of the C–H bond. The resulting anion **A** (Scheme 1) on quenching with MeI then affords **4** by electrophilic attack on the β-carbon atom.

This initial study was extended in two ways. First, treatment of compound **2** with SiMe$_3$Cl, $\overline{\text{CH}_2\text{CH}_2\text{O}}$, or allyl chloride afforded the trimethylsilyl- **5**, 2-ethanol- **6** and allyl- **8** substituted carbyne complexes (Scheme 3) all in moderate yield. In the case of the reaction with ethylene oxide disubstitution also occurred to form the diol **7**. Secondly, the corresponding chemistry of the neopentyl-substituted carbyne **10** was explored, and as is illustrated in Scheme 3 this led to the formation, again in moderate yield, of a range of β-functionalised carbyne complexes, all of which were obtained as moderately air-stable crystalline solids, characterised by elemental analysis and NMR spectroscopy. It is interesting that in the case of the neopentyl-substituted system there was no evidence for the formation of disubstituted complexes, in contrast with the corresponding reactions of the benzyl carbyne. As mentioned previously this can be explained by the enhanced 'acidity' of the carbyne β-CH present in the phenyl-substituted systems.

Since we intended to explore further the chemistry of the allyl-substituted carbynes **8** and **19** we sought to improve their yield by using the more reactive allyl bromide to quench the corresponding vinylidene anion. However, when the reaction of **11** with allyl bromide was examined only a slightly improved yield of **19** was obtained, but in addition a second minor purple crystalline product **20** was isolated (8%) by column chromatography. The elemental analysis and NMR spectra (see Experimental section) of **20** showed that the complex contained only one phosphite ligand together with a cyclopentadienyl ring and an organic fragment derived from the vinylidene and allyl moieties. Since an analogous product was only formed with allyl bromide and not with allyl chloride it was thought that by quenching **2** and **11** with the 'softer' allyl iodide an enhanced yield of this type of molecule might be obtained. This hypothesis proved to be correct only in the case of **11**.

Reaction of compound **2** with allyl iodide afforded a low yield (9%) of the purple crystalline material **9**, isostructural with **20**.



Scheme 3 L = P(OMe)$_3$. (*i*) +MeI; (*ii*) +EtBr; (*iii*) +SiMe$_3$Cl; (*iv*) + EtOCH$_2$Cl; (*v*) +MeSSMe; (*vi*) +$\overline{CH_2CH_2O}$; (*vii*) +Bu^{t}COCl; (*viii*) +CH$_2$=CHCH$_2$Cl

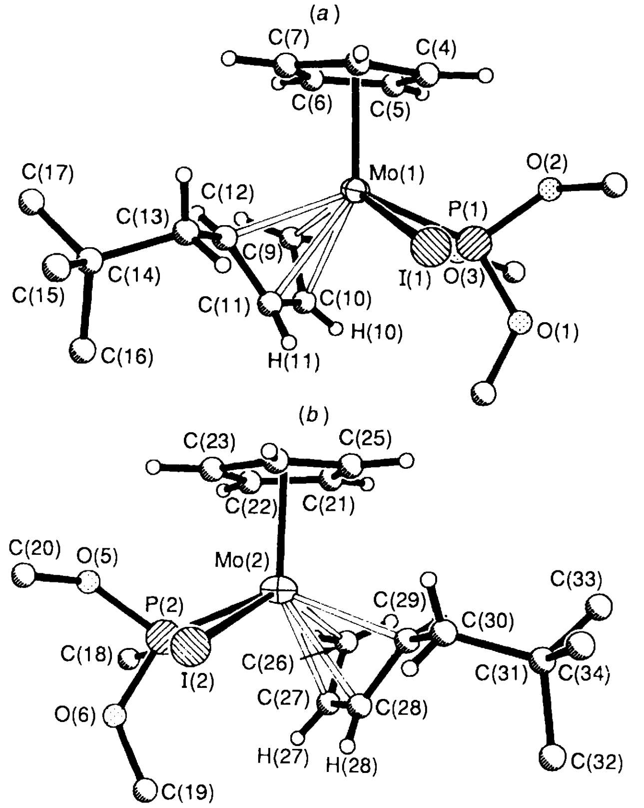


Fig. 1 Molecular structure of compound **21** showing labelling scheme for two independent molecules [(*a*) and (*b*)] present in the crystal structure, all methyl and cyclopentadienyl hydrogen atoms being omitted for clarity

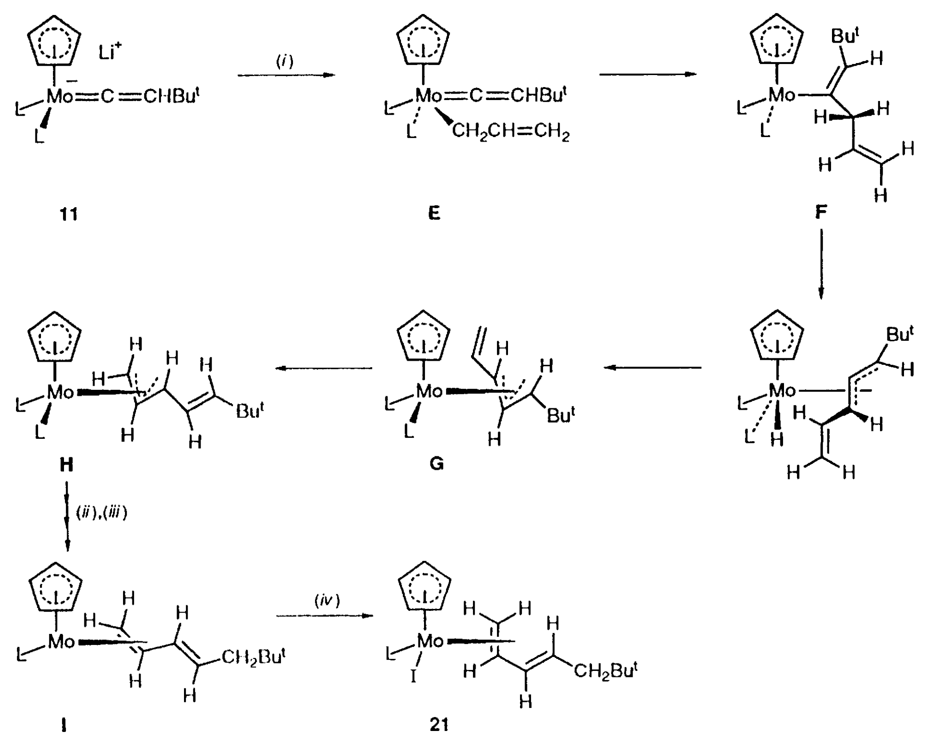
However, in the case of the reaction of **11** with allyl iodide there was no evidence for the formation of **19**, and a 47% yield of a purple crystalline material **21** was obtained. Examination of the NMR spectra together with the elemental analysis showed that this complex was structurally related to **9** and **20**. With this increased yield it was found possible to obtain crystals of **21** suitable for a single-crystal X-ray diffraction study.

The molecular geometry of one of the two crystallographically distinct molecules of compound **21** is illustrated in Fig. 1(*a*) selected bond lengths and angles being listed in Table 1; the geometry of the second molecule is essentially identical and is illustrated in Fig. 1(*b*). The purple complex is a molybdenum(II) 1,3-diene complex, where the molybdenum atom carries a η^5-cyclopentadienyl, a trimethyl phosphite, and an iodo ligand. In the solid state **21** exists as a racemic mixture of the enantiomer illustrated and its mirror image, and it is interesting that no other isomer is observed either in solution or in the solid state. The 1-neopentylbuta-1,3-diene adopts an *endo* configuration with respect to the η-C$_5$H$_5$ ligand, and is bonded asymmetrically. As might be expected the substituted end, which is effectively *trans* to the trimethyl phosphite ligand, is more weakly bonded.

