Reactions of Co-ordinated Ligands. Part 39.[1] The Synthesis of Carbyne Complexes from Alkyne Molybdenum and Tungsten Cations; Formation and Crystal Structures of $[\mathrm{Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$ and $[\overline{\mathrm{Mo\{=C(SiMe_3)C}}\mathrm{H_2\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}]$ *

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Thermolysis of the σ-vinyl complexes $[\mathrm{M\{\sigma\text{-}(}E\mathrm{)\text{-}CH{=}CHBu^t\}\{P(OMe)_3\}_3(\eta^5\text{-}C_{\mathit{m}}H_{\mathit{n}})}]$ (M = Mo or W; $m = n = 5$; $m = 9$, $n = 7$), formed by reaction of hydride-anion donors with the cations $[\mathrm{M(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta^5\text{-}C_{\mathit{m}}H_{\mathit{n}})}][\mathrm{BF_4}]$, leads to formation of the carbyne complexes $[\mathrm{M(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta^5\text{-}C_{\mathit{m}}H_{\mathit{n}})}]$. The η-cyclopentadienylmolybdenum carbyne complex was structurally characterised by *X*-ray crystallography. The molecule adopts a 'three-legged piano-stool' geometry with one of the legs being a Mo≡C triple bond [1.796(2) Å]. A similar reaction (−78 °C) between $[\mathrm{Mo(\eta^2\text{-}Pr^iC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$ and $\mathrm{K[BHBu^s_3]}$ in the presence of $\mathrm{P(OMe)_3}$ afforded the η³-allyl complex $[\mathrm{Mo(\eta^3\text{-}CH_2 \cdots CH \cdots CMe_2)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$, whereas the same cation with $\mathrm{NaBH_4\text{–}P(OMe)_3}$ gave the carbyne complex $[\mathrm{Mo(\equiv CCH_2Pr^i)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$. Possible mechanisms for these carbyne-forming reactions are discussed. In contrast, reaction of the trimethylsilyl-substituted cation $[\mathrm{Mo(\eta^2\text{-}Me_3SiC_2H)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}][\mathrm{BF_4}]$ with $\mathrm{K[BHBu^s_3]}$ or $\mathrm{Li(CuPh_2)}$ affords the η²-vinyl complexes $[\overline{\mathrm{Mo\{=C(SiMe_3)C}}\mathrm{HR\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}]$ (R = H or Ph). The phenyl-substituted η²-vinyl is also formed on reaction of $[\mathrm{Mo(\eta^2\text{-}Me_3SiC_2Ph)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}][\mathrm{BF_4}]$ with $\mathrm{K[BHBu^s_3]}$, the corresponding reaction with $\mathrm{Li(CuPh_2)}$ affording $[\overline{\mathrm{Mo\{=C(SiMe_3)C}}\mathrm{Ph_2\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}]$. The η²-vinyl species $\overline{\mathrm{Mo\{=C(SiMe_3)C}}\mathrm{HR\}}$ (R = H or Ph) thermally rearrange to the carbyne complexes $[\mathrm{Mo(\equiv CCH_2SiMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}]$ and $[\mathrm{Mo\{\equiv CCH(Ph)SiMe_3\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}]$. These trimethylsilyl-substituted carbynes are desilylated in NaF–H₂O–MeCN to form $[\mathrm{Mo(\equiv CCH_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}]$ and $[\mathrm{Mo(\equiv CCH_2Ph)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}]$. The molecular geometry of $[\overline{\mathrm{Mo\{=C(SiMe_3)C}}\mathrm{H_2\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)}]$ was established by *X*-ray crystallography. The η²-vinyl C–C bond lies nearly parallel to the Mo–P(1) vector the P(1)–Mo–C(8)–C(7) torsion angle being 13.8(2)°, with the carbene carbon C(8) nearer than C(7) to the plane of the indenyl ligand. The Mo–C(8) bond length is 1.955(3) Å, whereas Mo–C(7) is 2.258(4) Å.

The discovery[2] in 1973 of the first mononuclear transition metal carbyne alkylidyne complex stimulated considerable interest[3–11] in molecules containing metal to carbon triple bonds, and this eventually provided a fairly detailed understanding of the chemistry of such species. However, our observation[12] that the thermolysis of the σ-vinyl complex $[\mathrm{Mo\{\sigma\text{-}(}E\mathrm{)\text{-}CH{=}CHBu^t\}\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)}]$ (**1**) gave the bis-trimethyl phosphite-substituted carbyne $[\mathrm{Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$ (**2**) came as a surprise and posed two questions. Could this reaction be generalised and so allow the synthesis of other electron-rich carbynes, and secondly how did this apparent 1,2-hydrogen shift process occur? This paper is concerned with these two questions.

Results and Discussion

The tris-trimethyl phosphite-substituted σ-vinyl complex $[\mathrm{Mo\{\sigma\text{-}(}E\mathrm{)\text{-}CH{=}CHBu^t\}\{P(OMe)_3\}_3(\eta\text{-}C_5H_5)}]$ (**1**) is formed[12,13] on reaction of the four-electron donor alkyne cation $[\mathrm{Mo(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}][\mathrm{BF_4}]$ with $\mathrm{K[BHBu^s_3]}$ and $\mathrm{P(OMe)_3}$. When a solution of (**1**) in hexane was heated (80 °C) in a sealed vessel a bright yellow colour developed, and column chromatography on alumina afforded yellow crystals of (**2**). Elemental analysis, and ^{1}H, ^{13}C-{^{1}H}, and ^{31}P-{^{1}H} n.m.r. spectroscopy suggested that (**2**) was a molybdenum carbyne complex with the molecular formula $[\mathrm{Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)}]$. In particular the ^{13}C-{^{1}H} spectrum showed a low-field triplet [*J*(CP) 27.0 Hz] at 299.8 p.p.m. and the ^{1}H spectrum contained, in addition to signals assignable to $\mathrm{C_5H_5}$, $\mathrm{P(OMe)_3}$, and $\mathrm{Bu^t}$ groups, a triplet resonance centred at 2.20 p.p.m. [*J*(HP) 4.0 Hz], consistent with the presence of a $\mathrm{Mo{\equiv}CCH_2Bu^t}$ system. Because of the unusual nature of this reaction it was decided to confirm the postulated structure by *X*-ray crystallography. This established the molecular geometry shown in Figure 1, selected bond lengths and interbond angles being listed in Table 1. Although compound (**1**) crystallised with two independent molecules in the asymmetric unit no important geometric differences were found between the two and averaged structural parameters are therefore used in the discussion below.

The complex has a three-legged piano-stool geometry typical of $\mathrm{ML_3(\eta\text{-}C_5H_5)}$ species, the molybdenum being bonded to two trimethyl phosphite ligands, a neopentyl-substituted carbyne, and an η⁵-cyclopentadienyl ligand. The essentially linear nature of the $\mathrm{MoC_\alpha C_\beta}$ moiety [Mo–C(13)–C(14) 176.7(2)°] combined with a Mo–C(13) distance of 1.796(2) Å is consistent with the molecule being described as a carbyne complex with a Mo≡C triple bond. Previous *X*-ray crystallographic studies of molybdenum carbyne complexes have established the Mo–C-

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* η-Cyclopentadienyl(3,3-dimethylbutylidyne)bis(trimethyl phosphite)molybdenum and η⁵-indenylbis(trimethyl phosphite)(2-trimethylsilylethanylylidene)molybdenum respectively.

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

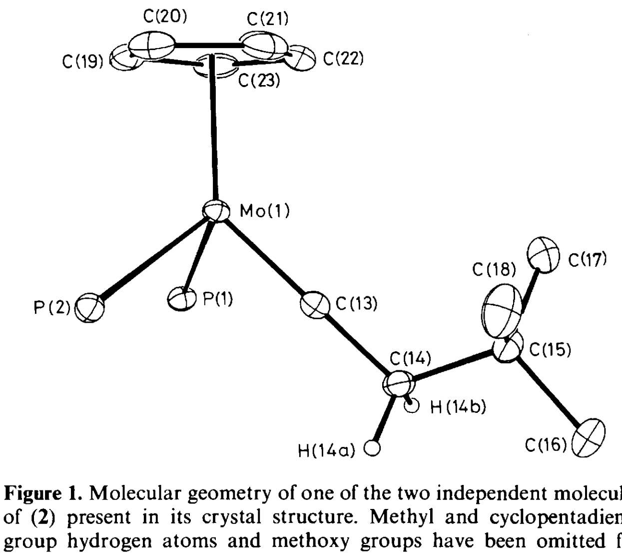


Figure 1. Molecular geometry of one of the two independent molecules of (**2**) present in its crystal structure. Methyl and cyclopentadienyl group hydrogen atoms and methoxy groups have been omitted for clarity. Ellipsoids enclose 30% probability density

(carbyne) distances [Mo(≡CPh)(CO)$_4${Re(CO)$_5$}], 1.835(3) Å,[14] [Mo(≡CCl)(CO)$_2${B(C$_3$H$_3$N$_2$)$_4$}], 1.89(9) Å,[15] and [Mo(≡CSC$_6$H$_4$NO$_2$-4)(CO)$_2${BH(C$_3$H$_3$N$_2$)$_3$}], 1.801(4) Å.[16] Although the molecule has potential mirror symmetry, in the solid state this is not found, the Bu^t group of the carbyne moiety lying to one side of the molecule. There is slight asymmetry in the Mo–P distances where the average length of the four independent Mo–P bonds is 2.329(1) Å, which compares with Mo–P(transoid) 2.352(1) Å and Mo–P(cisoid) 2.363(2) Å in the parent molecule [Mo{σ-(*E*)-CH=CHBu^t}{P(OMe)$_3$}$_3$(η-C$_5$H$_5$)].[13]

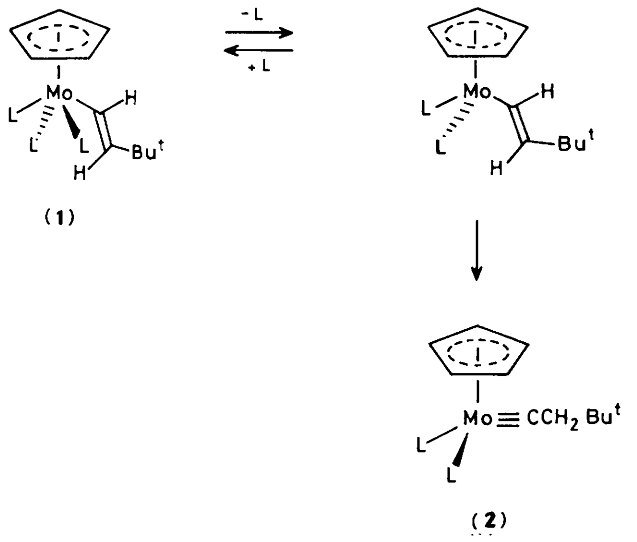
With structural confirmation of the rearrangement reaction which is illustrated in Scheme 1, it was first important to establish whether this reaction could be generalised. The corresponding η^5-indenyl complex [Mo{σ-(*E*)-CH=CHBu^t}{P(OMe)$_3$}$_3$(η^5-C$_9$H$_7$)] (**3**) was readily obtained (66%) on reaction of [Mo(η^2-Bu^{t}C$_2$H){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)][BF$_4$][17] with K[BHBu^s$_3$] and trimethyl phosphite, and when a solution of (**3**) in hexane was heated at 100 °C a deep yellow colour developed. Column chromatography of the thermolysis mixture gave an excellent yield (92%) of the carbyne [Mo(≡CCH$_2$Bu^t){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)] (**4**) which showed characteristic ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra (see Experimental section).

Table 1. Selected bond lengths (Å) and angles (°) for (**2**)

Mo(1)–P(1)	2.322(1)	Mo(1)–P(2)	2.337(1)	O(11)–C(11)	1.436(3)	O(12)–C(12)	1.436(4)
Mo(1)–C(13)	1.796(2)	Mo(1)–C(19)	2.427(3)	O(4)–C(4)	1.451(4)	O(5)–C(5)	1.426(4)
Mo(1)–C(20)	2.407(3)	Mo(1)–C(21)	2.375(3)	O(6)–C(6)	1.436(4)	O(7)–C(7)	1.437(3)
Mo(1)–C(22)	2.364(3)	Mo(1)–C(23)	2.384(3)	O(8)–C(8)	1.418(4)	O(9)–C(9)	1.372(4)
Mo(2)–P(3)	2.314(1)	Mo(2)–P(4)	2.343(1)	C(13)–C(14)	1.485(3)	C(14)–C(15)	1.549(4)
Mo(2)–C(24)	1.799(2)	Mo(2)–C(30)	2.393(3)	C(14)–H(14a)	0.989(26)	C(14)–H(14b)	0.943(36)
Mo(2)–C(31)	2.363(3)	Mo(2)–C(32)	2.367(3)	C(15)–C(16)	1.534(4)	C(15)–C(17)	1.522(4)
Mo(2)–C(33)	2.425(3)	Mo(2)–C(34)	2.418(3)	C(15)–C(18)	1.516(4)	C(19)–C(20)	1.394(4)
P(1)–O(1)	1.613(2)	P(1)–O(2)	1.628(2)	C(19)–C(23)	1.403(4)	C(20)–C(21)	1.381(5)
P(1)–O(3)	1.608(2)	P(2)–O(4)	1.607(2)	C(21)–C(22)	1.409(5)	C(22)–C(23)	1.408(5)
P(2)–O(5)	1.682(2)	P(2)–O(6)	1.612(2)	C(24)–C(25)	1.486(3)	C(25)–C(26)	1.552(3)
P(3)–O(7)	1.600(2)	P(3)–O(8)	1.609(2)	C(25)–H(25a)	0.988(26)	C(25)–H(25b)	1.143(31)
P(3)–O(9)	1.611(2)	P(4)–O(10)	1.608(2)	C(26)–C(27)	1.529(4)	C(26)–C(28)	1.531(4)
P(4)–O(11)	1.607(2)	P(4)–O(12)	1.625(2)	C(26)–C(29)	1.526(4)	C(30)–C(31)	1.418(5)
O(1)–C(1)	1.439(3)	O(2)–C(2)	1.430(4)	C(30)–C(34)	1.400(5)	C(31)–C(32)	1.405(4)
O(3)–C(3)	1.436(4)	O(10)–C(10)	1.440(3)	C(32)–C(33)	1.404(4)	C(33)–C(34)	1.391(4)

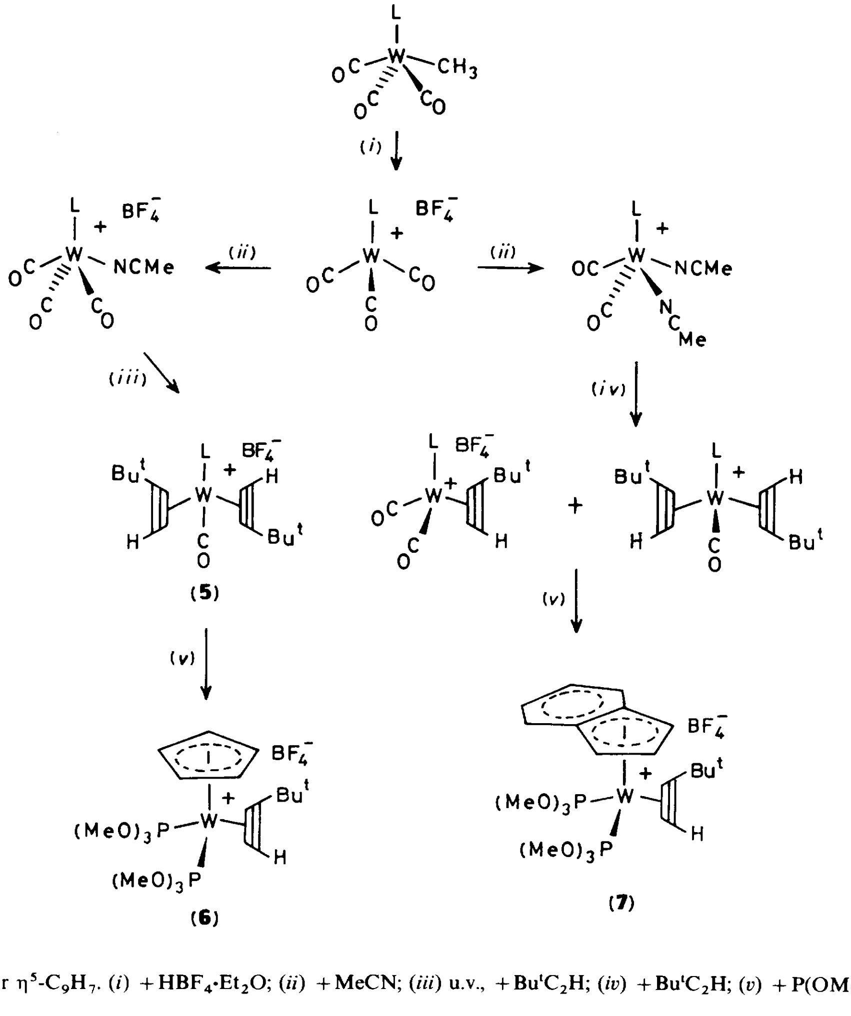
P(1)–Mo(1)–P(2)	92.9(1)	P(1)–Mo(1)–C(13)	86.3(1)	Mo(1)–P(1)–O(1)	125.7(1)	Mo(1)–P(1)–O(2)	118.5(1)
P(2)–Mo(1)–C(13)	90.4(1)	P(1)–Mo(1)–C(19)	101.8(1)	O(1)–P(1)–O(2)	94.9(1)	Mo(1)–P(1)–O(3)	112.0(1)
P(2)–Mo(1)–C(19)	103.1(1)	C(13)–Mo(1)–C(19)	163.7(1)	O(1)–P(1)–O(3)	98.7(1)	O(2)–P(1)–O(3)	103.2(1)
P(1)–Mo(1)–C(20)	134.3(1)	P(2)–Mo(1)–C(20)	91.1(1)	Mo(1)–P(2)–O(4)	115.3(1)	Mo(1)–P(2)–O(5)	119.3(1)
C(13)–Mo(1)–C(20)	139.2(1)	C(19)–Mo(1)–C(20)	33.5(1)	O(4)–P(2)–O(5)	101.7(1)	Mo(1)–P(2)–O(6)	121.1(1)
P(1)–Mo(1)–C(21)	148.8(1)	P(2)–Mo(1)–C(21)	112.3(1)	O(4)–P(2)–O(6)	104.3(1)	O(5)–P(2)–O(6)	91.2(1)
C(13)–Mo(1)–C(21)	110.5(1)	C(19)–Mo(1)–C(21)	56.0(1)	Mo(2)–P(3)–O(7)	117.7(1)	Mo(2)–P(3)–O(8)	121.0(1)
C(20)–Mo(1)–C(21)	33.6(1)	P(1)–Mo(1)–C(22)	116.4(1)	O(7)–P(3)–O(8)	102.5(1)	Mo(2)–P(3)–O(9)	118.5(1)
P(2)–Mo(1)–C(22)	146.1(1)	C(13)–Mo(1)–C(22)	107.3(1)	O(7)–P(3)–O(9)	96.6(1)	O(8)–P(3)–O(9)	95.8(1)
C(19)–Mo(1)–C(22)	56.5(1)	C(20)–Mo(1)–C(22)	56.5(1)	Mo(2)–P(4)–O(10)	125.7(1)	Mo(2)–P(4)–O(11)	110.9(1)
C(21)–Mo(1)–C(22)	34.6(1)	P(1)–Mo(1)–C(23)	92.1(1)	O(10)–P(4)–O(11)	98.9(1)	Mo(2)–P(4)–O(12)	119.4(1)
P(2)–Mo(1)–C(23)	136.5(1)	C(13)–Mo(1)–C(23)	133.0(1)	O(10)–P(4)–O(12)	95.0(1)	O(11)–P(4)–O(12)	103.1(1)
C(19)–Mo(1)–C(23)	33.9(1)	C(20)–Mo(1)–C(23)	56.3(1)	P(1)–O(1)–C(1)	120.9(2)	P(1)–O(2)–C(2)	120.3(2)
C(21)–Mo(1)–C(23)	57.0(1)	C(22)–Mo(1)–C(23)	34.5(1)	P(1)–O(3)–C(3)	122.0(2)	P(4)–O(10)–C(10)	119.9(2)
P(3)–Mo(2)–P(4)	93.5(1)	P(3)–Mo(2)–C(24)	83.0(1)	P(4)–O(11)–C(11)	122.0(2)	P(4)–O(12)–C(12)	120.4(2)
P(4)–Mo(2)–C(24)	91.8(1)	P(3)–Mo(2)–C(30)	150.3(1)	P(2)–O(4)–C(4)	121.0(2)	P(2)–O(5)–C(5)	117.5(2)
P(4)–Mo(2)–C(30)	110.1(1)	C(24)–Mo(2)–C(30)	112.9(1)	P(2)–O(6)–C(6)	119.9(2)	P(3)–O(7)–C(7)	121.6(2)
P(3)–Mo(2)–C(31)	118.7(1)	P(4)–Mo(2)–C(31)	144.5(1)	P(3)–O(8)–C(8)	119.5(2)	P(3)–O(9)–C(9)	125.2(2)
C(24)–Mo(2)–C(31)	105.7(1)	C(30)–Mo(2)–C(31)	34.7(1)	Mo(1)–C(13)–C(14)	176.7(2)	C(13)–C(14)–C(15)	115.2(2)
P(3)–Mo(2)–C(32)	93.3(1)	P(4)–Mo(2)–C(32)	139.3(1)	C(13)–C(14)–H(14a)	107.7(14)	C(15)–C(14)–H(14a)	111.5(15)
C(24)–Mo(2)–C(32)	128.9(1)	C(30)–Mo(2)–C(32)	57.1(1)	C(13)–C(14)–H(14b)	111.1(22)	C(15)–C(14)–H(14b)	106.7(22)
C(31)–Mo(2)–C(32)	34.6(1)	P(3)–Mo(2)–C(33)	101.1(1)	H(14a)–C(14)–H(14b)	104.2(27)	C(14)–C(15)–C(16)	108.4(2)
P(4)–Mo(2)–C(33)	105.3(1)	C(24)–Mo(2)–C(33)	162.0(1)	C(14)–C(15)–C(17)	110.1(2)	C(14)–C(15)–C(18)	110.0(2)
C(30)–Mo(2)–C(33)	56.2(1)	C(31)–Mo(2)–C(33)	56.8(1)	Mo(2)–C(24)–C(25)	172.8(2)	C(24)–C(25)–C(26)	114.7(2)
C(32)–Mo(2)–C(33)	34.1(1)	P(3)–Mo(2)–C(34)	132.9(1)	C(24)–C(25)–H(25a)	107.5(17)	C(26)–C(25)–H(25a)	109.1(17)
P(4)–Mo(2)–C(34)	91.0(1)	C(24)–Mo(2)–C(34)	143.7(1)	C(24)–C(25)–H(25b)	110.2(15)	C(26)–C(25)–H(25b)	108.0(15)
C(30)–Mo(2)–C(34)	33.8(1)	C(31)–Mo(2)–C(34)	56.8(1)	H(25a)–C(25)–H(25b)	107.1(22)	C(25)–C(26)–C(27)	109.3(2)
C(32)–Mo(2)–C(34)	56.3(1)	C(33)–Mo(2)–C(34)	33.4(1)	C(25)–C(26)–C(28)	107.8(2)	C(25)–C(26)–C(29)	109.6(2)

The possible extension of this chemistry to the corresponding tungsten compounds was next explored. In contrast with the molybdenum complexes the only previous study of alkyne tungsten cations described[18] the characterisation of the but-2-yne cation $\mathrm{[W(\eta^2\text{-}MeC_2Me)_2(CO)(\eta\text{-}C_5H_5)][PF_6]}$. The starting point for our investigation was the cation $\mathrm{[W(NCMe)(CO)_3(\eta\text{-}C_5H_5)][BF_4]}$ obtained in moderate yield by addition of $\mathrm{HBF_4{\cdot}Et_2O}$ to a solution of $\mathrm{[WMe(CO)_3(\eta\text{-}C_5H_5)]}$ in methylene chloride. Attempts to convert this cation into a bis-acetonitrile complex were unsuccessful; however, u.v. irradiation of a solution of $\mathrm{[W(NCMe)(CO)_3(\eta\text{-}C_5H_5)][BF_4]}$ in MeCN containing an excess of 3,3-dimethylbut-1-yne led to the formation of $\mathrm{[W(\eta^2\text{-}Bu^tC_2H)_2(CO)(\eta\text{-}C_5H_5)][BF_4]}$ (**5**), which was isolated as a yellow-brown crystalline material and characterised by elemental analysis, i.r., and n.m.r. spectroscopy. Addition of trimethyl phosphite to a solution of (**5**) in $\mathrm{CH_2Cl_2}$ afforded the red crystalline cation $\mathrm{[W(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]}$ (**6**). In the case of the corresponding η^5-indenyl chemistry, addition of $\mathrm{HBF_4{\cdot}Et_2O}$ to $\mathrm{[WMe(CO)_3(\eta^5\text{-}C_9H_7)]}$ followed by refluxing in acetonitrile afforded the red-brown *cis*-bis-acetonitrile cation $\mathrm{[W(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]}$, which was isolated as a monoacetonitrile solvate. This reacted with 3,3-dimethylbut-1-yne to give a mixture of $\mathrm{[W(\eta^2\text{-}Bu^tC_2H)(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]}$ and the required cation $\mathrm{[W(\eta^2\text{-}Bu^tC_2H)_2(CO)(\eta^5\text{-}C_9H_7)][BF_4]}$. Rather than attempt separation, the mixture was treated directly with an excess of trimethyl phosphite to give the maroon cation $\mathrm{[W(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]}$ (**7**). These reactions are summarised in Scheme 2.

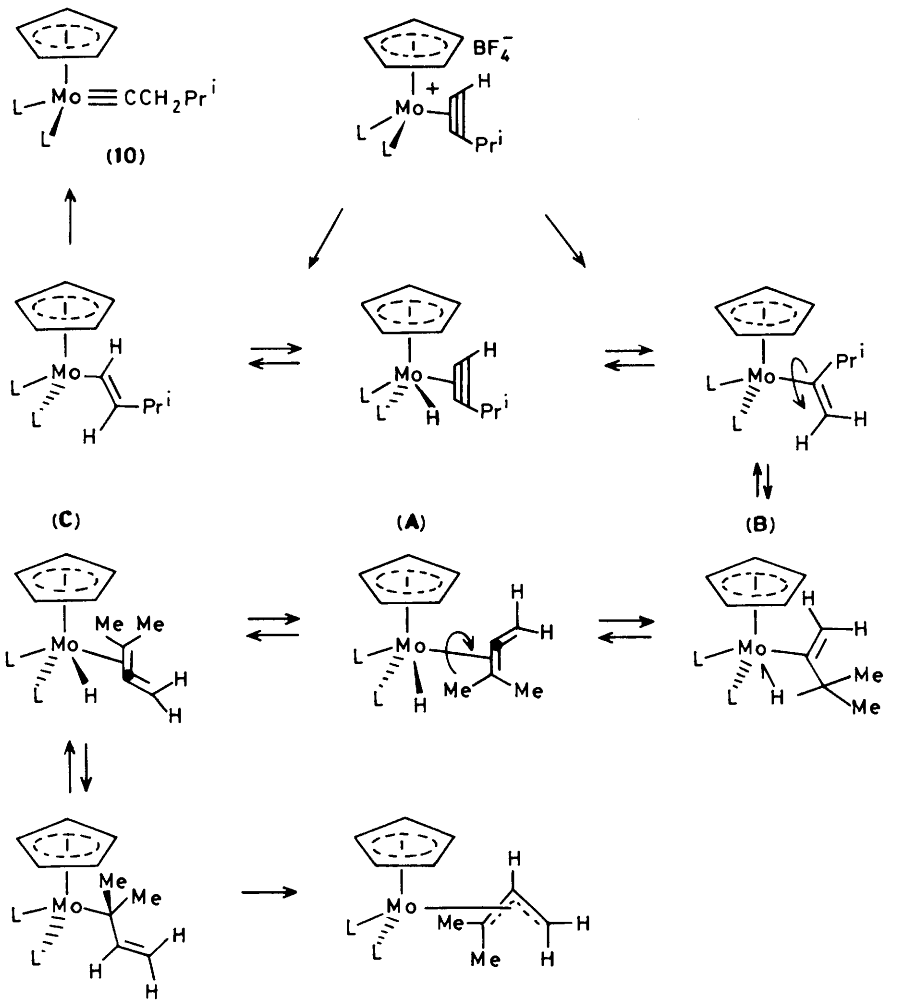


Scheme 1. L = $\mathrm{P(OMe)_3}$

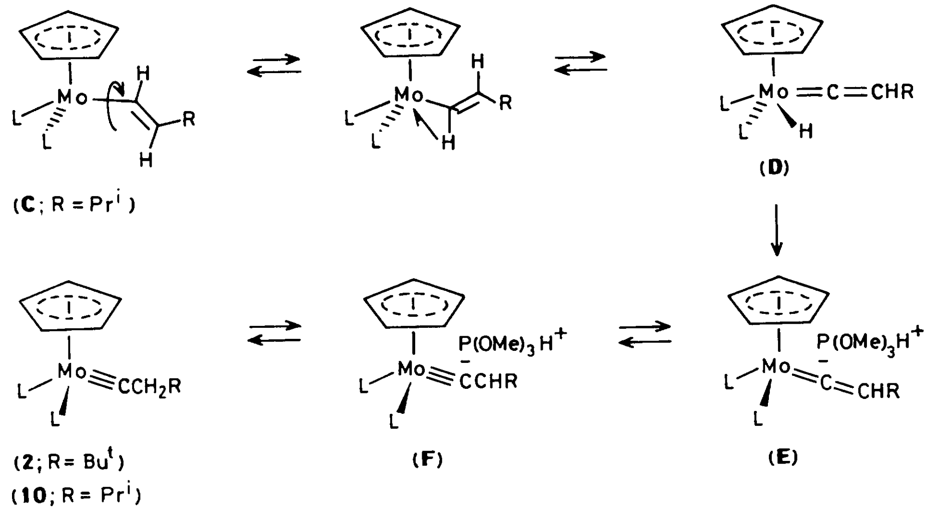
Both of these bis(trimethyl phosphite) cations reacted with sources of 'H$^-$'. Addition of a toluene solution of $\mathrm{Na[AlH_2(OCH_2CH_2OMe)_2]}$ to a toluene–trimethyl phosphite solution of (**6**) gave, on warming to room temperature followed by column chromatography, yellow crystals of $\mathrm{[W({\equiv}CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]}$ (**8**) showing similar n.m.r. characteristics to the molybdenum analogue (**2**). Reaction of the