It is not possible to understand with certainty the formation of compound **21** and by implication **9** and **20**, however this structural study strongly suggests that the vinylidene α-carbon becomes C(2) of the 1-neopentylbuta-1,3-diene ligand, the C$_5$ chain being formed by linking an allyl group with the vinylidene. An obvious way of achieving this is for allylation of **11** to occur regioselectively at the molybdenum centre, with the allyl and vinylidene fragments adopting a relative *cis* configuration. However, although such an intermediate, *i.e.* **E** in Scheme 4, has the potential for forming a C$_5$H$_6$Bu^t ligand by migration of the allyl group from the metal onto the α-carbon of the vinylidene, the isolated product **21** carries an additional hydrogen in that there is a C$_5$H$_7$Bu^t ligand present. Moreover, one of the trimethyl phosphite ligands has to be replaced by an iodo ligand. One way of achieving this is shown in Scheme 4. Migration of the allyl group in **E** onto the α-carbon generates a 16-electron vinyl-substituted species **F**, which would be

Table 1 Selected bond lengths (Å) and angles (°) for compound **21**

I(1)–Mo(1)	2.878(2)	Mo(1)–P(1)	2.404(2)	C(5)–C(6)	1.406(10)	C(6)–C(7)	1.391(13)
Mo(1)–C(4)	2.226(7)	Mo(1)–C(5)	2.240(7)	C(7)–C(8)	1.404(12)	C(9)–C(10)	1.407(10)
Mo(1)–C(6)	2.305(6)	Mo(1)–C(7)	2.345(8)	C(10)–C(11)	1.399(10)	C(11)–C(12)	1.370(10)
Mo(1)–C(8)	2.278(9)	Mo(1)–C(9)	2.271(9)	C(12)–C(13)	1.512(12)	C(13)–C(14)	1.504(10)
Mo(1)–C(10)	2.290(7)	Mo(1)–C(11)	2.356(6)	C(14)–C(15)	1.510(14)	C(14)–C(16)	1.493(16)
Mo(1)–C(12)	2.367(7)	I(2)–Mo(2)	2.873(2)	C(14)–C(17)	1.479(17)	P(2)–O(4)	1.578(5)
Mo(2)–P(2)	2.415(2)	Mo(2)–C(21)	2.306(8)	P(2)–O(5)	1.598(6)	P(2)–O(6)	1.599(6)
Mo(2)–C(22)	2.229(8)	Mo(2)–C(23)	2.245(10)	O(4)–C(18)	1.428(9)	O(5)–C(20)	1.425(11)
Mo(2)–C(24)	2.295(9)	Mo(2)–C(25)	2.350(8)	O(6)–C(19)	1.414(10)	C(21)–C(22)	1.394(17)
Mo(2)–C(26)	2.255(9)	Mo(2)–C(27)	2.286(8)	C(21)–C(25)	1.389(13)	C(22)–C(23)	1.429(15)
Mo(2)–C(28)	2.354(7)	Mo(2)–C(29)	2.388(7)	C(23)–C(24)	1.376(13)	C(24)–C(25)	1.381(16)
P(1)–O(1)	1.588(5)	P(1)–O(2)	1.595(5)	C(26)–C(27)	1.362(11)	C(27)–C(28)	1.412(9)
P(1)–O(3)	1.590(6)	P(1)–C(1)	1.408(8)	C(28)–C(29)	1.394(9)	C(29)–C(30)	1.500(10)
O(2)–C(2)	1.431(10)	O(3)–C(3)	1.427(10)	C(30)–C(31)	1.523(10)	C(31)–C(32)	1.515(13)
C(4)–C(5)	1.409(12)	C(4)–C(8)	1.439(11)	C(31)–C(33)	1.506(13)	C(31)–C(34)	1.546(11)
I(1)–Mo(1)–P(1)	85.1(1)	I(1)–Mo(1)–C(9)	140.1(2)	I(2)–Mo(2)–C(26)	137.7(2)	P(2)–Mo(2)–C(26)	86.6(2)
P(1)–Mo(1)–C(9)	87.5(2)	I(1)–Mo(1)–C(10)	104.2(2)	I(2)–Mo(2)–C(27)	102.8(2)	P(2)–Mo(2)–C(27)	80.4(2)
P(1)–Mo(1)–C(10)	81.1(2)	C(9)–Mo(1)–C(10)	35.9(3)	C(26)–Mo(2)–C(27)	34.9(3)	I(2)–Mo(2)–C(28)	80.8(2)
I(1)–Mo(1)–C(11)	81.3(2)	P(1)–Mo(1)–C(11)	105.2(2)	P(2)–Mo(2)–C(28)	105.4(2)	C(26)–Mo(2)–C(28)	62.1(3)
C(9)–Mo(1)–C(11)	63.1(3)	C(10)–Mo(1)–C(11)	35.0(3)	C(27)–Mo(2)–C(28)	35.4(2)	I(2)–Mo(2)–C(29)	87.6(2)
I(1)–Mo(1)–C(12)	86.5(2)	P(1)–Mo(1)–C(12)	138.9(2)	P(2)–Mo(2)–C(29)	139.6(2)	C(26)–Mo(2)–C(29)	73.3(3)
C(9)–Mo(1)–C(12)	73.9(3)	C(10)–Mo(1)–C(12)	62.2(3)	C(27)–Mo(2)–C(29)	62.9(2)	C(28)–Mo(2)–C(29)	34.2(2)
C(11)–Mo(1)–C(12)	33.7(2)	I(2)–Mo(2)–P(2)	84.4(1)	C(11)–C(12)–C(13)	121.8(7)	C(12)–C(13)–C(14)	117.2(7)
Mo(1)–C(9)–C(10)	72.8(5)	Mo(1)–C(10)–C(9)	71.3(4)	C(13)–C(14)–C(15)	110.3(7)	C(13)–C(14)–C(16)	109.5(7)
Mo(1)–C(10)–C(11)	75.0(4)	C(9)–C(10)–C(11)	119.2(7)	C(15)–C(14)–C(16)	105.7(9)	C(13)–C(14)–C(17)	112.1(8)
Mo(1)–C(11)–C(10)	70.0(4)	Mo(1)–C(11)–C(12)	73.6(4)	C(15)–C(14)–C(17)	109.8(9)	C(16)–C(14)–C(17)	109.2(10)
C(10)–C(11)–C(12)	120.9(6)	Mo(1)–C(12)–C(11)	72.7(4)	C(28)–C(29)–C(30)	123.8(6)	C(29)–C(30)–C(31)	115.6(7)
Mo(1)–C(12)–C(13)	125.6(5)	Mo(2)–C(26)–C(27)	73.8(5)	C(30)–C(31)–C(32)	110.3(6)	C(30)–C(31)–C(33)	112.0(6)
Mo(2)–C(27)–C(26)	71.3(5)	Mo(2)–C(27)–C(28)	74.9(4)	C(32)–C(31)–C(33)	110.3(8)	C(30)–C(31)–C(34)	108.7(7)
C(26)–C(27)–C(28)	118.2(6)	Mo(2)–C(28)–C(27)	69.7(4)	C(32)–C(31)–C(34)	107.9(7)	C(33)–C(31)–C(34)	107.7(7)
Mo(2)–C(28)–C(29)	74.3(4)	C(27)–C(28)–C(29)	121.0(6)				
Mo(2)–C(29)–C(28)	71.6(4)	Mo(2)–C(29)–C(30)	126.0(5)				



Scheme 4 L = P(OMe)$_3$. (*i*) +C_3H_5I, −LiI; (*ii*) −P(OMe)$_3$; (*iii*) +$C_3H_5PO(OMe)_2$, −$C_3H_4PO(OMe)_2$; (*iv*) isomerisation, +I^-

expected to rearrange by analogy with earlier work[9] into the η^3-pentadienyl species **G**. Slippage *via* a $\eta^3 \longrightarrow \sigma \longrightarrow \eta^3$ transformation would then access **H**. If the trimethyl phosphite ligands present in **H** are labile then allyl iodide would capture a free P(OMe)$_3$ ligand forming a co-ordinatively unsaturated molybdenum species **I** and $CH_2{=}CHCH_2PO(OMe)_2$. The molecule of dimethyl allylphosphonate could act as a proton donor to the end carbon of the unco-ordinated double bond of the η^3-pentadienyl ligand thus generating the cation $[\mathrm{Mo}(\eta^4\text{-}s\text{-}trans\text{-}\mathrm{C_5H_7Bu^t})\{\mathrm{P(OMe)_3}\}(\eta\text{-}\mathrm{C_5H_5})]^+$. A *trans* to *cis* isomerisation of the 1,3-diene[10,11] followed by capture of the cation with iodide anion then generates **21**. The stabilised carbanion $[\mathrm{CH_2}\cdots\mathrm{CH}\cdots\mathrm{CHPO(OMe)_2}]^-$ formed in the crucial proton-transfer step would be captured by the excess of allyl iodide present in the reaction mixture.

A key aspect of this explanation for the formation of the 1,3-diene complexes **9**, **20** and **21** is the suggestion that the use of 'soft' allyl iodide directs allylation to the 'soft' molybdenum centre of the ambident nucleophile $\mathrm{Li}[\mathrm{Mo(CCHBu^t)}\{\mathrm{P(OMe)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})]$. However, it should be remembered that both 'soft' methyl iodide and 'hard' pivaloyl chloride react at the β-carbon to form **12** and **18** respectively, implying that the factors which control the regioselectivity of these reactions are far from simple.

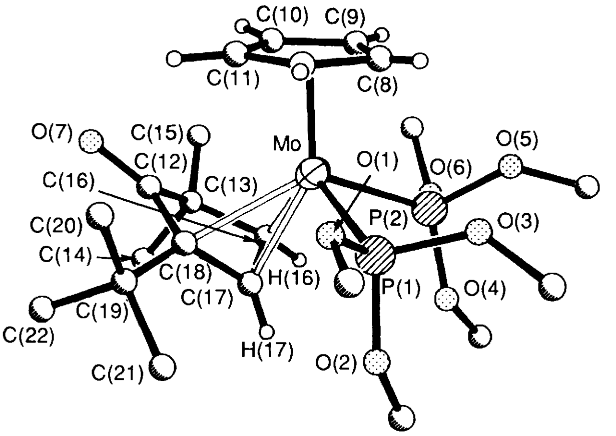
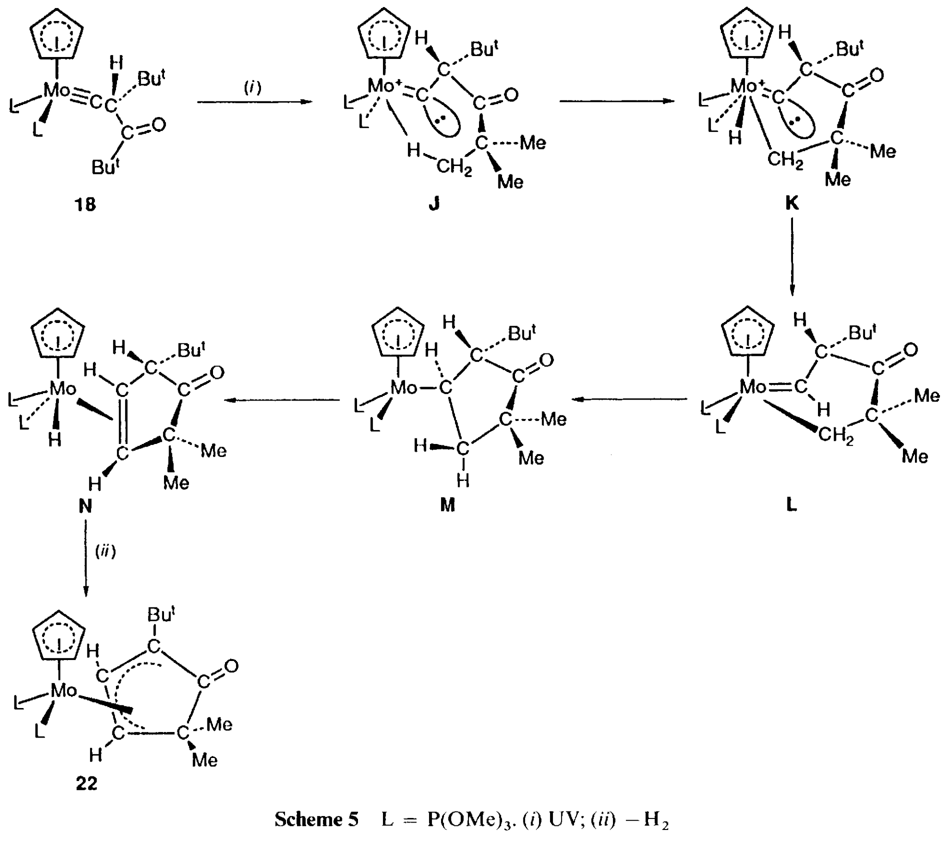


Fig. 2 Molecular structure of compound **22** showing labelling scheme. All methyl and cyclopentadienyl group hydrogen atoms have been omitted for clarity; only the high-occupancy sites for oxygen atoms O(5) and O(6) are shown

In considering the potential reactivity of these functionalised carbynes, attention was focused on the keto-substituted complex **18** in the belief that it might be possible to initiate a photochemical reaction *via* a n $\longrightarrow$ π^* transition. In the event an unexpected photochemical reaction intervened. Monitoring the photolysis of a hexane solution of **18** in a water-cooled quartz reaction vessel by infrared spectroscopy showed that over 24 h the CO stretching absorption at 1696 $\mathrm{cm^{-1}}$ disappeared to be replaced by another strong absorbance at 1642 $\mathrm{cm^{-1}}$ while the solution darkened from yellow to orange. Column chromatography of the reaction mixture led to the isolation (40% yield) of an orange crystalline solid, **22**, whose ^{1}H NMR spectrum contained resonances due to a cyclopentadienyl and two inequivalent trimethyl phosphite ligands but only one $\mathrm{Bu^t}$ group, the presence of signals corresponding to two methyl groups and two single protons suggesting that one of the $\mathrm{Bu^t}$ groups had been involved in an unusual reaction during the course of the photolysis. This was confirmed by a single-crystal X-ray diffraction study. The molecular geometry of **22** is shown in Fig. 2, selected bond lengths and interbond angles being listed in Table 2.

The molecule carries a bis(trimethyl phosphite)cyclopentadienylmolybdenum fragment bonded to a η^3-4,4-dimethyl-5-oxocyclopentenyl ligand, in which the η^3-allyl adopts an *endo* configuration. As with many[12] molybdenum(II) η^3-allyls the inner carbon C(17) is closer to the metal than the outer carbons C(16) and C(18) [Mo–C(16) 2.310(5), Mo–C(17) 2.217(5), Mo–C(18) 2.362(5) Å]. The $\mathrm{C_5}$ ring has a flattened envelope conformation which is presumably reinforced by conjugation between the η^3-allyl group and the ketonic carbonyl. This is reflected in the C(12)–C(18) distance of 1.478(8) Å, which is significantly shorter than a normal [1.53(1) Å] carbon–carbon single bond. The ketonic carbonyl bond distance of C(12)–O(7) 1.234(6) Å also indicates some delocalisation. It is suggested that in this unusual cyclisation reaction the original carbyne contact carbon present in **18** becomes the central η^3-allylic carbon C(17) of the keto-η^3-allylic complex **22**.



Scheme 5 L = $\mathrm{P(OMe)_3}$. (*i*) UV; (*ii*) $-\mathrm{H_2}$

Table 2 Selected bond lengths (Å) and angles (°) for compound **22**

Mo–P(1)	2.381(2)	Mo–P(2)	2.400(2)	P(1)–Mo–P(2)	85.9(1)	P(1)–Mo–C(16)	119.0(1)
Mo–C(7)	2.318(6)	Mo–C(8)	2.278(6)	P(2)–Mo–C(16)	75.4(1)	P(1)–Mo–C(17)	87.5(2)
Mo–C(9)	2.306(6)	Mo–C(10)	2.356(8)	P(2)–Mo–C(17)	91.4(1)	C(16)–Mo–C(17)	37.2(2)
Mo–C(11)	2.357(6)	Mo–C(16)	2.310(5)	P(1)–Mo–C(18)	93.8(1)	P(2)–Mo–C(18)	127.3(1)
Mo–C(17)	2.217(6)	Mo–C(18)	2.362(5)	C(16)–Mo–C(18)	58.9(2)	C(17)–Mo–C(18)	36.1(2)
P(1)–O(1)	1.599(4)	P(1)–O(2)	1.606(4)	O(7)–C(12)–C(13)	123.9(5)	O(7)–C(12)–C(18)	127.7(4)
P(1)–O(3)	1.599(5)	P(2)–O(4)	1.574(5)	C(13)–C(12)–C(18)	108.1(4)	C(12)–C(13)–C(14)	106.6(4)
P(2)–O(5)	1.585(5)	P(2)–O(5′)	1.632(28)	C(12)–C(13)–C(15)	115.5(5)	C(14)–C(13)–C(15)	108.1(5)
P(2)–O(6)	1.621(5)	P(2)–O(6′)	1.618(19)	C(12)–C(13)–C(16)	98.1(4)	C(14)–C(13)–C(16)	111.4(5)
O(1)–C(1)	1.404(9)	O(2)–C(2)	1.397(8)	C(15)–C(13)–C(16)	116.6(4)	Mo–C(16)–C(13)	110.1(3)
O(3)–C(3)	1.389(11)	O(4)–C(4)	1.433(7)	Mo–C(16)–C(17)	67.9(4)	C(13)–C(16)–C(17)	107.7(4)
O(5)–C(5)	1.437(6)	O(5′)–C(5)	1.476(21)	Mo–C(17)–C(16)	74.9(3)	Mo–C(17)–C(18)	77.5(3)
O(6)–C(6)	1.399(8)	O(6′)–C(6)	1.392(26)	C(16)–C(17)–C(18)	106.3(4)	Mo–C(18)–C(12)	93.9(3)
O(7)–C(12)	1.234(6)	C(7)–C(8)	1.398(8)	Mo–C(18)–C(17)	66.4(2)	C(12)–C(18)–C(17)	107.6(4)
C(7)–C(11)	1.372(10)	C(8)–C(9)	1.397(10)	Mo–C(18)–C(19)	132.0(4)	C(12)–C(18)–C(19)	118.2(4)
C(9)–C(10)	1.385(10)	C(10)–C(11)	1.377(8)	C(17)–C(18)–C(19)	126.1(5)	C(18)–C(19)–C(20)	112.2(4)
C(12)–C(13)	1.543(6)	C(12)–C(18)	1.478(8)	C(18)–C(19)–C(21)	112.0(4)	C(20)–C(19)–C(21)	109.6(5)
C(13)–C(14)	1.532(8)	C(13)–C(15)	1.524(8)	C(18)–C(19)–C(22)	108.4(4)	C(20)–C(19)–C(22)	109.3(4)
C(13)–C(16)	1.521(8)	C(16)–C(17)	1.445(7)	C(21)–C(19)–C(22)	105.1(5)		
C(17)–C(18)	1.428(6)	C(18)–C(19)	1.537(6)				
C(19)–C(20)	1.526(8)	C(19)–C(21)	1.541(9)				
C(19)–C(22)	1.538(8)						