Scheme 2. L = η^5-$\mathrm{C_5H_5}$ or η^5-$\mathrm{C_9H_7}$. (*i*) +$\mathrm{HBF_4{\cdot}Et_2O}$; (*ii*) +MeCN; (*iii*) u.v., +$\mathrm{Bu^tC_2H}$; (*iv*) +$\mathrm{Bu^tC_2H}$; (*v*) +$\mathrm{P(OMe)_3}$



Scheme 3. L = $P(OMe)_3$



Scheme 4. L = $P(OMe)_3$

more soluble indenyl cation (7) in tetrahydrofuran (thf) with $K[BHBu^s_3]$ in the absence of trimethyl phosphite at low temperature (−78 °C) gave, on warming to room temperature and chromatography on alumina, bright yellow crystals (56% yield) of $[W(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ (9).

In all these reactions a neopentyl-substituted carbyne is formed, and it was therefore also of interest to examine related reactions with complexes carrying different substituents on the co-ordinated alkyne. However, earlier[13] experiments with $[Mo(\eta^2\text{-}Pr^iC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ had already

Table 2. Selected bond lengths (Å) and angles (°) for (**11**)

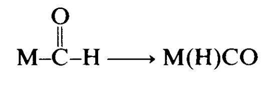
Mo–P(1)	2.351(1)	Mo–P(2)	2.358(1)	O(2)–C(2)	1.426(7)	O(3)–C(3)	1.457(4)
Mo–C(7)	2.258(4)	Mo–C(8)	1.955(3)	O(4)–C(4)	1.444(4)	O(5)–C(5)	1.431(5)
Mo–C(12)	2.341(4)	Mo–C(13)	2.369(4)	O(6)–C(6)	1.453(6)	C(7)–C(8)	1.437(6)
Mo–C(14)	2.439(5)	Mo–C(19)	2.426(4)	C(7)–H(7a)	0.922(39)	C(7)–H(7b)	1.023(39)
Mo–C(20)	2.339(3)	P(1)–O(1)	1.614(3)	C(12)–C(13)	1.412(7)	C(12)–C(20)	1.421(4)
P(1)–O(2)	1.631(3)	P(1)–O(3)	1.627(2)	C(13)–C(14)	1.422(5)	C(14)–C(15)	1.422(7)
P(2)–O(4)	1.610(3)	P(2)–O(5)	1.622(2)	C(14)–C(19)	1.449(5)	C(15)–C(16)	1.359(5)
P(2)–O(6)	1.609(3)	Si–C(8)	1.849(4)	C(16)–C(17)	1.423(6)	C(17)–C(18)	1.358(8)
Si–C(9)	1.879(5)	Si–C(10)	1.875(4)	C(18)–C(19)	1.424(5)	C(19)–C(20)	1.435(7)
Si–C(11)	1.874(4)	O(1)–C(1)	1.430(4)				

P(1)–Mo–P(2)	91.8(2)	P(1)–Mo–C(7)	72.8(1)	C(14)–Mo–C(20)	58.1(2)	C(19)–Mo–C(20)	35.0(2)
P(2)–Mo–C(7)	88.8(1)	P(1)–Mo–C(8)	110.8(1)	Mo–P(1)–O(1)	124.2(1)	Mo–P(1)–O(2)	120.7(1)
P(2)–Mo–C(8)	96.2(1)	C(7)–Mo–C(8)	39.0(2)	O(1)–P(1)–O(2)	95.4(2)	Mo–P(1)–O(3)	112.8(1)
P(1)–Mo–C(12)	129.3(1)	P(2)–Mo–C(12)	83.9(1)	O(1)–P(1)–O(3)	97.4(2)	O(2)–P(1)–O(3)	101.8(1)
C(7)–Mo–C(12)	156.8(1)	C(8)–Mo–C(12)	119.9(1)	Mo–P(2)–O(4)	119.3(1)	Mo–P(2)–O(5)	118.0(1)
P(1)–Mo–C(13)	151.8(1)	P(2)–Mo–C(13)	105.2(1)	O(4)–P(2)–O(5)	91.3(1)	Mo–P(2)–O(6)	116.7(1)
C(7)–Mo–C(13)	128.7(1)	C(8)–Mo–C(13)	89.9(1)	O(4)–P(2)–O(6)	105.1(2)	O(5)–P(2)–O(6)	102.4(1)
C(12)–Mo–C(13)	34.9(2)	P(1)–Mo–C(14)	122.6(1)	C(8)–Si–C(9)	106.9(2)	C(8)–Si–C(10)	115.3(2)
P(2)–Mo–C(14)	138.8(1)	C(7)–Mo–C(14)	120.7(2)	C(8)–Si–C(11)	107.8(2)	P(1)–O(1)–C(1)	124.3(3)
C(8)–Mo–C(14)	92.1(2)	C(12)–Mo–C(14)	57.4(2)	P(1)–O(2)–C(2)	120.6(2)	P(1)–O(3)–C(3)	121.3(2)
C(13)–Mo–C(14)	34.4(1)	P(1)–Mo–C(19)	94.2(1)	P(2)–O(4)–C(4)	120.5(3)	P(2)–O(5)–C(5)	120.2(3)
P(2)–Mo–C(19)	134.2(1)	C(7)–Mo–C(19)	136.1(2)	P(2)–O(6)–C(6)	121.5(3)	Mo–C(7)–C(8)	59.0(2)
C(8)–Mo–C(19)	123.3(2)	C(12)–Mo–C(19)	57.8(1)	Mo–C(7)–H(7a)	114.8(22)	C(8)–C(7)–H(7a)	117.3(17)
C(13)–Mo–C(19)	57.8(1)	C(14)–Mo–C(19)	34.7(1)	Mo–C(7)–H(7b)	121.2(17)	C(8)–C(7)–H(7b)	115.3(25)
P(1)–Mo–C(20)	97.0(1)	P(2)–Mo–C(20)	99.2(1)	H(7a)–C(7)–H(7b)	116.7(30)	Mo–C(8)–Si	151.4(2)
C(7)–Mo–C(20)	167.3(1)	C(8)–Mo–C(20)	147.7(2)	Mo–C(8)–C(7)	81.9(2)	Si–C(8)–C(7)	123.7(3)
C(12)–Mo–C(20)	35.3(1)	C(13)–Mo–C(20)	58.7(1)				

demonstrated the existence of an alternative reaction pathway where it was found that reaction with K[BHBu$^s_3$] in thf at −78 °C did not give the expected MoCH=CHPr^i system, but led instead to the formation of the η^3-allyl complex [Mo(η^3-CH$_2$⋯CH⋯CMe$_2$){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)]. Nevertheless, re-examination of this reaction under different reaction conditions showed that this cation with Na[BH$_4$] in the presence of P(OMe)$_3$ at *room temperature* in thf gave directly in good yield the yellow carbyne complex [Mo($\equiv$CCH$_2$Pr^i){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] (**10**).

We can understand these apparently confusing observations if we assume that the reaction of H$^-$ with [Mo(η^2-Pr^{i}C$_2$H){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][BF$_4$] provides access to the 18-electron hydrido–alkyne species (**A**) illustrated in Scheme 3. Such an intermediate could be formed either by direct attack on the molybdenum with a change [η^2(4e) to η^2(2e)] in the bonding mode of the 3-methylbut-1-yne ligand, or by attack on carbon forming an η^2-vinyl complex[19] which then opens [η^2(3e) to σ(1e)] and undergoes a β-hydrogen elimination reaction. Since the 3-methylbut-1-yne ligand in (**A**) could also rotate then an equilibrium could be set up allowing formation of the two isomeric 16-electron σ-vinyl species (**B**) and (**C**) carrying respectively the groups MoC(Pr^i)=CH$_2$ and MoCH=CHPr^i. Rotation of the σ-vinyl group in (**B**) about the Mo–C single bond then places the β-hydrogen atom of the Pr^i groups in such a position that interaction can occur with the unsaturated molybdenum centre leading to a hydrido allene complex, thus providing a path to the η^3-allyl complex. At room temperature the equilibrium could favour the σ-vinyl complex (**C**), which rearranges to the carbyne (**10**). A similar reaction could be involved in the formation of (**2**) on thermolysis of (**1**) where dissociative loss of trimethyl phosphite from (**1**) gives the related species [Mo{σ-(*E*)-CH=CHBu^t}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)], which then rearranges to the carbyne. Of course, this leaves unanswered how this last step might occur.

If we consider the possible reaction pathways available to a 16-electron σ-vinyl complex such as (**C**) in Scheme 3, then an obvious reaction is an α-hydrogen elimination. Specifically, if rotation occurs about the Mo–C σ-vinyl bond then the vinyl α-hydrogen is then correctly orientated so as to allow an agostic interaction with the unsaturated molybdenum centre. When further developed, this interaction leads to the formation of the 18-electron hydrido vinylidene complex (**D**) (Scheme 4). In the case of the formation of the carbynes (**2**) and (**4**), and also (**8**) and (**10**), the reaction mixture also contains the relatively strong base trimethyl phosphite. It is conceivable that this deprotonates the hydrido vinylidene, for example (**D**), affording the vinylidene anion (**E**). In separate studies[20,21] we have shown that such ambident anions are also formed on deprotonation of the carbyne (**2**), and that reaction with electrophiles including a proton leads to selective attack on the β-carbon atom. Clearly the series of reactions shown in Scheme 4 could therefore effect the transformation of an σ-vinyl complex into a carbyne, a prerequisite being an α-hydrogen substituent and the presence of a base. Although there are no previous examples of α-hydrogen elimination reactions from σ-vinyl complexes there is an interesting analogy with the known[22] ability of formyl complexes to rearrange to hydrido carbonyl species (below).



$$\mathrm{M{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}H} \longrightarrow \mathrm{M(H)CO}$$

An indication that this might not be the complete story came from two observations. As was previously mentioned the tungsten cation (**7**) reacts with K[BHBu$^s_3$] in thf in the *absence* of P(OMe)$_3$ to give directly a good yield of the carbyne [W($\equiv$CCH$_2$Bu^t){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)]. This indicated that there may be an alternative pathway from [W{σ-CH=CHBu^t}{P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)] to the carbyne, which did not require the presence of a base. An insight into how this might occur came from a study[23] of the reaction of [Mo(η^2-Me$_3$SiC$_2$H){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)][BF$_4$] with K[BHBu$^s_3$].

Reaction (−78 °C) in thf afforded a labile neutral complex (**11**), which was isolated as deep blue crystals by low-temperature (−40 °C) column chromatography on alumina. Examination of the ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra suggested the molecular formula $[Mo\{=C(SiMe_3)CH_2\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$; in particular the ^{13}C spectrum showed a triplet [*J*(CP) 6 Hz] at low field (276.5 p.p.m.) characteristic of the α-carbon of an η^2-vinyl complex. This was confirmed by low-temperature (−50 °C) single-crystal *X*-ray crystallography, the molecular structure being illustrated in Figure 2, and selected bond lengths and angles are listed in Table 2.

The molecular geometry is related to that found for the η-cyclopentadienyl η^2-vinyl complexes $[Mo\{=C(Ph)CHPh\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ and $[Mo\{=C(Bu^t)CHPh\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$[19] (rather than that of $[Mo\{=C(Me)CPh_2\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$[19]); the vinyl C–C bond lies nearly parallel to the Mo–P(1) vector with the P(1)–Mo–C(8)–C(7) torsion angle equal to 13.8(2)°, placing the carbene carbon C(8) nearer than C(7) to the plane of the indenyl ligand. The saturated or β-carbon atom of the η^2-vinyl fragment carries only hydrogen substituents, so that adoption of this orientation minimises non-bonding interactions between the vinyl substituents and the phosphite ligands. The bond lengths about the metallacyclopropene ring are similar to those found[19] for the Mo=C(Ph)CHPh and Mo=C(Bu^t)CHPh systems; the Mo–C(8) bond is 1.955(3) Å and the Mo–C(7) bond is 2.258(4) Å. The ring is completed by the C(7)–C(8) bond of 1.437(6) Å. There is no structural evidence for d_π–p_π interaction between the carbene carbon C(8) and the silicon of the SiMe$_3$ substituent. Whilst the Si–C(8) distance of 1.849(4) Å is shorter than the average Si–C(methyl) bond length of 1.876(4) Å, a substantial part of this discrepancy is due to the radial contraction observed for sp^2 *versus* sp^3 carbon.

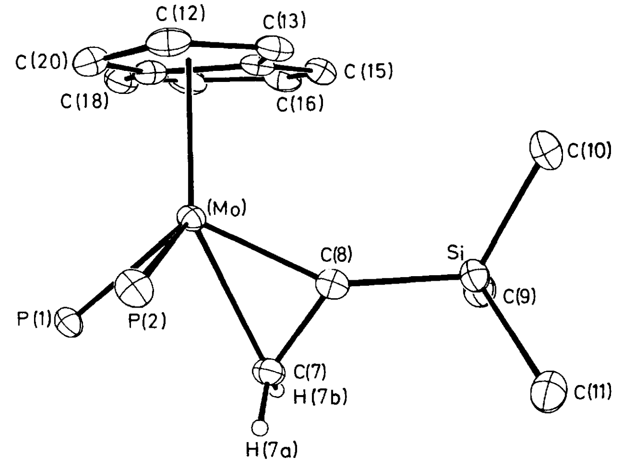
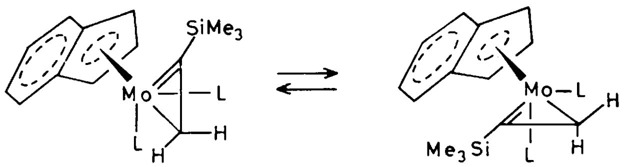


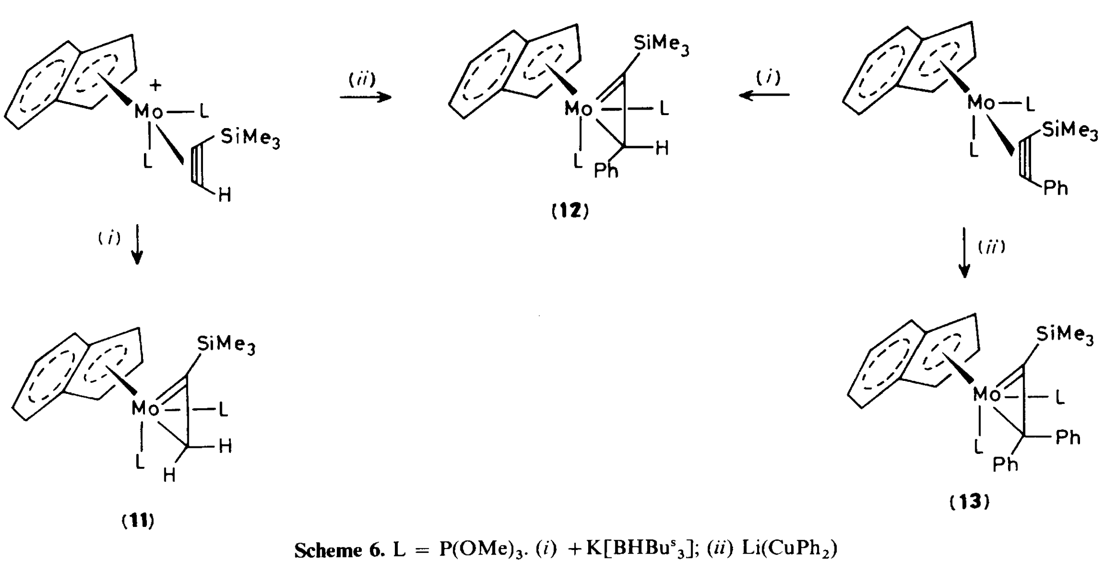
Figure 2. Molecular geometry of (**11**), with methoxy groups and methyl and indenyl group hydrogen atoms omitted for clarity. Ellipsoids are drawn to enclose 30% probability density



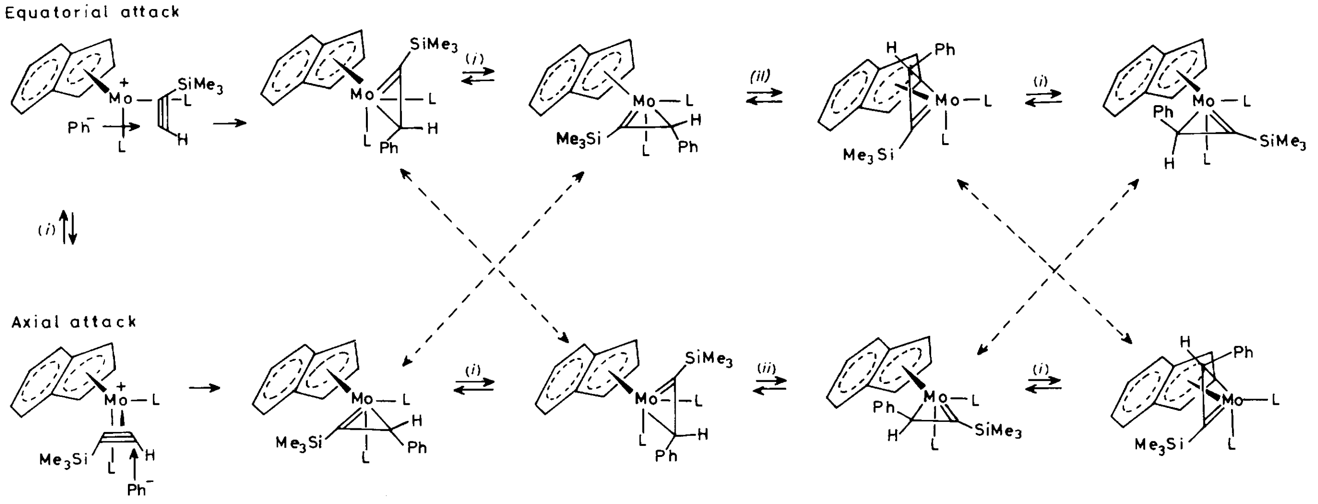
Scheme 5. L = P(OMe)$_3$

As previously[19,23] discussed the ^{31}P-{^{1}H} spectrum of (**11**) shows only a single resonance and the ^{1}H spectrum indicates apparent equivalence of the methylene hydrogens of the η^2-vinyl fragment at −70 °C. This equivalence of the trimethyl phosphite ^{31}P, and similarly the methylene ^{1}H, environments can be explained by the occurrence of a facile 'windscreen-wiper' motion of the kind previously discussed and which is illustrated in Scheme 5. Simple extended Hückel molecular orbital calculation suggests that the barrier to such a process is *ca.* 20 kJ mol^{-1}. Related η^2-vinyl complexes were obtained by reaction of $[Mo(\eta^2\text{-}Me_3SiC_2H)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$ with Li(CuPh$_2$) in thf which gives a neutral green crystalline material, identified by analysis and n.m.r. spectroscopy as the complex $[Mo\{=C(SiMe_3)CHPh\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ (**12**). This complex was also obtained on reaction of K[BHBu$^s_3$] with the cation $[Mo(\eta^2\text{-}Me_3SiC_2Ph)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$. This trimethylsilyl(phenyl)ethyne-substituted cation also reacted with Li(CuPh$_2$) to give the diphenyl-substituted η^2-vinyl complex (**13**). These reactions are summarised in Scheme 6.

In the formation of (**12**) a phenyl group is delivered by the cuprate to the unsubstituted end of the trimethylsilylethyne ligand, and it is interesting to recall that the same regioselectivity is shown in the reaction of $[Mo(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ with Li(CuPh$_2$) affording the η^2-vinyl complex $[Mo\{=C(Bu^t)CHPh\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$.[19] In considering the frontier orbitals involved in this latter reaction we have previously[19] discussed how attack could



Scheme 6. L = P(OMe)$_3$. (*i*) +K[BHBu$^s_3$]; (*ii*) Li(CuPh$_2$)



Scheme 7. L = $\mathrm{P(OMe)_3}$. (*i*) windscreen-wiper motion; (*ii*) 180° rotation

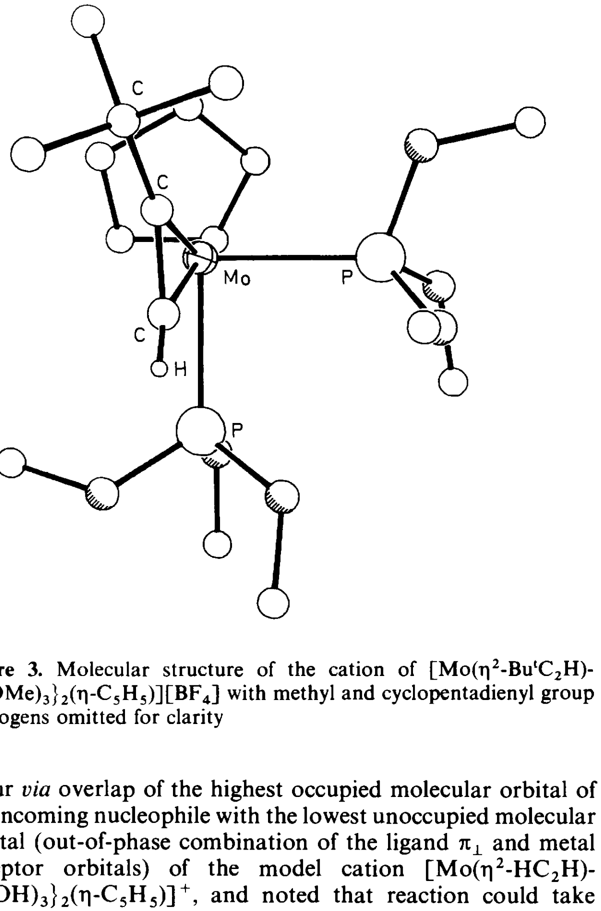


Figure 3. Molecular structure of the cation of $[\mathrm{Mo}(\eta^2\text{-}\mathrm{Bu^tC_2H})\{\mathrm{P(OMe)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})][\mathrm{BF_4}]$ with methyl and cyclopentadienyl group hydrogens omitted for clarity

occur *via* overlap of the highest occupied molecular orbital of the incoming nucleophile with the lowest unoccupied molecular orbital (out-of-phase combination of the ligand $\pi_\perp$ and metal acceptor orbitals) of the model cation $[\mathrm{Mo}(\eta^2\text{-}\mathrm{HC_2H})\{\mathrm{P(OH)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})]^+$, and noted that reaction could take place at either the metal centre or at one of the two alkyne carbons. In the case of perpendicular attack on the $\pi_\perp$ orbital of an *unsymmetrical* alkyne the observed regioselectivity could arise either from a difference in the relative magnitudes of the coefficients of the π orbitals associated with the two alkyne carbon atoms, or from the relative ease of access by the species delivering the '$\mathrm{Ph^-}$' group to one of the co-ordinated alkyne carbons.

If the reaction was electronically controlled and involved either a two- or one-electron transfer[*] reaction then clearly replacement of a $\mathrm{Bu^t}$ group by a $\mathrm{SiMe_3}$ group should have a marked influence on the regioselectivity. The fact that there is no such effect suggests dominant steric control of the reaction. This can be assessed by considering the structures of the cations $[\mathrm{Mo}(\eta^2\text{-}\mathrm{RC_2H})\{\mathrm{P(OMe)_3}\}_2(\eta\text{-}\mathrm{C_5H_5})]^+$ (R = $\mathrm{Bu^t}$ or $\mathrm{SiMe_3}$). In the case of the 3,3-dimethylbut-1-yne-substituted cation the geometry in the solid state has been determined by *X*-ray crystallography,[24] and is illustrated in Figure 3. The same conformation is adapted in solution for both the cyclopentadienyl and indenyl cations since the $^{13}\mathrm{C}\text{-}\{^1\mathrm{H}\}$ n.m.r. shows alkyne contact carbons for the $\eta\text{-}\mathrm{C_5H_5}$ complex at 244.9 [t, $C\mathrm{Bu^t}$, $^2J(\mathrm{CP})$ 9.1 Hz] and 201.7 p.p.m. [t, CH, $^2J(\mathrm{CP})$ 23.9 Hz], and at 245 [$C\mathrm{Bu^t}$, $^2J(\mathrm{CP}) < 2$] and 204.7 p.p.m. [t, CH, $^2J(\mathrm{CP})$ 24.3 Hz] for the $\eta^5\text{-}\mathrm{C_9H_7}$ cation where the triplet coupling arises from a 'windscreen-wiper' motion of the alkyne. In the case of the trimethylsilylethyne η^5-indenyl complex the corresponding $^{13}\mathrm{C}$ signals are at 224.5 [t, $C\mathrm{SiMe_3}$, $^2J(\mathrm{CP})$ 2.0 Hz] and 205.0 p.p.m. [t, CH, $^2J(\mathrm{CP})$ 23.4 Hz], implying that the same geometry is adopted as for the 3,3-dimethylbut-1-yne cation.

If it is remembered that delivery of a phenyl group occurs *via* attack on the alkyne $\pi_\perp$ orbital then inspection of Figure 3 suggests that the least-hindered direction of approach to the co-ordinated alkyne is onto the CH carbon. In other words the steric bulk of R in co-ordinated $\eta^2\text{-}\mathrm{RC_2H}$ controls both the orientation of the alkyne and the site preference for delivery of $\mathrm{Ph^-}$. Examination of Scheme 7 shows that delivery of a phenyl group onto the unsubstituted alkyne carbon can occur from either of two directions leading to the formation of diastereoisomers, which are interrelated by 'windscreen-wiper' and 'rotational' processes.[19] In other words the stereochemistry of the product is thermodynamically controlled. It is interesting to note that, although the same regioselectivity is observed in the reaction of the 3,3-dimethylbut-1-yne and trimethylsilylethyne cations, the $CH\mathrm{Ph}$ resonance of the η^2-vinyl $\overline{\mathrm{Mo{=}C(Bu^t)C}}\mathrm{HPh}$ occurs at 3.78 p.p.m., whereas the corresponding resonance in (**12**) is at 4.70 p.p.m. suggesting that these two complexes may adopt different conformations. This will be discussed more fully in a subsequent paper.