The initial step in the photochemical reaction possibly involves a singlet ($\pi \longrightarrow \pi^*$) transition to a linear excited state (Franck–Condon principle) followed by relaxation to a more stable bent dipolar form, the resulting 16-electron molybdenum centre interacting with one of the pivaloyl, Bu^t methyl C–H bonds to form the intermediate **J** (Scheme 5). Complete transfer of the agostic hydrogen present in **J** to the molybdenum followed by proton transfer to the carbanionic α-carbon would then form the 4-metallacyclohex-3-enone **L**. The C_5 ring present in the final product **22** is then created *via* a ring contraction resulting from migration of the CH_2CMe_2 chain from the molybdenum to the carbene carbon. β-Hydrogen abstraction followed by protolysis of the Mo–H bond by the relatively acidic α-keto hydrogen then results in H_2 loss and formation of **22**. In agreement with this suggestion photolysis of the deuterio analogue of **18**, *i.e.* [Mo{≡CCD(Bu^t)COBu^t}{P(OMe)$_3$}$_2$(η-C_5H_5)], afforded **22** with no deuterium content as determined by ^{2}D NMR and mass spectrometry.

In conclusion we have shown that carbynes of the type [Mo(≡CCH$_2$R){P(OMe)$_3$}$_2$(η-C_5H_5)] can be deprotonated to form vinylidene anions, which can be quenched with a range of electrophiles. Although reaction occurs predominantly at the β-carbon of the vinylidene there is evidence that certain electrophiles can also attack the molybdenum centre. There are indications that carbyne complexes might have an interesting photochemistry.

Experimental

The ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} NMR spectra were recorded on JEOL FX90Q, FX200, or Bruker W-360 spectrometers as appropriate. Data are given for room-temperature measurements, and coupling constants are in Hz. Chemical shifts are positive to high frequency of the reference $SiMe_4$ for ^{13}C and ^{1}H and H_3PO_4 (84% external) for ^{31}P. Infrared spectra were recorded on a Perkin-Elmer 983 G spectrophotometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled and degassed solvents.

Reactions of Li[Mo(CCHPh){P(OMe)$_3$}$_2$(η-C_5H_5)] **2**.—(*a*) *With iodomethane*. A solution of butyllithium (0.40 mmol) in hexane was added to a cooled (−30 °C) solution of [Mo(≡CCH$_2$Ph){P(OMe)$_3$}$_2$(η-C_5H_5)]^2 **1** (0.20 g, 0.39 mmol) in diethyl ether (10 cm^3). On warming to −10 °C the solution changed from yellow to bright red due to the formation of **2**. NMR (C_6D_6, thf, −30 °C): ^{13}C-{^{1}H}, δ 317.4 [t, Mo=C, ^2J(CP) 17.7], 139.2–124 (s, Ph), 122.5 (s, MoC*C*), 87.1 (s, C_5H_5) and 50.3 (s, POMe) [in the proton-coupled spectrum the singlet at δ 122.5 appears as a doublet, ^1J(CH) 144.0 Hz]; ^{31}P-{^{1}H}, δ 212.5 (s, POMe). The red solution of **2** was recooled to −30 °C and iodomethane (0.2 cm^3, 0.46 g, 3.21 mmol) added. On warming to room temperature the colour changed from red to yellow. The volatile material was removed in vacuo, the residue extracted into hexane and chromatographed on alumina. Elution with hexane–diethyl ether (4:1) gave first a yellow band, which on recrystallisation (−40 °C) from hexane afforded yellow *crystals* of [Mo{≡CCH(Me)Ph}{P(OMe)$_3$}$_2$(η-C_5H_5)] **3** (0.09 g, 44%) (Found: C, 45.4; H, 6.0. $C_{20}H_{32}MoO_6P_2$ requires C, 45.6; H, 6.1%). NMR (C_6D_6): ^{1}H, δ 7.37–7.10 (m, 5 H, Ph), 5.21 (s, 5 H, C_5H_5), 3.50 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.8], 3.38 [d, 9 H, POMe′, |^3J(HP) + ^5J(HP′)| 11.4], 3.31 (m, 1 H, Mo≡CCH) and 1.47 [d, 3 H, Me, ^3J(HH′) 7.4]; ^{13}C-{^{1}H}, δ 298.0 [t, Mo≡C, ^2J(CP) 25], 145.2–122.0 (s, Ph), 90.1 (s, C_5H_5), 63.2 (s, MoC*C*), 51.2 (s, POMe) and 32.3 (s, Me); ^{31}P-{^{1}H}, δ 214.2 [d, POMe, ^2J(PP′) 60.6 Hz]. Further elution afforded a second yellow band which on recrystallisation (−40 °C) from hexane gave yellow *crystals* of [Mo(≡CCMe$_2$Ph){P(OMe)$_3$}$_2$(η-C_5H_5)] **4** 0.05 g, 24%) identified by comparison with published NMR data.

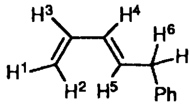
(*b*) *With chlorotrimethylsilane*. Similarly, reaction (−30 °C) of compound **2** (0.39 mmol) with $SiMe_3Cl$ (3.0 cm^3, 2.57 g, 23.6 mmol) followed by chromatographic work-up gave on recrystallisation (−78 °C) from hexane yellow *crystals* of [Mo{≡CCH(SiMe$_3$)Ph}{P(OMe)$_3$}$_2$(η-C_5H_5)] **5** (0.16 g, 39%) (Found: C, 45.2; H, 6.4. $C_{22}H_{38}MoO_6P_2Si$ requires C, 45.2; H, 6.5%). NMR (C_6D_6): ^{1}H, δ 7.28–7.12 (m, 5 H, Ph), 5.21 [t, 5 H, C_5H_5, ^3J(HP) 0.9], 3.56 [t, 1 H, Mo≡CCH, ^4J(HP) 4.4], 3.46 [at (apparent triplet), 18 H, POMe, |^3J(HP) + ^5J(HP′)| 11.8], and 0.12 (s, 9 H, $SiMe_3$); ^{13}C-{^{1}H}, δ 292.7 [t, Mo≡C, ^2J(CP) 28.6 Hz], 141.7, 139.1, 125.9, 124.7 (s, Ph), 89.1 (s, C_5H_5), 64.1 (s, Mo≡C*C*), 50.8 (s, POMe) and −1.9 (s, $SiMe_3$); ^{31}P-{^{1}H}, δ 213.2 (s, POMe).