Clearly a similar sequence of reactions can be pictured for the formation of (**11**) on reaction of $[\mathrm{Mo}(\eta^2\text{-}\mathrm{Me_3SiC_2H})$-

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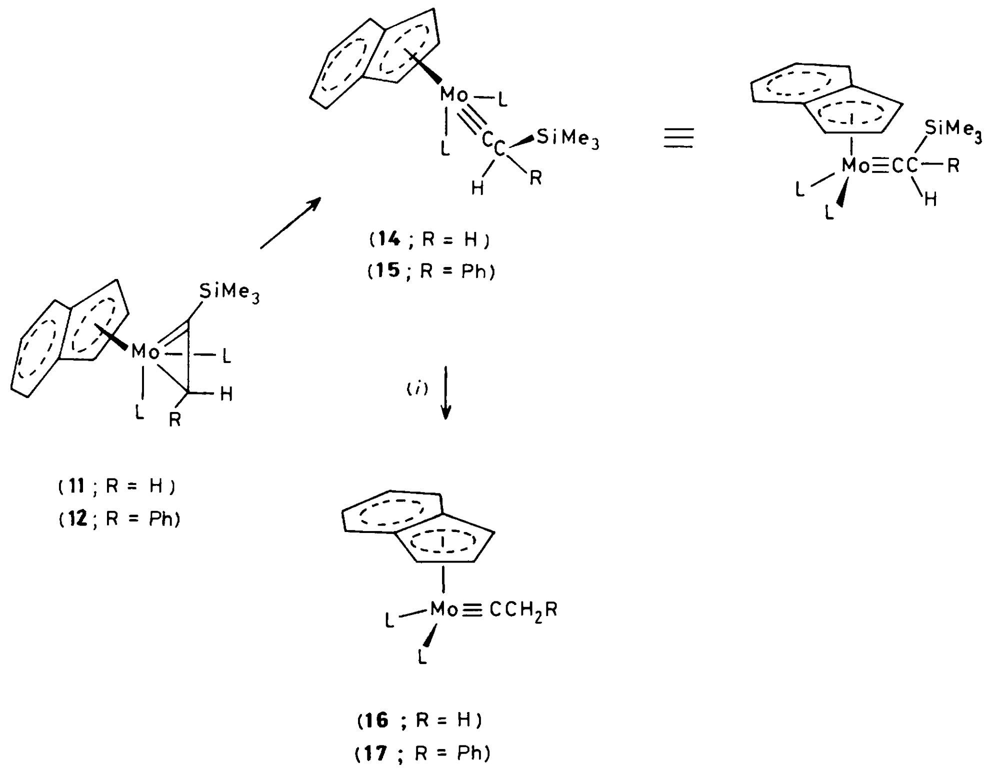
[*] Electrochemical experiments show that these cations readily undergo a reversible one-electron reduction reaction, and the cuprate reactions could involve such a process. If this was the case then it is reasonable to assume that the same steric factors could control the conformation of the 17-electron species $[\mathrm{Mo}(\eta^2\text{-}\mathrm{RC_2H})\{\mathrm{P(OMe)_3}\}_2(\eta^5\text{-}\mathrm{C}_m\mathrm{H}_n)]$ ($n = m = 5$; $n = 7, m = 9$).



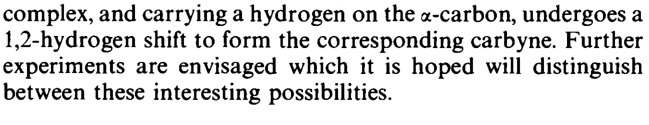
Scheme 8. L = $P(OMe)_3$. (*i*) NaF, H_2O–MeCN

$\{P(OMe)_3\}_2(\eta^5-C_9H_7)][BF_4]$ with $K[BHBu^s_3]$. However, it is important to recall that the related reaction between $[Mo(\eta^2-Bu^tC_2H)\{P(OMe)_3\}_2(\eta^5-C_9H_7)][BF_4]$ and $K[BHBu^s_3]$ leads to the isolation of (3),[13] a σ-vinyl complex containing the arrangement Mo–σ-(*E*)-CH=CHBu^t. This difference in regioselectivity could arise either from a competing reaction at the molybdenum centre or by ring-opening [η^2(3e) to σ(1e)] of an η^2-vinyl complex followed by a β-hydrogen elimination reaction and subsequent rotation of the alkyne and insertion into the molybdenum hydride.

The η^2-vinyl complexes (**11**) and (**12**), which carry a trimethylsilyl substituent on the α-carbon atom of the C_2 fragment, undergo a remarkable rearrangement reaction, which is related to the formations of the carbyne complexes (**2**), (**4**), and (**8**)—(**10**). In toluene solution at room temperature the blue complex (**11**) rearranges ($t_{\frac{1}{2}}$ *ca.* 45 min) in quantitative yield into the yellow carbyne complex (**14**). A similar rearrangement occurs with the green phenyl-substituted η^2-vinyl (**12**), but under more forcing conditions (hexane, 70 °C, 7 d), to give the yellow carbyne complex (**15**) (see Scheme 8). Whereas, in contrast, the diphenyl-substituted η^2-vinyl (**13**) showed no tendency to rearrange. Reaction of these trimethylsilyl-substituted carbynes with a solution of NaF in MeCN–H_2O leads to desilylation and formation in high yield of the methyl- and benzyl-substituted carbyne complexes (**16**) and (**17**).

The desilylation reaction can be readily understood in terms of the nucleophilic attack by F^- on silicon with displacement of the anions $[Mo(CCHR)\{P(OMe)_3\}_2(\eta^5-C_9H_7)]^-$ (R = H or Ph).[20,21] These anions then simply protonate on the β-carbon atom, forming the corresponding carbynes. In contrast, the initial rearrangement, which affords (**14**) and (**15**), is less easily understood.

If the η^2-vinyl complex (**11**) opened to a 16-electron η^2-vinyl complex then in principle the $SiMe_3$ group could migrate onto the molybdenum forming a trimethylsilyl vinylidene complex. However, there is no precedent for such a reaction, and moreover, once formed it is difficult to envisage how this molecule could then rearrange to the carbyne (**14**). A more likely pathway from (**11**) to (**14**), and (**12**) to (**15**), is *via* a concerted 1,2-trimethylsilyl shift driven by the formation of a thermodynamically stable Mo≡C triple bond. As is illustrated in Scheme 9, a related intramolecular process could be involved in the formation of (**2**), (**4**), and (**8**)—(**10**) where an η^2-vinyl species $\overline{\mathrm{Mo{=}CHC}}\mathrm{HR}$ formed by collapse of a 16-electron σ-vinyl complex, and carrying a hydrogen on the α-carbon, undergoes a 1,2-hydrogen shift to form the corresponding carbyne. Further experiments are envisaged which it is hoped will distinguish between these interesting possibilities.



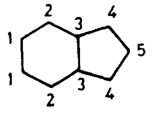
Scheme 9. R = $SiMe_3$ or H; R′ = H, Ph, Pr^i, or Bu^t

Experimental

Hydrogen-1, $^{13}C-\{^1H\}$, and $^{31}P-\{^1H\}$ n.m.r. spectra were recorded on JEOL FX 90Q or FX200 spectrometers, as appropriate. Data given are for room-temperature measurements unless otherwise indicated, and coupling constants are in Hz. 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. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Preparation of Starting Materials.—cis-*Bis*(*acetonitrile*)*dicarbonyl*(η^5-*indenyl*)*molybdenum*(II) *tetrafluoroborate.* A slight excess of $HBF_4 \cdot Et_2O$ (1.7 g, 10.5 mmol) was added dropwise to a stirred, cooled (−78 °C) solution of $[MoMe(CO)_3(\eta^5\text{-}C_9H_7)]$ (3.1 g, 10 mmol) in CH_2Cl_2 (30 cm^3). The reaction mixture was allowed to warm to room temperature, the colour changing from yellow to deep maroon. After 30 min at room temperature the resultant dark solution was cooled (−78 °C) and an excess of acetonitrile (5 cm^3, 96 mmol) added. On warming to room temperature this gave a deep red colour. After 30 min diethyl ether was added to give an orange powder which was washed with diethyl ether (3 × 50 cm^3), dried, and recrystallised (0 °C) from methylene chloride–diethyl ether to give red *crystals* of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$[25] (3 g, 70%), identified by i.r. and n.m.r. spectroscopy.

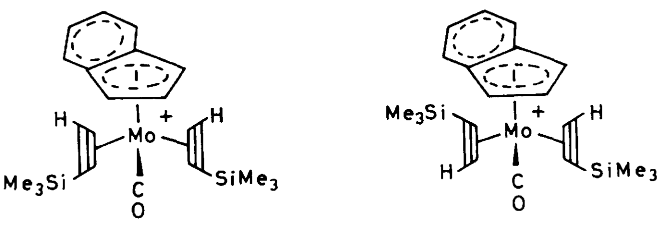
cis-*Bis*(*acetonitrile*)*dicarbonyl*(η^5-*indenyl*)*tungsten*(II) *tetrafluoroborate.* A solution of $[WMe(CO)_3(\eta^5\text{-}C_9H_7)]$ (10.0 g, 25.13 mmol) in CH_2Cl_2 (40 cm^3) was cooled (−78 °C) and treated dropwise with one equivalent of $HBF_4 \cdot Et_2O$ (4.1 g, 25 mmol). The reaction mixture was allowed to warm and stirred at room temperature for 1.5 h. The resultant red solution was cooled (−78 °C) and treated with an excess of acetonitrile (20 cm^3, 3.84 mol) then allowed to warm to room temperature. The reaction mixture was heated under reflux for 2 h, then reduced to dryness *in vacuo*. The red-brown residue was dissolved in acetonitrile (200 cm^3) and filtered through Celite. The solvent was reduced (20 cm^3) *in vacuo*, resulting in the precipitation of red-brown *crystals* of $[W(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4] \cdot MeCN$ (10.0 g, 70%) (Found: C, 36.1; H, 2.8; N, 7.4. $C_{17}H_{16}BF_4N_3O_2W$ requires C, 36.1; H, 2.8; N, 7.4%); ν_{CO}(MeCN) at 1 959s and 1 879s cm^{-1}. N.m.r.: ^1H (CD_3NO_2), δ 7.72 (AA′BB′ multiplet, 4 H, indenyl), 6.44 [d, 2 H, H^4, $J(H^4H^5)$ 3], 6.10 [t, 1 H, H^5, $J(H^4H^5)$ 3], 2.62 (s, 3 H, MeCN solvate), 2.01 (s, 6 H, MeCN); $^{13}C\text{-}\{^1H\}$ (CD_3NO_2), δ 141.7 (CN), 135.7 (CN), 132.7 (indenyl C^1), 128.1 (indenyl C^2), 116.0 (indenyl C^3), 91.5 (indenyl C^5), 80.3 (indenyl C^4), 4.9 (*Me*CN solvate), 1.3 p.p.m. (*Me*CN).



Acetonitriletricarbonyl(η-*cyclopentadienyl*)*tungsten*(II) *tetrafluoroborate.* One equivalent of $HBF_4 \cdot Et_2O$ (0.23 g, 1.4 mmol) was added to a stirred (−78 °C) solution of $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ (0.5 g, 1.4 mmol) in CH_2Cl_2 (10 cm^3). On warming to room temperature the solution changed colour from lemon-yellow to deep purple. The solution was cooled (−78 °C) and an excess of MeCN (40 cm^3) was added, and stirred at room temperature for 12 h. The volume of the solvent was reduced (20 cm^3) *in vacuo*, the solution filtered through Celite and reduced to dryness. The residue was dissolved in CH_2Cl_2 (10 cm^3) and diethyl ether (5 cm^3) added; cooling (−20 °C) afforded orange-red *crystals* of $[W(NCMe)(CO)_3(\eta\text{-}C_5H_5)][BF_4]$ (0.23 g, 35%) (Found: C, 26.0; H, 1.7; N, 2.8. $C_{10}H_8BF_4NO_3W$ requires C, 26.0; H, 1.8; N, 3.0%); ν_{CO}(MeCN) at 2 067s, 1 973s cm^{-1}. N.m.r.: ^1H(CD_3CN), δ 6.03 (s, 5 H, C_5H_5) and 2.56 p.p.m. (s, 3 H, MeCN).

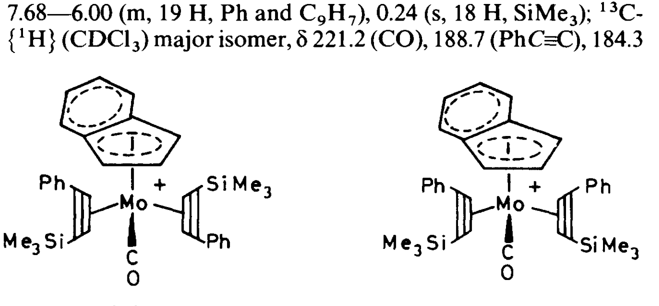
(3,3-*Dimethylbut*-1-*yne*)(η-*indenyl*)*bis*(*trimethyl phosphite*)*molybdenum*(II) *tetrafluoroborate.* An excess of trimethyl phosphite (0.5 cm^3, 4.7 mmol) was added dropwise to a stirred (room temperature) solution of $[Mo(\eta^2\text{-}Bu^tC_2H)_2(CO)(\eta\text{-}C_9H_7)][BF_4]$ (0.98 g, 2.0 mmol) in CH_2Cl_2 (20 cm^3). After 2 h the reaction mixture was filtered through a Celite pad, the volume of the solvent reduced *in vacuo*, and diethyl ether added to give purple *crystals* of $[Mo(\eta^2\text{-}Bu^tC_2H)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$ (1.14 g, 90%) (Found: C, 39.9; H, 5.9. $C_{21}H_{35}BF_4MoO_6P_2$ requires C, 40.2; H, 5.7%). N.m.r.: $^1H(CDCl_3)$, δ 11.9 [t, 1 H, *H*C≡C, *J*(HP) 17], 7.38 (m, 4 H, indenyl), 6.11 (m, 2 H, indenyl H^4), 5.66 (m, 1 H, indenyl H^5), 3.51 [apparent t, 18 H, POMe, $|J(HP) + J(HP')|$ 11.5], 1.39 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$ ($CDCl_3$), δ 245 [Bu^t*C*≡C, *J*(CP) > 2], 204.7 [t, Bu^tC≡*C*H, *J*(CP) 24.3], 128.3 (indenyl C^1), 126.0 (indenyl C^2), 116.5 (indenyl C^3), 94.5 (indenyl C^5), 82.8 (indenyl C^4), 53.6 (POMe), 43.7 (Me_3*C*C≡CH), 31.0 (*Me*$_3$CC≡C); $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ 174.8 p.p.m. (POMe).

Carbonyl(η-*indenyl*)*bis*(*trimethylsilylethyne*)*molybdenum*(II) *tetrafluoroborate.* A simple extension of the previously published procedure afforded yellow-orange *crystals* of $[Mo(\eta^2\text{-}Me_3SiC_2H)_2(CO)(\eta\text{-}C_9H_7)][BF_4]$ (85%) (Found: C, 46.3; H, 5.4. $C_{20}H_{27}BF_4MoOSi_2$ requires C, 46.0; H, 5.2%); ν_{CO}(Nujol) at 2 043s cm^{-1}. N.m.r.: $^1H(CD_3NO_2)$, major isomer, δ 10.60 (s, 1 H, HC≡C), 9.48 (s, 1 H, HC≡C), 7.7—5.5 (m, 7 H, C_9H_7), 0.38 (s, 9 H, HC≡CSi*Me*$_3$), 0.05 (s, 9 H, HC≡CSi*Me*$_3$); minor isomer, δ 10.28 (s, 2 H, *H*C≡CSiMe$_3$), 0.20 (s, 18 H, HC≡CSi*Me*$_3$); $^{13}C\text{-}\{^1H\}$ $CDCl_3$), major isomer, δ 173.9 (HC≡*C*SiMe$_3$), 170.4 (H*C*≡CSiMe$_3$), 158.9 (H*C*≡CSiMe$_3$), 133.8 (indenyl C^1), 131.5 (indenyl), 130.1 (indenyl), 126.1 (indenyl), 122.5 (indenyl), 119.0 (indenyl), 107.9 (indenyl), 92.9 (indenyl C^5), 80.9 (indenyl C^4), −0.4 (HC≡CSi*Me*$_3$), −0.7 p.p.m. (HC≡CSi*Me*$_3$).



Major Minor

Carbonyl(η-*indenyl*)*bis*(*trimethylsilylphenylethyne*)*molybdenum*(II) *tetrafluoroborate.* Similarly, reaction of $[Mo(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$ (3.50 g, 8.03 mmol) in CH_2Cl_2 (40 cm^3) with PhC_2SiMe_3 (4.2 g, 24.1 mmol) gave yellow *crystals* of $[Mo(\eta^2\text{-}Me_3SiC_2Ph)_2(CO)(\eta^5\text{-}C_9H_7)][BF_4]$ (4.0 g, 74%) (Found: C, 57.1; H, 5.0. $C_{32}H_{35}BF_4MoOSi_2$ requires C, 57.0; H, 5.2%); $\nu_{CO}(CH_2Cl_2)$ at 2 052s cm^{-1}. N.m.r.: $^1H(CDCl_3)$, major isomer, δ 7.68—6.00 (m, 19 H, Ph and C_9H_7), 0.48 (s, 9 H, $SiMe_3$), 0.16 (s, 9 H, $SiMe_3$); minor isomer, 7.68—6.00 (m, 19 H, Ph and C_9H_7), 0.24 (s, 18 H, $SiMe_3$); $^{13}C\text{-}\{^1H\}$ ($CDCl_3$) major isomer, δ 221.2 (CO), 188.7 (Ph*C*≡C), 184.3 (Ph*C*≡C), 171.2 (C≡*C*SiMe$_3$), 165.5 (C≡*C*SiMe$_3$), 140.6—115.0 (C_9H_7), 110.0 (indenyl C^3), 108.5 (indenyl C^3), 93.6, 85.0, 84.4 (indenyl C^4 and C^5), −0.5 ($SiMe_3$), −0.8 p.p.m. ($SiMe_3$).



Major Minor

η-*Indenylbis*(*trimethyl phosphite*)(*trimethylsilylethyne*)*molybdenum*(II) *tetrafluoroborate.* A similar procedure afforded blue *crystals* of $[Mo(\eta^2\text{-}Me_3SiC_2H)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$ (Found: C, 37.3; H, 5.4. $C_{20}H_{35}BF_4MoO_6P_2Si$ requires C, 37.3; H, 5.4%). N.m.r.: $^1H(CDCl_3)$, δ 11.30 [t, 1 H, CH, *J*(HP) 13.8], 7.76—7.31 (m, 4 H, C_9H_7), 6.14 (m, 2 H, C_9H_7), 5.30 (s, br, 1 H, C_9H_7), 3.51 [apparent t, 18 H, POMe,

|*J*(HP) + *J*(HP′)| 10.9], 0.17 (s, 9 H, SiMe$_3$); ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 224.5 [t, Me$_3$Si*C*≡CH, *J*(CP) 2], 205.0 [t, Me$_3$SiC≡*C*H, *J*(CP) 23.4], 129.1, 126.0, 115.8, 95.6, 93.1, 86.1 (C$_9$H$_7$), 53.4 (POMe), −0.7 (SiMe$_3$); ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ 178.5 p.p.m. (POMe).

η-*Indenylbis(trimethyl phosphite)[trimethylsilyl(phenyl)ethyne]molybdenum*(II) *tetrafluoroborate*. Addition of P(OMe)$_3$ (1.0 cm^3, 8.48 mmol) to a CH$_2$Cl$_2$ (20 cm^3) solution of [Mo(η^2-Me$_3$SiC$_2$Ph)$_2$(CO)(η^5-C$_9$H$_7$)][BF$_4$] (2.8 g, 4.15 mmol) resulted in a colour change from yellow to green and following addition of Et$_2$O the isolation of dark green *crystals* of [Mo(η^2-Me$_3$SiC$_2$Ph){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)][BF$_4$] (2.86 g, 96%) (Found: C, 44.2; H, 5.2. C$_{26}$H$_{39}$BF$_4$MoO$_6$P$_2$Si requires C, 43.4; H, 5.5%). N.m.r.: ^{1}H (CDCl$_3$), δ 7.68—6.66 (m, 7 H, Ph and C$_9$H$_7$), 6.07 (m, C$_9$H$_7$), 5.68 (m, 2 H, C$_9$H$_7$), 5.30 (m, 1 H, C$_9$H$_7$), 3.56 [apparent t, 9 H, POMe, |*J*(HP) + *J*(HP′)| 10.5], 3.52 [apparent t, 9 H, POMe, |*J*(HP) + *J*(HP′)| 10.5], 0.09 (s, 9 H, SiMe$_3$); ^{13}C-{^{1}H} (CDCl$_3$), δ 199.6 [t, Ph*C*≡C, *J*(CP) 23.4], 178.2 [C≡*C*SiMe$_3$, *J*(CP) <2], 141.7—121.0 (C$_9$H$_7$), 114.2, 112.8, 87.1, 85.4, 80.4 (C$_9$H$_7$), 53.1 [d, POMe, *J*(CP) 3.9], −0.2 (SiMe$_3$); ^{31}P-{^{1}H} (CDCl$_3$), δ 177.1 [d, POMe, *J*(PP′) 19.5], 174.6 p.p.m. [d, POMe, *J*(PP′) 19.5].

Thermolysis of (η-*Cyclopentadienyl*) (η-(E)-2-*t-butylvinyl*]-*tris(trimethyl phosphite)molybdenum*(II).—A solution of [Mo{σ-(*E*)-CH=CHBu^t}{P(OMe)$_3$}$_3$(η-C$_5$H$_5$)] (0.35 g, 0.5 mmol) in hexane (10 cm^3) contained in an evacuated sealed tube (50 cm^3) fitted with a Westoff stopcock was heated at 80 °C for 12 h. The reaction mixture became bright yellow. The volatile material was removed *in vacuo* and the residue dissolved in diethyl ether (5 cm^3) and chromatographed on an alumina-packed column. Elution with hexane gave a bright yellow band, which was collected, the volume of the solvent reduced (5 cm^3), and cooling (−78 °C, 3 d) afforded bright yellow *crystals* of [Mo(≡CCH$_2$Bu^t){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] (**2**) (0.21 g, 85%) (Found: C, 41.3; H, 7.1. C$_{17}$H$_{34}$MoO$_6$P$_2$ requires C, 41.5; H, 6.9%). N.m.r.: ^{1}H(C$_6$D$_6$), δ 5.2 [t, C$_5$H$_5$, *J*(HP) 1.0], 3.5 [apparent t, 18 H, POMe, |*J*(HP) + *J*(HP′)| 12.0], 2.2 [t, 2 H, CH$_2$Bu^t, *J*(HP) 4.0], 1.1 (s, 9 H, Bu^t); ^{13}C-{^{1}H} (C$_6$D$_6$), δ 299.8 [t, Mo≡C, *J*(CP) 27.0], 89.3 (C$_5$H$_5$), 62.5 (CH$_2$), 50.9 (POMe), 33.0 (CH$_2$*C*Me$_3$), 29.9 p.p.m. (C*Me*$_3$).

Formation of (η-*Indenyl*)[σ-(E)-2-*t-butylvinyl*]*tris(trimethyl phosphite)molybdenum*(II).—A solution of the purple crystalline cation [Mo(η^2-Bu^{t}C$_2$H){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)][BF$_4$] (0.93 g, 1.4 mmol) in tetrahydrofuran (25 cm^3) was cooled (−78 °C) and one equivalent of trimethyl phosphite (0.2 cm^3, 1.88 mmol) added. A slight excess of K[BHBu$^s_3$] (1.5 cm^3 of a 1 mol dm^{-3} solution in thf) was added dropwise with stirring. After 15 min the solvent was removed *in vacuo* and the red oil extracted with diethyl ether (50 cm^3). The resultant solution was filtered through a plug of Celite and the volume of the solvent reduced (5 cm^3); cooling (−78 °C, 2 d) afforded red *crystals* of [Mo{σ-(*E*)-CH=CHBu^t}{P(OMe)$_3$}$_3$(η^5-C$_9$H$_7$)] (**3**) (0.70 g, 66%) (Found: C, 43.3; H, 6.7. C$_{24}$H$_{45}$MoO$_9$P$_3$ requires 43.2; H, 6.8%). N.m.r.: ^{1}H(C$_6$D$_6$), δ 7.13 (m, 4 H, C$_9$H$_7$), 6.85 (m, 1 H, C*H*=CHBu^t), 5.69 (m, 1 H, C$_9$H$_7$), 5.49 (m, 2 H, C$_9$H$_7$), 5.33 [dt, 1 H, CH=C*H*Bu^t, *J*(HH) 14, *J*(HP) 4.5], 3.48 (m, 27 H, POMe), 1.24 (s, 9 H, Bu^t); ^{13}C-{^{1}H} (C$_6$D$_6$), δ 153.1 [dt, MoCH=*C*HBu^t, *J*(CP) 8.55, *J*(CP) 3.74], 133.4 [dt, Mo*C*H=CHBu^t, *J*(CP) 44.68, *J*(CP) 7.81], 128.0, 110.8, 88.2, 77.2 (C$_9$H$_7$), 51.9 (POMe), 36.8 (*C*Me$_3$), 30.5 (C*Me*$_3$); ^{31}P-{^{1}H} (C$_6$D$_6$), AB$_2$ spin system, δ$_A$ 204.8, δ$_B$ 190.9 p.p.m. [*J*(P$_A$P$_B$) 113.9].

Formation of [Mo(≡CCH$_2$Bu^t){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)] *by Thermolysis of* (η-*Indenyl*)[σ-(E)-*t-butylvinyl*]*tris(trimethyl phosphite)molybdenum*(II).—Similarly, thermolysis (100 °C, 12 h) of a solution of (**3**) (0.4 g, 0.6 mmol) in hexane (10 cm^3) gave after column chromatography and recrystallisation (−78 °C, 3 d) from diethyl ether yellow *crystals* of [Mo(≡CCH$_2$Bu^t){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)] (**4**) (0.3 g, 92%) (Found: C, 46.5; H, 6.7. C$_{21}$H$_{36}$MoO$_6$P$_2$ requires C, 46.5; H, 6.7%). N.m.r.: ^{1}H(C$_6$D$_6$), δ 6.92 (AA′BB′ multiplet, 4 H, indenyl), 5.82 [d, 2 H, indenyl H^4, *J*(HH) 2.5], 5.51 [t, 1 H, indenyl H^5, *J*(HH) 2.5], 3.35 [apparent t, 18 H, POMe, |*J*(HP + *J*(HP′)| 11.0], 2.07 [t, 2 H, C*H*$_2$Bu^t, *J*(HP) 4.5], 1.08 (s, 9 H, Bu^t); ^{13}C-{^{1}H} (C$_6$D$_6$), 302.2 [t, Mo≡C, *J*(CP), 31.5], 123.4 (indenyl C^2), 122.2 (indenyl C^1), 118.5 (indenyl C^3), 93.8 (indenyl C^5), 74.4 (indenyl C^4), 62.9 (*C*H$_2$Bu^t), 50.8 (POMe), 33.1 (*C*Me$_3$), 30.0 (C*Me*$_3$); ^{31}P-{^{1}H} (C$_6$D$_6$), δ 207.5 p.p.m. (s).

Synthesis of Carbonyl(η-*cyclopentadienyl*)*bis*(3,3-*dimethylbut*-1-*yne*)*tungsten*(II) *Tetrafluoroborate*.—A solution of [W(NCMe)(CO)$_3$(η-C$_5$H$_5$)][BF$_4$] (6.0 mmol) and 3,3-dimethylbut-1-yne (3.35 g, 41 mmol) in MeCN (60 cm^3), which was contained in a water-jacketed quartz vessel, was irradiated (u.v., 500-W lamp) for 6 h. Volatile material was removed *in vacuo*, the residue dissolved in CH$_2$Cl$_2$ (600 cm^3), and filtered through a plug of Al$_2$O$_3$. The volume of the solvent was reduced to 15 cm^3, and diethyl ether added resulting in the formation of yellow-brown *crystals* of [W(η^2-Bu^{t}C$_2$H)$_2$(CO)(η-C$_5$H$_5$)][BF$_4$] (**5**) (0.6 g, 19%) (Found: C, 40.7; H, 4.9. C$_{18}$H$_{25}$BF$_4$OW requires C, 40.9; H, 4.8%); ν$_{CO}$(Nujol) at 2 071s cm^{-1}. N.m.r.: ^{1}H(CDCl$_3$), δ 11.13 (s, 1 H, HC≡C), 9.79 (s, 1 H, HC≡C), 6.16 (s, 5 H, C$_5$H$_5$), 1.39 (s, 9 H, Bu^t), 1.32 (s, 9 H, Bu^t); ^{13}C-{^{1}H} (CDCl$_3$), δ 207.9 (CO), 187.3 (Bu^t*C*≡C), 165.1 (Bu^t*C*≡C), 149.9 (Bu^{t}C≡*C*H), 132.8 (Bu^{t}C≡*C*H), 99.0 (C$_5$H$_5$), 40.4 (Me$_3$*C*C≡C), 37.2 (Me$_3$*C*C≡C), 30.7 (*Me*$_3$CC≡C), 29.9 p.p.m. (*Me*$_3$CC≡C).

Synthesis of η-*Cyclopentadienyl*(3,3-*dimethylbut*-1-*yne*)*bis*(*trimethyl phosphite*)*tungsten*(II) *Tetrafluoroborate*.—An excess of trimethyl phosphite (0.30 g, 0.25 cm^3, 2.4 mmol) was added to a stirred solution of [W(η^2-Bu^{t}C$_2$H)$_2$(CO)(η-C$_5$H$_5$)][BF$_4$] (0.6 g, 1.1 mmol) in CH$_2$Cl$_2$ (10 cm^3). After 30 min, diethyl ether (10 cm^3) was added affording red *crystals* of [W(η^2-Bu^{t}C$_2$H){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][BF$_4$] (**6**) (0.4 g, 53%) (Found: C, 30.5; H, 5.2. C$_{17}$H$_{33}$BF$_4$O$_6$P$_2$W requires C, 30.6; H, 5.0%). N.m.r.: ^{1}H(CDCl$_3$), δ 12.55 [t, 1 H, HC≡C, *J*(HP) 15.2], 5.65 (s, 5 H, C$_5$H$_5$), 3.57 [m, 18 H, POMe, |*J*(HP) + *J*(HP′)| 11.0], 1.33 (s, 9 H, Bu^t); ^{13}C-{^{1}H} (CD$_2$Cl$_2$), δ 242.6 [Bu^t*C*≡C, *J*(CW) 63.7], 199.9 [t, H*C*≡C, *J*(CP) 20.8], 92.3 (C$_5$H$_5$), 53.4 (POMe), 42.9 (Me$_3$*C*C≡C), 31.4 (*Me*$_3$CC≡C); ^{31}P-{^{1}H}, δ 143.2 p.p.m. [s, *J*(PW) 537.6].