(*c*) *With ethylene oxide*. A similar reaction (−30 °C) between compound **3** (0.61 mmol) and ethylene oxide (1.5 cm^3, 1.34 g, 30.5 mmol) followed by quenching with MeOH (2 cm^3) gave on chromatographic work-up and elution with diethyl ether a yellow band which on recrystallisation (−30 °C) from hexane–diethyl ether gave yellow *crystals* of [Mo{≡CCH(CH$_2$CH$_2$OH)Ph}{P(OMe)$_3$}$_2$(η-C_5H_5)] **6** (0.12 g, 35%) (Found: C, 45.3; H, 6.5. $C_{21}H_{34}MoO_7P_2$ requires C, 45.3; H, 6.1%). NMR (C_6D_6): ^{1}H, δ 7.33–7.04 (m, 5 H, Ph) 5.22 (s, 5 H, C_5H_5), 3.66 [t, 2 H,

CH_2OH, ^3J(HH′) 7.4], 3.50 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.33 [d, 9 H, POMe′, |^3J(HP) + ^5J(HP′)| 11.4], 2.23 (m, 2 H, CH_2CH_2OH) and 2.00 (m, 1 H, Mo≡CCH); ^{13}C-{^{1}H}, δ 300.1 [t, Mo≡C, ^2J(CP) 28.6], 143.5 (s, *ipso*-Ph), 130.0, 128.8, 126.1 (s, Ph), 89.2 (s, C_5H_5), 61.4, 60.8 (s, Mo≡C*C* and CH_2OH), 51.0 [d, POMe, ^2J(CP) 4.4] and 40.4 (s, CH_2CH_2OH); ^{31}P-{^{1}H}, δ 212.9 [d, POMe, ^2J(PP′) 61.0] and 211.9 [d, POMe′, ^2J(PP′) 61.0 Hz]. Further elution with diethyl ether–thf (3:2) and recrystallisation (−78 °C) from diethyl ether afforded pale yellow *crystals* of [Mo{≡CC(CH_2CH_2OH)$_2$Ph}{P(OMe)$_3$}$_2$(η-C_5H_5)] **7** (0.02 g, 5%) (Found: C, 45.7; H, 6.2. $C_{23}H_{38}MoO_8P_2$ requires C, 46.0, H, 6.3%). ^{1}H NMR (C_6D_6): δ 7.39–6.87 (m, 5 H, Ph), 4.93 [t, 5 H, C_5H_5, ^3J(HP) 0.9], 3.45 [t, 4 H, CH_2OH, ^3J(HH′) 7.0], 3.10 [at, 18 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4] and 2.00 [t, 4 H, CH_2CH_2OH, ^3J(HH′) 7.0 Hz].

(*d*) *With allyl chloride.* An analogous reaction between compound **2** (0.82 mmol) and allyl chloride (2.0 cm^3, 1.87 g, 24.4 mmol) gave on chromatography and crystallisation (−78 °C) from hexane yellow *crystals* of [Mo{≡CCH($CH_2CH{=}CH_2$)Ph}{P(OMe)$_3$}$_2$(η-C_5H_5)] **8** (0.18 g, 40%) (Found: C, 47.8; H, 6.4. $C_{22}H_{34}MoO_6P_2$ requires C, 47.8; H, 6.2%). NMR (C_6D_6): ^{1}H, δ 7.42–6.97 (m, 5 H, Ph), 5.22 (m, 1 H, $CH{=}CH_2$), 5.21 [t, 5 H, C_5H_5, ^3J(HP) 0.9], 4.98 (m, 2 H, $CH{=}CH_2$), 3.50 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.8], 3.34 [d, 9 H, POMe′, |^3J(HP′) + ^5J(HP)| 11.8], and 3.16–2.44 [m, 3 H, Mo≡C CH(Ph)CH_2]; ^{31}P-{^{1}H}, δ 213.6 [d, POMe, ^2J(PP′) 61.0] and 212.8 [d, POMe′, ^2J(PP′) 61.0 Hz].

(*e*) *With allyl iodide*. Similarly, reaction of compound **2** (0.42 mmol) with allyl iodide (2.0 cm^3, 3.67 g, 21.9 mmol) afforded purple *crystals* of [MoI(η^4-$CH_2{=}CHCH{=}CHCH_2Ph$){P(OMe)$_3$}(η-C_5H_5)] **9** (0.2 g, 9%) (Found: C, 40.1; H, 4.7. $C_{18}H_{26}IMoO_3P$ requires C, 39.7; H, 4.8%). NMR (C_6D_6): ^{1}H, δ 7.34–7.06 (m, 5 H, Ph), 5.78 (m, 1 H, H^3), 5.57 [dd, 1 H, H^4, ^3J(H^{4}H^5) 6.7, ^3J(H^{4}H^3) 3.1], 4.73 [d, 5 H, C_5H_5, ^3J(HP) 1.3], 3.34 [d, 9 H, POMe, ^3J(HP) 10.1 Hz], 2.72 (m, 1 H, H^7), 1.76 (m, 1 H, H^1), 1.32 (m, 1 H, H^6), 0.94 (m, 1 H, H^5) and −0.12 (m, 1 H, H^2); ^{31}P-{^{1}H}, δ 182.5 (s, POMe).



Reaction of Li[Mo(CCHBu^t){P(OMe)$_3$}$_2$(η-C_5H_5)] **11**.—(*a*) *With iodomethane.* A solution of butyllithium (1.42 mmol) in hexane was added to a cooled (−30 °C) solution of [Mo(≡CCH_2Bu^t){P(OMe)$_3$}$_2$(η-C_5H_5)][2] **10** (1.42 mmol) in diethyl ether (30 cm^3). The reaction mixture was allowed to warm to −10 °C and then recooled to −30 °C, becoming deep red due to the presence of compound **11**. NMR: ^{13}C-{^{1}H} (C_6D_6, thf, −30 °C), δ 322.8 [t, Mo=C, ^2J(CP) 17 Hz], 121.8 (s, MoC*C*), 87.0 (s, C_5H_5), 50.2 (s, POMe), 33.1 (s, *C*Me$_3$) and 27.2 (s, C*Me*$_3$); ^{31}P-{^{1}H} ([$^2H_8$]thf, −30 °C), δ 213.4 (s). Iodomethane (2.0 cm^3, 4.55 g, 32.1 mmol) was added to the red solution and the reaction mixture allowed to warm to room temperature. The volatile material was removed *in vacuo*, the residue extracted into hexane and chromatographed on an alumina-packed column. Elution with hexane–diethyl ether (4:1) gave a single yellow band which was collected and recrystallised (−78 °C) from hexane to give yellow *crystals* of [Mo{≡CCH(Me)Bu^t}{P(OMe)$_3$}$_2$(η-C_5H_5)] **12** (0.31 g, 43%) (Found: C, 42.3; H, 7.5. $C_{18}H_{36}MoO_6P_2$ requires C, 42.7; H, 7.2%). NMR (C_6D_6); ^{1}H, δ 5.18 (s, 5 H, C_5H_5), 3.50 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.48 [d, 9 H, POMe′, |^3J(HP) + ^5J(HP′)| 11.8], 2.07 (m, 1 H, Mo≡CCH), 1.1 [d, 3 H, Me, ^3J(HH′) 7.0] and 1.0 (s, 9 H, Bu^t); ^{13}C-{^{1}H}, δ 308.4 [t, Mo≡C, ^2J(CP) 27.5], 89.4 (s, C_5H_5), 62.3 (s, Mo≡C*C*), 50.8 (s, POMe), 34.7 (s, *C*Me$_3$), 28.3 (s, C*Me*$_3$), and 14.7 (s, Me); ^{31}P-{^{1}H}, δ 214.6 [d, POMe, ^2J(PP′) 61.0] and 212.7 [d, POMe′, ^2J(PP′) 61.0 Hz].

(*b*) *With bromoethane.* A similar reaction between compound **11** (1.38 mmol) and bromoethane (1.5 cm^3, 3.19 g, 29.6 mmol) followed by chromatography and recrystallisation (−78 °C) from hexane gave yellow *crystals* of [Mo{≡CCH(Et)Bu^t}{P(OMe)$_3$}$_2$(η-C_5H_5)] **13** (0.32 g, 45%) (Found: C, 44.0; H, 7.4. $C_{19}H_{38}MoO_6P_2$ requires C, 43.8; H, 7.3%). NMR (C_6D_6): ^{1}H, δ 5.57 (s, 5 H, C_5H_5), 3.53 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.51 [d, 9 H, POMe′, |^3J(HP′) − ^5J(HP)| 10.5], 3.27 (m, 2 H, CH_2), 2.65 (m, 1 H, Mo≡CCH), 1.48 (s, 9 H, Bu^t) and 1.11 [t, 3 H, Me, ^3J(HH) 7.0]; ^{13}C-{^{1}H}, δ 310.9 [t, Mo≡C, ^2J(CP) 24.2], 90.4 (s, C_5H_5), 70.9 (s, Mo≡C*C*), 51.1 (s, POMe), 35.7 (s, *C*Me$_3$), 32.3 (s, CH_2), 30.5 (s, C*Me*$_3$) and 15.5 (s, Me); ^{31}P-{^{1}H}, δ 207.4 [d, POMe, ^2J(PP′) 59.8] and 205.8 [d, POMe′, ^2J(PP′) 59.8].