Synthesis of (3,3-*Dimethylbut*-1-*yne*)(η-*indenyl*)*bis*(*trimethyl phosphite*)*tungsten*(II) *Tetrafluoroborate*.—A solution of [W(NCMe)$_2$(CO)$_2$(η^5-C$_9$H$_7$)][BF$_4$] (1.7 g, 3 mmol) and 3,3-dimethylbut-1-yne (0.7 g, 17 mmol) in CH$_2$Cl$_2$ (10 cm^3) was stirred at room temperature for 24 h. The volume of the solvent was reduced (5 cm^3) *in vacuo* and diethyl ether (5 cm^3) added with stirring to give a yellow solid identified by i.r. and ^{1}H n.m.r. as a mixture of [W(η^2-Bu^{t}C$_2$H)(CO)$_2$(η^5-C$_9$H$_7$][BF$_4$] and [W(η^2-Bu^{t}C$_2$H)$_2$(CO)(η^5-C$_9$H$_7$)][BF$_4$]. This mixture was dissolved in CH$_2$Cl$_2$ (10 cm^3), and treated with trimethyl phosphite (1.2 g, 9.4 mmol). After 2 h at room temperature, diethyl ether (10 cm^3) was added resulting in the precipitation of a maroon coloured oil. This was washed with diethyl ether (5 × 10 cm^3) giving maroon *microcrystals* of [W(η^2-Bu^{t}C$_2$H){P(OMe)$_3$}$_2$(η^5-C$_9$H$_7$)][BF$_4$] (**7**) (1.1 g, 51%) (Found: C, 35.0; H, 5.0. C$_{21}$H$_{35}$BF$_4$O$_6$P$_2$W requires C, 35.2; H, 4.9%). N.m.r.: ^{1}H(CDCl$_3$), δ 12.49 [t, 1 H, HC≡C, *J*(HP) 14.7], 7.35 (m, 4 H, C$_9$H$_7$), 6.00 (m, 2 H, C$_9$H$_7$), 5.67 (m, 1 H, C$_9$H$_7$), 3.45 [apparent t, 18 H, POMe, |*J*(HP) + *J*(HP′)| 11.4], 1.36 (s, 9 H, Bu^t); ^{13}C-{^{1}H}, δ 245.0 [t, Bu^t*C*≡C, *J*(CP) 2.0], 204.3 [t, Bu^{t}C≡*C*H, *J*(CP) 22.0], 128.7 (indenyl C^1), 126.0 (indenyl C^2), 115.8 (indenyl C^3), 89.29 (indenyl C^5), 78.0 (indenyl C^4), 53.8 [t, POMe, J(CP) 4.1], 43.5 ($Me_3CC{\equiv}CH$), 31.1 ($Me_3CC{\equiv}C$); $^{31}P\text{-}\{^1H\}$ ($CDCl_3$), δ 139.6 p.p.m.

Formation of $[W(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$.—Trimethyl phosphite (0.15 g, 1.23 mmol) was added to (**6**) (0.75 g, 1.13 mmol) in toluene (50 cm^3). The resultant solution was cooled (0 °C) and treated with stirring with a solution of $Na[AlH_2(OCH_2CH_2OMe)_2]$ [0.28 g, 1.4 mmol, 0.4 cm^3 of 70% (w/w) solution in toluene]. The reaction mixture was stirred (1 h, 0 °C) and then allowed to warm to room temperature. After 1 h the solvent was removed *in vacuo* and the residue extracted with hexane (5 × 10 cm^3). The resultant orange solution was filtered through Celite, the volume reduced, and chromatographed on an alumina-packed column. Elution with hexane–diethyl ether (2:1) gave a yellow band, which was collected and recrystallised (−78 °C, 24 h) to give yellow *crystals* of $[W(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**8**) (0.3 g, 45%) (Found: C, 35.3; H, 6.0. $C_{17}H_{34}O_6P_2W$ requires C, 35.2; H, 5.9%). N.m.r.: $^1H(C_6D_6)$, 5.16 (s, 5 H, C_5H_5), 3.51 [apparent t, 18 H, POMe, $|J(HP) + J(HP')|$ 11.8], 1.75 [t, 2 H, CH_2Bu^t, J(HP) 3.8], 1.08 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$ (C_6D_6), δ 284.5 [t, W≡C, J(CP), 17.1], 87.4 (C_5H_5), 64.4 [t, CH_2Bu^t, J(CW) 20.8], 51.4 (POMe), 32.1 (CMe_3), 30.0 (CMe_3); $^{31}P\text{-}\{^1H\}$ (C_6D_6), 181.4 p.p.m. [d, J(PW) 867.2].

Formation of $[W(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$.—A mixture of $[W(\eta^2\text{-}Bu^tC_2H)_2(CO)(\eta^5\text{-}C_9H_7)][BF_4]$ and $[W(\eta^2\text{-}Bu^tC_2H)(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]$, obtained from $[W(NCMe)_2(CO)_2(\eta^5\text{-}C_9H_7)][BF_4]\cdot MeCN$ (1.7 g, 3 mmol), was dissolved in CH_2Cl_2 (10 cm^3) and treated with $P(OMe)_3$ (1 cm^3, 1.2 g, 9.4 mmol). The solution was stirred (2 h) at room temperature and then the solvent removed *in vacuo*. The resultant maroon coloured oil was dissolved in thf (20 cm^3) and cooled (−78 °C). A solution of $K[BHBu^s_3]$ (3.2 cm^3, 3.2 mmol of 1 mol dm^{-3} solution in thf) was added, and the reaction mixture allowed to warm to room temperature. After 30 min the solvent was removed *in vacuo*, the residue extracted with diethyl ether, and the extracts chromatographed on alumina. Elution with diethyl ether gave a yellow band, which was collected and recrystallised (−78 °C, 3 d) from hexane–diethyl ether (2:1) to give bright yellow *crystals* of $[W(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ (**9**) (1.08 g, 56%) (Found: C, 40.5; H, 5.8. $C_{21}H_{36}O_6P_2W$ requires C, 40.0; H, 5.7%). N.m.r.: $^1H(C_6D_6)$, δ 7.00 (m, 4 H, C_9H_7), 5.98 (m, 2 H, C_9H_7), 5.39 [t, 1 H, C_9H_7, J(HH) 2.93], 3.38 [apparent t, 18 H, POMe, $|J(HP) + J(HP')|$ 11.7], 1.77 [t, 2 H, CH_2Bu^t, J(HP) 4.4], 1.08 (s, 9 H, Bu^t); $^{13}C\text{-}\{^1H\}$ (C_6D_6), 286.2 [t, W≡C, J(CP), 19.8], 123.8 (indenyl C^2), 123.0 (indenyl C^1), 117.7 (indenyl C^3), 88.8 (indenyl C^5), 71.3 (indenyl C^4), 64.3 (CH_2Bu^t), 51.2 (POMe), 32.1 (CMe_3), 30.0 (CMe_3); $^{31}P\text{-}\{^1H\}$ (C_6D_6), δ 177.58 p.p.m. [J(PW) 671.4].

Formation of $[Mo(\equiv CCH_2Pr^i)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$.—A suspension of $[Mo(\eta^2\text{-}Pr^iC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (0.5 g, 0.9 mmol) in thf (20 cm^3), with the addition of trimethyl phosphite (0.5 cm^3), was stirred (room temperature) with a slight excess of $NaBH_4$ (0.05 g, 1.3 mmol). After 2 h the volatile material was removed *in vacuo*, and the residue extracted with hexane. Column chromatography of the extracts and elution with hexane–diethyl ether (5:1) gave a primrose-yellow band which was collected. Recrystallisation (−78 °C) from pentane gave large yellow *crystals* of $[Mo(\equiv CCH_2Pr^i)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**10**) (0.25 g, 58%) (Found: C, 40.6; H, 7.2. $C_{16}H_{32}MoO_6P_2$ requires C, 40.2; H, 6.7%). N.m.r.: $^1H(CD_2Cl_2)$, δ 5.12 (s, 5 H, C_5H_5), 3.50 [apparent t, 18 H, POMe, $|J(HP) + J(HP')|$ 11.0], 2.00 [dt, 2 H, CH_2Pr^i, J(HH) 4.0, J(HP) 3.0], 1.82 (m, 1 H, $CHMe_2$), 0.94 [d, 6 H, $CHMe_2$, J(HH) 6]; $^{13}C\text{-}\{^1H\}$ (CD_2Cl_2), δ 302.5 [t, Mo≡C, J(CP) 29], 89.1 (C_5H_5), 59.3 (CH_2Pr^i), 51.0 (POMe), 29.5 ($CHMe_2$), 22.8 ($CHMe_2$); $^{31}P\text{-}\{^1H\}$ (C_6D_6), δ 213.5 p.p.m. (s).

Reactions of η*-Indenylbis(trimethyl phosphite)(trimethylsilylethyne)molybdenum*(II) *Tetrafluoroborate*.—(*a*) *With* $K[BHBu^s_3]$. A suspension of $[Mo(\eta^2\text{-}Me_3SiC_2H)\{P(OMe)_3\}_2(\eta\text{-}C_9H_7)][BF_4]$ (2.1 g, 3.2 mmol) in thf (30 cm^3) was cooled to −78 °C, and one equivalent of $K[BHBu^s_3]$ (3.2 cm^3, 3.2 mmol of 1 mol dm^{-3} solution in thf) added dropwise with stirring. After 5 min the volatile material was removed *in vacuo*, and the residue extracted (0 °C) with hexane, and chromatographed on an alumina-packed column with a jacket kept at −40 °C. Elution with diethyl ether–hexane (1:4) afforded a deep blue band, which was collected, and recrystallised (−78 °C) from hexane to give deep blue *crystals* of $[Mo\{{=}C(SiMe_3)CH_2\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ (**11**) (1.2 g, 58%) (Found: C, 43.3; H, 6.5. $C_{20}H_{36}MoO_6P_2Si$ requires C, 43.0; H, 6.5%). N.m.r.: $^1H([^2H_8]$toluene, −70 °C), δ 7.51 (m, 2 H, C_9H_7), 6.72 (m, 2 H, C_9H_7), 6.07 (m, 1 H, C_9H_7), 5.72 (m, 2 H, C_9H_7), 3.26 (m, 18 H, POMe), 2.01 [t, 2 H, CH_2, J(HP) 7], 0.54 (s, 9 H, $SiMe_3$); $^{13}C\text{-}\{^1H\}$ ($[^2H_8]$toluene, −70 °C), 276.5 [t, Mo≡C, J(CP) 6], 125.6 (indenyl C^1), 122.5 (indenyl C^2), 112.8 (indenyl C^3), 97.2 (indenyl C^5), 79.5 (indenyl C^5), 51.4 (POMe), 23.9 (s, br, $MoCH_2$), 1.2 ($SiMe_3$); $^{31}P\text{-}\{^1H\}$ ($[^2H_8]$toluene, −70 °C), δ 207.8 p.p.m. (s).

(*b*) *With* $Li(CuPh_2)$. A solution of $Li(CuPh_2)$ (3.2 mmol) in thf (10 cm^3) was added dropwise to a stirred (−78 °C) suspension of $[Mo(\eta^2\text{-}Me_3SiC_2H)\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$ (2.1 g, 3.2 mmol) in thf (20 cm^3). An immediate change in colour to dark green was observed. The reaction mixture was allowed to warm to room temperature, and the solvent removed *in vacuo*. The residue was dissolved in diethyl ether and chromatographed on alumina. Elution with diethyl ether–hexane (1:10) gave a dark green band, which was collected and recrystallised (−78 °C) from hexane–diethyl ether to give dark green *crystals* of $[Mo\{{=}C(SiMe_3)CHPh\}\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)]$ (**12**) (1.3 g, 63%) (Found: C, 49.0; H, 6.5. $C_{25}H_{40}MoO_6P_2Si$ requires C, 49.2; H, 6.4%). N.m.r.: $^1H(C_6D_6)$, δ 7.6—6.1 (m, H, C_9H_7, Ph), 5.35 (m, 1 H, C_9H_7), 4.70 [dd, 1 H, CHPh, $|J(HP) + J(HP')|$ 11.5], 3.30 [d, 9 H, POMe, $|J(HP) + J(HP')|$ 11.5], 2.90 [d, 9 H, POMe, $|J(HP) + J(HP')|$ 11.5], 0.40 (s, 9 H, $SiMe_3$); $^{13}C\text{-}\{^1H\}$ (C_6D_6), δ 288.3 [d, Mo=C, $|J(CP) + J(CP')|$ 16], 155.5 (*ipso*-Ph), 128.6, 127.6, 126.4, 124.4, 122.8, 122.2, 121.6 (C_9H_7, Ph), 115.0 (indenyl), 113.9 (indenyl C^3), 97.3 (indenyl C^5), 79.8 (indenyl C^5), 78.6 (indenyl), 51.6 [d, POMe, $|J(CP) + J(CP')|$ 6], 44.2 [d, MoCHPh, $|J(CP) + J(CP')|$ 9.0], 1.9 ($SiMe_3$); $^{31}P\text{-}\{^1H\}$ (C_6D_6), 199.7 [d, POMe, J(PP) 82], 193.2 p.p.m. [d, POMe, J(PP) 82].

Reactions of $[Mo(\eta^2\text{-}Me_3SiC_2Ph)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$.—(*a*) *With* $K[BHBu^s_3]$. A solution of $K[BHBu^s_3]$ (0.7 mmol in 0.75 cm^3 thf) was added dropwise to a stirred cooled (−78 °C) suspension of $[Mo(\eta^2\text{-}Me_3SiC_2Ph)\{P(OMe)_3\}_2(\eta^5\text{-}C_9H_7)][BF_4]$ (0.50 g, 0.69 mmol) in thf (15 cm^3). The reaction mixture was allowed to warm to room temperature and stirred for 1.5 h, after which time the solvent was removed *in vacuo*. The residue was extracted into hexane and chromatographed on alumina. Elution with diethyl ether–hexane (1:4) gave a green band, which was collected and recrystallised (−78 °C) from hexane–diethyl ether to give (**12**) (0.26 g, 59%), identical (n.m.r.) with that described above.