(*c*) *With chlorotrimethylsilane*. Similarly, reaction (−30 °C) of compound **11** (1.20 mmol) and $SiMe_3Cl$ (1.5 cm^3, 1.29 g, 11.8 mmol) afforded yellow *crystals* of [Mo{≡CCH($SiMe_3$)Bu^t}{P(OMe)$_3$}$_2$(η-C_5H_5)] **14** (0.26 g, 38%) (Found: C, 42.7; H, 7.5. $C_{20}H_{42}MoO_6P_2Si$ requires C, 42.6; H, 7.4%). NMR (C_6D_6): ^{1}H, δ 5.18 (s, 5 H, C_5H_5), 3.54 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.48 [d, 9 H, POMe′, |^3J(HP) + ^5J(HP)| 11.4], 2.29 [t, 1 H, Mo≡CCH, ^4J(HP) 4.2], 1.12 (s, 9 H, Bu^t) and 0.10 (s, 9 H, $SiMe_3$); ^{13}C-{^{1}H}, δ 304.7 [t, Mo≡C, ^2J(CP) 25.7], 89.5 (s, C_5H_5), 70.2 (s, Mo≡C*C*), 51.0 (s, POMe), 35.2 (s, *C*Me$_3$), 28.6 (s, C*Me*$_3$) and −1.9 (s, $SiMe_3$); ^{31}P-{^{1}H}, δ 213.4 [d, POMe, ^2J(PP′) 60.2] and 211.6 [d, POMe′, ^2J(PP′) 60.2 Hz].

(*d*) *With chloromethyl ethyl ether*. Quenching of compound **11** (0.84 mmol) with $EtOCH_2Cl$ (1.5 cm^3, 1.44 g, 15.2 mmol) and subsequent column chromatography followed by crystallisation (−78 °C, hexane) gave yellow *crystals* of [Mo{≡CCH(CH_2OEt)Bu^t}{P(OMe)$_3$}$_2$(η-C_5H_5)] **15** (0.12 g, 32%) (Found: C, 43.3; H, 7.2. $C_{20}H_{40}MoO_7P_2$ requires C, 43.6; H, 7.3%). NMR (C_6D_6); ^{1}H, δ 5.22 (s, 5 H, C_5H_5), 4.60 [dd, 2 H, CH_2OEt, ^2J(HH′) 6.6, ^3J(HH′) 7.4], 3.52 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.49 [d, 9 H, POMe′, |^3J(HP′) + ^5J(HP)| 11.8], 3.40 [q, 2 H, CH_2CH_3, ^3J(HH′) 7.0], 2.41 (m, 1 H, Mo≡CC*H*), 1.26 (s, 9 H, Bu^t) and 1.11 [t, 3 H, Me, ^3J(HH′) 7.0]; ^{31}P-{^{1}H}, δ 214.5 [d, POMe, ^2J(PP′) 61.7] and 212.3 [d, POMe′, ^2J(PP′) 61.7 Hz].

(*e*) *With dimethyl disulphide*. A similar reaction between compound **11** (1.63 mmol) and MeSSMe (2.0 cm^3, 2.09 g, 22.2 mmol) gave yellow *crystals* of [Mo{≡CCH(SMe)Bu^t}{P(OMe)$_3$}$_2$(η-C_5H_5)] **16** (0.43 g, 49%) (Found: C, 40.3, H, 6.9. $C_{18}H_{36}MoO_6P_2S$ requires C, 40.1; H, 6.7%). NMR (C_6D_6): ^{1}H, δ 5.19 (s, 5 H, C_5H_5), 3.54 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.47 [d, 9 H, POMe′, |^3J(HP′) + ^5J(HP)| 11.4], 2.77 [t, 1 H, Mo≡CCH, |^4J(HP) + ^4J(HP′)| 8.3], 2.14 (s, 3 H, SMe) and 1.20 (s, 9 H, Bu^t); ^{13}C-{^{1}H}, δ 294.5 [t, Mo≡C, |^2J(CP) + ^2J(CP′)| 55.0], 89.6 (s, C_5H_5), 74.3 (s, Mo≡C*C*), 51.1 [d, POMe, ^2J(CP) 6.6 Hz], 37.3 (s, *C*Me$_3$), 28.5 (s, C*Me*$_3$) and 17.3 (s, SMe); ^{31}P-{^{1}H}, δ 211.8 (s, POMe).

(*f*) *With ethylene oxide*. An excess of $\overline{CH_2CH_2O}$ (1.5 cm^3, 1.34 g, 30.5 mmol) was added to a cooled (−30 °C) solution of compound **11** (1.06 mmol) and the reaction mixture was allowed to warm to room temperature; no visible change in colour occurred. After 1 h the solution was cooled to −30 °C and quenched with methanol (5 cm^3), this causing an immediate colour change from red to yellow. Work-up of the reaction mixture afforded yellow *crystals* of [Mo{≡CCH(CH_2CH_2OH)Bu^t}{P(OMe)$_3$}$_2$(η-C_5H_5)] **17** (0.18 g, 33%) (Found: C, 42.7; H, 7.3 $C_{19}H_{38}MoO_7P_2$ requires C, 42.5; H, 7.1%). NMR (C_6D_6): ^{1}H, δ 5.20 (s, 5 H, C_5H_5), 3.85 [t, 2 H, CH_2OH, |^3J(HH) + ^3J(HH′)| 12.7], 3.47 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.37 [d, 9 H, POMe′, |^3J(HP′) + ^5J(HP)| 11.4], 2.53 (br s, 1 H, OH), 2.07 (m, Mo≡CCH), 1.75 (m, 2 H, CH_2CH_2OH) and 1.11 (s, 9 H, Bu^t); ^{13}C-{^{1}H}, δ 309.6 [t, Mo≡C, ^2J(CP) 26.4], 89.4 (s, C_5H_5), 64.5 (s, Mo≡C*C*), 62.1 (s, CH_2OH), 51.1 (s, POMe), 35.2 (s, *C*Me$_3$), 33.6 (s, CH_2CH_2OH) and 28.5 (s, C*Me*$_3$); ^{31}P-{^{1}H}, δ 212.8 [d, POMe, ^2J(PP′) 59.8] and 210.5 [d, POMe′, ^2J(PP′) 59.8 Hz].

(*g*) *With* 2,2-*dimethylpropanoyl chloride*. Reaction of compound **11** (1.42 mmol) with Bu^{t}COCl (2.0 cm^3, 1.96 g, 16.2 mmol) gave, on chromatography and crystallisation (−78 °C hexane), yellow *crystals* of [Mo{≡CCH(COBu^t)Bu^t}-

Table 3 Structure analyses[a]

Compound	**21**	**22**
Crystal data		
Formula	$C_{17}H_{30}IMoO_3P$	$C_{22}H_{40}MoO_7P_2$
M	536.2	574.4
a/Å	12.922(8)	10.122(9)
b/Å	15.479(5)	27.265(13)
c/Å	21.991(15)	10.059(9)
β/°	102.84(5)	111.35(6)
U/Å^3	4288(4)	2583(3)
Z	8	4
D_c/g cm^{-3}	1.66	1.48
F(000)	2128	1200
μ(Mo-Kα) cm^{-1}	21.0	6.5
Data collection and reduction		
Crystal dimensions (mm)	0.05 × 0.35 × 0.7	0.5 × 0.2 × 0.2
2θ range (°)	4–45	3–50
Total data	6155	4972
Unique data	5624	4556
'Observed' data, N_o	4665	3617
Observation criterion [$F^2 > n\sigma(F^2)$]	1.5	2
Crystal faces [distance from origin (mm)]	(100) [0.35], $(00\bar{1})$ [0.025], (001) [0.025], $(\bar{1}\bar{1}1)$ [0.35], $(0\bar{1}0)$ [0.175], (010) [0.175]	—
No. of azimuthal scan data	—	302
Minimum, Maximum transmission coefficient	0.709–0.949	0.762–0.907
Refinement		
Disordered atoms	None	O(5), O(6)
Least-squares variables, N_v	507	359
R^b	0.041	0.048
R'^b	0.049	0.050
S^b	1.44	1.85
g	0.0005	0.0002
Final difference map features (e Å^{-3})	+0.59, −0.69	+1.4, −1.7

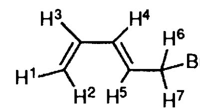
[a] Details in common: monoclinic, space group $P2_1/n$ (no. 14); 295 K; λ (Mo-Kα) 0.710 69 Å; ω–2θ scans; scan width 1.0 + $\Delta\alpha_1\alpha_2$; [b] $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = [\Sigma w\Delta^2/\Sigma wF_o^{\,2}]^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$; $w = [\sigma_c^{\,2}(F_o) + gF_o^{\,2}]^{-1}$, $\sigma_c^{\,2}(F_o)$ = variance in F_o due to counting statistics.

{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **18** (0.32 g, 39%) (Found: C, 46.1 H, 7.5. $C_{22}H_{42}MoO_7P_2$ requires C, 45.8; H, 7.3%), ν$_{CO}$(hexane) 1696 cm^{-1}. NMR (C$_6$D$_6$): ^{1}H, δ 5.18 (s, 5 H, C$_5$H$_5$), 3.67 [t, 1 H, Mo≡CCH, |^4J(HP) + ^4J(HP′)| 8.3], 3.47 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.45 [d, 9 H, POMe′, ^3J(HP′) + ^5J(HP)| 11.4], 1.21 (s, 9 H, Bu^t) and 1.19 (s, 9 H, Bu^t); ^{13}C-{^{1}H}, δ 294.5 [t, Mo≡C, ^2J(CP) 26.4], 209.2 (s, CO), 89.5 (s, C$_5$H$_5$), 74.9 (s, Mo≡C*C*), 51.0 (s, POMe), 44.7 (s, CO*C*Me$_3$), 37.0 (s, *C*Me$_3$), 29.0 (s, COC*Me*$_3$) and 27.3 (s, C*Me*$_3$); ^{31}P-{^{1}H}, δ 211.2 [d, POMe, ^2J(PP′) 59.2] and 210.4 [d, POMe′, ^2J(PP′) 59.2 Hz].

(*h*) *With allyl chloride*. Reaction of compound **11** (0.91 mmol) with allyl chloride (2.0 cm^3, 1.87 g, 24.4 mmol) afforded on column chromatography one product, which on crystallisation (−78 °C, hexane) gave yellow *crystals* of [Mo{≡CCH(CH$_2$-CH=CH$_2$)Bu^t}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **19** (0.15 g, 31%) (Found: C, 45.1; H, 7.4. $C_{20}H_{38}MoO_6P_2$ requires C, 45.1; H, 7.2%). NMR (C$_6$D$_6$): ^{1}H, δ 6.29 (m, 1 H, C*H*=CH$_2$), 5.21 (s, 5 H, C$_5$H$_5$), 5.04 (m, 2 H, CH=C*H*$_2$), 3.49 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 11.4], 3.48 [d, 9 H, POMe′, |^3J(HP′) + ^5J(HP)| 11.4], 2.76–1.82 (m, 3 H, Mo≡CC*HCH*$_2$) and 1.13 (s, 9 H, Bu^t); ^{13}C-{^{1}H}, δ 307.7 [t, Mo≡C, ^2J(CP) 25.3], 141.3 (s, C=*C*H), 113.3 (s, C=*C*H$_2$), 89.5 (s, C$_5$H$_5$), 68.3 (s, Mo≡C*C*), 51.0 (s, POMe), 35.6 (s, CH$_2$), 32.6 (s, *C*Me$_3$) and 28.7 (s, C*Me*$_3$); ^{31}P-{^{1}H}, δ 213.7 [d, POMe, ^2J(PP′) 61.0] and 212.1 [d, POMe′, ^2J(PP′) 61.0 Hz].

(*i*) *With allyl bromide*. After quenching compound **11** (0.81 mmol) with allyl bromide (2.0 cm^3, 2.80 g, 23.1 mmol), column chromatography gave two bands. Elution with hexane–diethyl ether (3:2) gave a yellow band, which on crystallisation (−78 °C, hexane) gave yellow *crystals* of **19** (0.17 g, 39%).

Further elution with diethyl ether gave a maroon band, which was crystallised [−78 °C, hexane–diethyl ether (4:1)] to give purple *crystals* of [MoBr(η^4-CH$_2$=CHCH=CHCH$_2$Bu^t)-{P(OMe)$_3$}(η-C$_5$H$_5$)] **20** (0.03 g, 8%) (Found: C, 41.5; H, 6.4. $C_{17}H_{30}BrMoO_3P$ requires C, 41.7; H, 6.1%). NMR (C$_6$D$_6$): ^{1}H, δ 6.32 (m, 1 H, H^3), 5.47 [br dd, 1 H, H^4, ^3J(H^{4}H^5) 10.3, ^3J(H^{4}H^3) 5.9], 4.71 [d, 5 H, C$_5$H$_5$, ^3J(HP) 1.8], 3.46 [d, 9 H, POMe, ^3J(HP) 10.1], 2.48 (m, 1 H, H^7), 1.97 [br d, 1 H, H^1, ^3J(H^{1}H^3) 6.5 Hz], 1.59 (m, 1 H, H^6), 1.30 (m, 1 H, H^5), 1.08 (s, 9 H, Bu^t) and −0.08 (m, 1 H, H^2); ^{31}P-{^{1}H}, δ 183.4 (s, POMe).



(*j*) *With allyl iodide*. Similarly, reaction of compound **11** (1.22 mmol) with allyl iodide (2.0 cm^3, 3.67 g, 21.9 mmol) and subsequent chromatographic work-up gave only a purple band, which on crystallisation [−78 °C, hexane–diethyl ether (4:1)] gave purple *crystals* of [MoI(η^4-CH$_2$=CHCH=CHCH$_2$Bu^t)-{P(OMe)$_3$}(η-C$_5$H$_5$)] **21** (0.31 g, 47%) (Found: C, 38.4; H, 6.1; I, 23.7. $C_{17}H_{30}IMoO_3P$ requires C, 38.1; H, 5.7; I, 23.7%). NMR (C$_6$D$_6$): ^{1}H, δ 5.96 [ddd, 1 H, H^3, ^3J(H^{3}H^4) 5.9, ^3J(H^{3}H^2) 7.8, ^3J(H^{3}H^1) 6.8], 5.73 [dd, 1 H, H^4, ^3J(H^{4}H^3) 5.9, ^3J(H^{4}H^5) 9.8], 4.55 [d, 5 H, C$_5$H$_5$, ^3J(HP) 1.5], 3.32 [d, 9 H, POMe, ^3J(HP) 10.3], 2.68 [dd, 1 H, H^7, ^3J(H^{7}H^5) 11.2, ^2J(H^{7}H^6) 14.7] 1.94 (m, 1 H, H^1), 1.66 (m, 1 H, H^5), 1.60 [dd, 1 H, H^6, ^3J(H^{6}H^5) 2.7, ^2J(H^{6}H^7) 14.7], and 0.96 (s, 9 H, Bu^t), −0.15 [br t, 1 H, H^2, ^3J(H^{2}H^3) 7.8, ^3J(HP) 7.8]; ^{13}C-{^{1}H}, δ 128.9, 115.2 (s, =CHCH=), 89.8 (s, =*C*HCH$_2$Bu^t), 89.4 (s, =CH$_2$), 89.2 (s, C$_5$H$_5$), 53.8 [d, POMe, ^2J(CP) 6.6 Hz], 48.4 (s, CH$_2$), 32.5 (s, *C*Me$_3$) and 29.4 (s, C*Me*$_3$); ^{31}P-{^{1}H}, δ 181.9 (s, POMe).

Photolysis of [Mo{≡CCH(COBu^t)Bu^t}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] **18**.—A solution of compound **18** (0.20 g, 0.35 mmol) in hexane (50 cm^3) was irradiated with UV light (250 W, quartz) at room temperature for 24 h. The solution was reduced in volume and chromatographed on alumina. Elution with hexane–diethyl ether (2:3) gave an orange band which on crystallisation (−78 °C, hexane) afforded orange *crystals* of compound **22** (0.08 g, 40%) (Found: C, 46.1; H, 7.2. $C_{22}H_{40}MoO_7P_2$ requires C, 46.0; H, 7.1%), ν$_{CO}$ (hexane) 1642 cm^{-1}. NMR (C$_6$D$_6$): ^{1}H, δ 5.11 [dd, 1 H, C*H*CBu^t, ^3J(HH′) 4.8, ^3J(HP) 2.6], 4.93 [t, 5 H, C$_5$H$_5$, ^3J(HP) 0.9], 3.21 [d, 9 H, POMe, |^3J(HP) + ^5J(HP′)| 10.1], 2.44 [dd, 1 H, C*H*CMe$_2$, ^3J(HH′) 4.8, ^3J(HP) 13.6], 1.65 (s, 9 H, Bu^t), 1.43 (s, 3 H, Me) and 1.25 (s, 3 H, Me); ^{13}C-{^{1}H}, δ 199.8 (s, CO), 89.4 (s, C$_5$H$_5$), 82.5 (s, *C*Bu^t), 78.3 (s, *C*HCBu^t), 52.4, 52.1 (s, POMe), 50.7 (d, *C*HCMe$_2$), 37.8 (s, Me), 33.4 (s, *C*Me$_2$), 30.6 (s, C*Me*$_3$) and 24.9 (s, Me); ^{31}P-{^{1}H}, δ 195.4 [d, POMe, ^2J(PP′) 82.4] and 191.8 [d, POMe′, ^2J(PP′) 82.4 Hz].

Structure Determinations for Compounds **21** *and* **22**.—Many of the details of the structure analyses carried out on compounds, **21** and **22** are listed in Table 3. X-Ray diffraction measurements were made using Nicolet four-circle P3m diffractometers on single crystals mounted in thin-walled glass capillaries under N$_2$ at room temperature. Cell dimensions for each analysis were determined from the setting angle values of 25 centred reflections.

For each structure analysis, intensity data were collected for unique portions of reciprocal space and corrected for Lorentz, polarisation and long-term intensity fluctuations, the latter on the basis of the intensities of three check reflections repeatedly measured during data collection. Corrections for X-ray

Table 4 Atomic coordinates (× 10^4) for compound **21**

Atom	*x*	*y*	*z*
I(1)	8 950(1)	6 558(1)	2 121(1)
Mo(1)	7 313(1)	5 558(1)	2 488(1)
I(2)	3 538(1)	4 308(1)	1 476(1)
Mo(2)	2 043(1)	3 178(1)	1 864(1)
P(1)	8 346(1)	5 749(1)	3 532(1)
O(1)	8 970(5)	6 604(3)	3 791(3)
O(2)	9 302(4)	5 094(3)	3 773(2)
O(3)	7 662(4)	5 535(4)	4 032(2)
C(1)	8 635(7)	7 452(4)	3 617(4)
C(2)	10 346(6)	5 235(6)	3 672(5)
C(3)	8 110(10)	5 517(9)	4 686(4)
C(4)	8 295(5)	4 378(4)	2 480(4)
C(5)	7 465(6)	4 167(4)	2 774(4)
C(6)	6 508(5)	4 224(4)	2 322(4)
C(7)	6 713(7)	4 469(4)	1 752(4)
C(8)	7 816(6)	4 573(5)	1 839(4)
C(9)	5 843(6)	5 742(5)	2 879(4)
C(10)	6 274(5)	6 567(4)	2 828(3)
C(11)	6 372(5)	6 861(4)	2 242(3)
C(12)	6 094(6)	6 345(5)	1 725(4)
C(13)	6 270(6)	6 624(6)	1 097(4)
C(14)	5 353(6)	7 045(5)	655(3)
C(15)	5 711(9)	7 416(9)	101(4)
C(16)	4 696(12)	7 796(8)	970(5)
C(17)	4 464(11)	6 437(10)	439(7)
P(2)	802(1)	3 754(1)	970(1)
O(4)	−385(4)	3 557(4)	998(2)
O(5)	787(4)	3 332(3)	305(2)
O(6)	772(5)	4 738(3)	747(3)
C(18)	−1 271(6)	3 722(7)	495(4)
C(19)	981(8)	5 483(5)	1 128(4)
C(20)	1 495(7)	3 583(5)	−76(4)
C(21)	1 766(7)	1 740(5)	2 051(6)
C(22)	1 463(7)	1 925(5)	1 415(6)
C(23)	2 405(8)	2 158(5)	1 216(5)
C(24)	3 229(7)	2 129(5)	1 733(5)
C(25)	2 853(7)	1 867(5)	2 245(5)
C(26)	720(6)	3 282(5)	2 378(4)
C(27)	1 113(5)	4 096(4)	2 359(3)
C(28)	2 190(5)	4 242(4)	2 643(3)
C(29)	2 845(6)	3 566(4)	2 914(3)
C(30)	4 013(6)	3 661(4)	3 183(3)
C(31)	4 330(6)	3 765(4)	3 888(3)
C(32)	3 877(9)	4 595(6)	4 085(5)
C(33)	3 984(9)	3 006(7)	4 223(5)
C(34)	5 553(7)	3 823(6)	4 086(4)

Table 5 Atomic coordinates (× 10^4) for compound **22**

Atom	*x*	*y*	*z*
Mo	2271(1)	1503(1)	4805(1)
P(1)	325(1)	1591(1)	5581(1)
P(2)	3637(1)	1295(1)	7239(1)
O(1)	−940(4)	1897(1)	4459(5)
O(2)	−651(4)	1173(1)	5876(4)
O(3)	723(5)	1917(2)	6995(5)
O(4)	3044(4)	860(2)	7887(4)
O(5)	3900(4)	1754(2)	8271(4)
O(5′)	3293(26)	1621(9)	8436(25)
O(6)	5216(4)	1062(2)	7711(4)
O(6′)	5326(20)	1398(8)	7938(22)
O(7)	2089(4)	1129(1)	1149(3)
C(1)	−2278(7)	1996(3)	4518(10)
C(2)	−221(7)	756(2)	6735(8)
C(3)	218(8)	1890(3)	8105(8)
C(4)	3791(8)	514(3)	8974(7)
C(5)	4462(7)	1722(3)	9801(5)
C(6)	6297(6)	1260(3)	7321(6)
C(7)	1626(6)	2286(2)	3903(7)
C(8)	2677(7)	2318(2)	5265(6)
C(9)	3920(6)	2122(2)	5183(7)
C(10)	3617(7)	1972(2)	3788(7)
C(11)	2210(7)	2070(2)	3013(6)
C(12)	2164(5)	963(2)	2316(5)
C(13)	3444(5)	671(2)	3321(5)
C(14)	3242(6)	140(2)	2789(6)
C(15)	4894(5)	845(2)	3374(6)
C(16)	3137(5)	727(2)	4685(5)
C(17)	1614(5)	728(2)	4297(5)
C(18)	1043(5)	960(2)	2933(5)
C(19)	−512(5)	942(2)	1905(5)
C(20)	−1020(6)	1435(2)	1181(6)
C(21)	−1513(6)	770(2)	2656(7)
C(22)	−647(7)	551(2)	759(6)

absorption effects were applied for **21** on the basis of the indexed crystal faces and dimensions and for **22** on the basis of azimuthal scan data. The structures were solved by heavy-atom (Patterson and Fourier difference) methods, and refined by blocked-cascade least squares against *F* until shift/e.s.d. values were < 0.1. The two independent molecules present in the crystal structure of **21** differ only in small changes in methyl group orientations. Two of the methoxy groups on P(2) in **22** were subject to a two site disorder with O(5) and O(6) having occupancy 0.88(1) and O(5′) and O(6′) having occupancy 0.12(1). The O–C and P–O distances involving the low-occupancy oxygen atoms were constrained to be close to 1.4 and 1.6 Å respectively. All non-hydrogen atoms other than O(5′) and O(6′) were assigned anisotropic displacement parameters. All methyl and cyclopentadienyl hydrogen atoms (except the cyclopentadienyl hydrogen atoms in **22** were constrained to ideal geometries (with C–H 0.96 Å), other hydrogen positions being refined with C–H lengths constrained to be close to a refined common value [0.89(2) Å] in **21**, and without positional constraints for **22**. All hydrogen atoms were assigned isotropic displacement parameters; these were fixed for the methyl and cyclopentadienyl hydrogens of **21** and refined without constraints for all other hydrogens.

Final difference syntheses showed no chemically significant features, the largest being close to the metal atoms. Refinements converged smoothly to residuals given in Table 3. Tables 4 and 5 report the positional parameters for these structure determinations.

All calculations were made with programs of the SHELXTL[13] system as implemented on a Nicolet R3m/E structure determination system. Complex neutral-atom scattering factors were taken from ref. 14.

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

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