(*b*) *With* $Li(CuPh_2)$. Reaction of $[Mo(\eta^2\text{-}Me_3SiC_2Ph)\{P(OMe)_3\}_2(\eta\text{-}C_9H_7)][BF_4]$ (0.50 g, 0.69 mmol) with $Li(CuPh_2)$ (0.75 mmol) in thf (20 cm^3) at −78 °C followed by chromatography and crystallisation (−78 °C) from hexane gave green *crystals* of $[Mo\{{=}C(SiMe_3)CPh_2\}\{P(OMe)_3\}_2(\eta^5\text{-}$

$C_9H_7)]$ (**13**) (0.24 g, 49%) (Found: C, 53.1; H, 6.3. $C_{32}H_{44}MoO_6P_2Si$ requires C, 53.3; H, 6.3%). N.m.r.: $^1H(C_6D_6)$, δ 7.95—7.86 (m, 2 H, Ph), 7.37—6.54 (m, 10 H, C_9H_7, Ph), 6.61 [d, 1 H, C_9H_7, *J*(HH) 3.9], 6.53 [d, 1 H, C_9H_7, *J*(HH) 3.9], 5.78 (m, 1 H, C_9H_7), 5.28 (m, 2 H, C_9H_7), 3.15 [d, 9 H, POMe, |*J*(HP) + *J*(HP′)| 10.9], 2.91 [d, 9 H, POMe, |*J*(HP) + *J*(HP′)| 10.5], 0.28 (s, 9 H, $SiMe_3$); $^{13}C-\{^1H\}$ (C_6D_6), δ 276.9 [t, Mo=C, |*J*(CP) + *J*(CP′)| 52.8], 156.1, 154.1 (*ipso*-Ph), 130.8—121.3 (s, Ph, C_9H_7), 116.5, 115.5, 95.7, 82.9, 77.0 (C_9H_7), 51.3 [d, POMe, *J*(CP) 3.9], 29.1 [d, Mo–*C*Ph_2, *J*(CP) 9.8], 0.6 ($SiMe_3$); $^{31}P-\{^1H\}$ (C_6D_6), δ 199.3 [d, POMe, *J*(PP′) 85.5], 189.9 p.p.m. [d, POMe, *J*(PP′) 85.5].

Rearrangement of $[Mo\{=C(SiMe_3)CH_2\}\{P(OMe)_3\}_2(\eta^5-C_9H_7)]$ (**11**).—A solution of (**11**) (1.1 g, 2 mmol) in toluene (10 cm^3) was stirred at room temperature for 24 h, the blue colour changing to yellow. The solvent was removed *in vacuo*, and the residue chromatographed on alumina. Elution with hexane–diethyl ether (4:1) gave a yellow band. This was collected and recrystallised (−78 °C, 5 d) from pentane to give yellow *crystals* of $[Mo(\equiv CCH_2SiMe_3)\{P(OMe)_3\}_2(\eta^5-C_9H_7)]$ (**14**) (1.0 g, 98%) (Found: C, 43.0; H, 6.7. $C_{20}H_{36}MoO_6P_2Si$ requires C, 43.0; H, 6.5%). N.m.r.: $^1H(C_6D_6)$, δ 7.08 (m, 2 H, C_9H_7), 6.54 (m, 2 H, C_9H_7), 5.64 (m, 2 H, C_9H_7), 5.37 [t, 1 H, C_9H_7, *J*(HH) 3.0], 3.18 [apparent t, 18 H, POMe, |*J*(HP) + *J*(HP′)| 11.5], 1.90 [t, 3 H, $Mo\equiv CCH_2$, *J*(HP) 5.5], −0.04 (s, 9 H, $SiMe_3$); $^{13}C-\{^1H\}$ ($[^2H_8]$toluene), δ 297.3 [t, Mo≡C, *J*(CP) 31], 124.2 (indenyl C^2), 122.7 (indenyl C^1), 118.8 (indenyl C^3), 93.6 (indenyl C^5), 78.8 (indenyl C^4), 51.3 (POMe), 45.7 (Mo≡C*C*H_2), −0.2 ($SiMe_3$); $^{31}P-\{^1H\}$ ($[^2H_8]$toluene), δ 207.6 p.p.m. (s, POMe).

Rearrangement of $[Mo\{=C(SiMe_3)CHPh\}\{P(OMe)_3\}_2(\eta^5-C_9H_7)]$ (**12**).—A solution of (**12**) (0.20 g, 0.32 mmol) in hexane (15 cm^3) contained in a sealed tube (50 cm^3) fitted with a Young's tap, was heated (70 °C, 7 d), during which time the colour changed from green to yellow. The solvent was removed *in vacuo*, and the residue chromatographed on alumina. Elution with hexane–diethyl ether (3:2) gave a yellow band, which was collected and recrystallised (−78 °C) from hexane to afford yellow *crystals* of $[Mo\{\equiv CCH(Ph)SiMe_3\}\{P(OMe)_3\}_2(\eta^5-C_9H_7)]$ (**15**) (0.14 g, 70%) (Found: C, 49.4; H, 6.6. $C_{26}H_{40}MoO_6P_2Si$ requires C, 49.2; H, 6.4%). N.m.r.: $^1H(C_6D_6)$, δ 7.66—6.75 (m, 9 H, C_9H_7, Ph), 6.02 (m, 2 H, C_9H_7), 5.71 [t, 1 H, C_9H_7, *J*(HH) 6.1], 3.50 [t, 1 H, Mo≡CCH, *J*(HP) 5.1], 3.34 [d, 9 H, POMe, |*J*(HP) + *J*(HP′)| 11.7], 3.19 [d, 9 H, POMe, |*J*(HP) + *J*(HP′)| 11.5], 0.16 (s, 9 H, $SiMe_3$); $^{13}C-\{^1H\}$ (C_6D_6), δ 297.1 [t, Mo≡C, *J*(CP) 29.4], 141.3 (*ipso*-Ph), 132.2—122.0 (series of singlets due to Ph and C_9H_7), 118.6 (C_9H_7), 118.1 (C_9H_7), 93.2, 74.2, 73.7 (C_9H_7), 64.6 (Mo≡C*C*), 50.7, 50.6 (POMe), −1.8 ($SiMe_3$); $^{31}P-\{^1H\}$ (C_6D_6), δ 205.6 p.p.m. (s, POMe).

Desilylation of $[Mo(\equiv CCH_2SiMe_3)\{P(OMe)_3\}_2(\eta^5-C_9H_7)]$.—A solution of (**14**) (0.1 g, 2 mmol), and NaF (0.1 g, 2 mmol) in acetonitrile (10 cm^3) and water (1 cm^3) was stirred at room temperature for 24 h. The solvent was removed *in vacuo*, the residue extracted with hexane, and the extract chromatographed on an alumina-packed column. Elution with hexane–diethyl ether (4:1) gave a yellow band, which was collected, and recrystallised (−78 °C, 7 d) from pentane to give yellow *crystals* of $[Mo(\equiv CCH_3)\{P(OMe)_3\}_2(\eta^5-C_9H_7)]$ (**16**) (0.07 g, 80%) (Found: C, 42.4; H, 6.1. $C_{17}H_{28}MoO_6P_2$ requires C, 42.0; H, 5.8%). N.m.r.: $^1H(C_6D_6)$, δ 7.15 (m, 2 H, C_9H_7), 6.65 (m, 2 H, C_9H_7), 5.70 (m, 2 H, C_9H_7), 5.42 [t, 1 H, C_9H_7, *J*(HH) 6.0], 3.35 [apparent t, 18 H, POMe, |*J*(HP) + *J*(HP′)| 11.5], 1.90 [t, 3 H, Mo≡CMe, *J*(HP) 5]; $^{13}C-\{^1H\}$ (C_6D_6), δ 295.8 [t, Mo≡C, *J*(CP) 29.5], 123.4 (indenyl C^2), 122.1 (indenyl C^1), 118.4 (indenyl C^3), 92.5 (indenyl C^5), 74.3 (indenyl C^4), 50.7 (POMe), 36.0 (Mo≡C*Me*); $^{31}P-\{^1H\}$ (C_6D_6), δ 207.7 p.p.m. (s, POMe).

Table 3. Structure analyses

	(**2**)	(**11**)
(*a*) Data collection		
Crystal colour and habitat	Pale yellow hexagonal prism	Blue block
Solvent [θ_c/°C]	Hexane–ether (3:1) [−78]	Hexane [−78]
Approx. crystal size (mm)	0.5 × 0.55 × 0.2	0.5 × 0.4 × 0.15
Method of data collection	θ/2θ	Wyckoff, ω scans
T/K	230	230
Scan speeds (° min^{-1})		
minimum	3.0	2.9
maximum	58.6	29.3
Scan width (°)	$2.0 + \Delta_{\alpha_1\alpha_2}$	1.0
2θ Range (°)	3—55	4—45
Check reflections	−2,−7,−6,4,3,5	3,−1,−1,0,−4,2
No. of data collected	9 223	3 456
No. of unique data	8 107	3 093
No. of observed data (N_o)	7 816	2 830
Transmission coefficient range	0.742—0.919	
(*b*) Refinement		
Anisotropic atoms	Mo, C, O, P	Mo, C, O, Si, P
Isotropic atoms	H	H
No. of parameters refined (N_v)	621	306
* Final *R*	0.026	0.026
R′	0.027	0.026
g	0.002	0.0002
S	1.369	1.32
Largest final difference electronic-density features (e $Å^{-3}$)	+1.1, −0.7	±0.5

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w^{\frac{1}{2}}|F_o| - |F_c|/\Sigma w^{\frac{1}{2}}F_o]$; $S = [\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]$.

Desilylation of $[Mo\{\equiv CCH(Ph)SiMe_3\}\{P(OMe)_3\}_2(\eta^5-C_9H_7)]$.—A solution of (**15**) (0.15 g, 0.24 mmol) in acetonitrile (10 cm^3) containing water (1 cm^3) and sodium fluoride (0.1 g, 2.38 mmol) was stirred at room temperature for 24 h. Removal of the solvent *in vacuo*, extraction with hexane, followed by chromatography on alumina, gave on elution with hexane–diethyl ether (4:1) a yellow band, which was collected and recrystallised (−78 °C) from hexane to give yellow *crystals* of $[Mo(\equiv CCH_2Ph)\{P(OMe)_3\}_2(\eta^5-C_9H_7)]$ (**17**) (0.12 g, 80%) (Found: C, 48.9; H, 5.9. $C_{23}H_{32}MoO_6P_2$ requires C, 49.1; H, 5.7%). N.m.r.: $^1H(C_6D_6)$, δ 7.3—7.15 (m, 7 H, C_9H_7, Ph), 6.76 (m, 2 H, C_9H_7), 5.87 (m, 2 H, C_9H_7), 5.54 [t, 1 H, C_9H_7, *J*(HH) 3.0], 3.48 [t, 2 H, $Mo\equiv CCH_2$, *J*(HP) 5], 3.34 [apparent t, 18 H, POMe, |*J*(HP) + *J*(HP′)| 11.5]; $^{31}P-\{^1H\}$ (C_6D_6), δ 207.6 p.p.m. (s, POMe).

Crystal Structure Analysis.—Single-crystal *X*-ray diffraction studies of (**2**) and (**11**) were carried out at low temperature using a Nicolet P3m diffractometer fitted with the LT-1 crystal cooling device. The crystals were sealed in thin-walled glass capillaries [(**2**) under N_2, (**11**) under Ar]. Intensity data were collected with Mo-K_α *X*-radiation (graphite monochromator, $\bar{\lambda}$ = 0.710 69 Å) for unique volumes of reciprocal space using variable-speed scans. The scan speed employed was determined on the basis of a 2 s pre-scan of the reflection; if below a low threshold value on the pre-scan, the reflection was not recorded for any 2θ in the case of (**2**), and for 40 < 2θ < 45° in the case of (**11**). Two check reflection intensities were remeasured after every 50 reflections; these showed no significant variation over the period of data collection. Further details of data collection, reduction and structure solution and refinement are given in Table 3.

Table 4. Atomic co-ordinates (× 10^4) for (**2**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	3 615(1)	7 584(1)	5 998(1)	C(11)	6 932(4)	−1 114(2)	8 403(2)
Mo(2)	6 566(1)	2 540(1)	9 224(1)	C(12)	5 545(3)	1 360(3)	7 468(2)
P(1)	1 983(1)	7 773(1)	5 083(1)	C(13)	2 521(2)	6 407(2)	6 228(1)
P(2)	2 492(1)	8 760(1)	6 718(1)	C(14)	1 607(3)	5 414(2)	6 376(1)
P(3)	8 501(1)	2 568(1)	9 997(1)	C(15)	2 365(3)	4 434(2)	6 075(1)
P(4)	7 333(1)	1 101(1)	8 543(1)	C(16)	1 279(3)	3 478(2)	6 813(2)
O(1)	440(2)	8 197(2)	5 135(1)	C(17)	3 416(3)	4 017(2)	6 232(2)
O(2)	1 474(2)	6 672(2)	4 606(1)	C(18)	3 103(4)	4 815(3)	7 388(2)
O(3)	2 530(2)	8 654(2)	4 542(1)	C(19)	5 568(3)	8 772(2)	5 672(2)
O(10)	8 928(2)	841(1)	8 467(1)	C(20)	5 839(3)	8 513(3)	6 357(2)
O(11)	6 770(2)	−103(1)	8 789(1)	C(21)	5 963(3)	7 374(3)	6 399(2)
O(12)	6 894(2)	1 047(2)	7 725(1)	C(22)	5 759(3)	6 898(3)	5 731(2)
O(4)	868(2)	8 434(2)	6 777(1)	C(23)	5 498(3)	7 772(3)	5 280(2)
O(5)	3 059(2)	8 917(2)	7 521(1)	C(24)	7 604(2)	3 583(2)	8 812(1)
O(6)	2 571(2)	10 096(1)	6 627(1)	C(25)	8 503(3)	4 510(2)	8 558(1)
O(7)	9 966(2)	2 355(2)	9 702(1)	C(26)	7 758(3)	5 260(2)	8 030(1)
O(8)	8 516(2)	1 802(2)	10 660(1)	C(27)	6 521(3)	5 754(2)	8 347(1)
O(9)	8 993(3)	3 722(2)	10 409(1)	C(28)	8 808(3)	6 198(2)	7 853(2)
C(1)	−632(3)	7 496(3)	5 412(2)	C(29)	7 255(3)	4 564(2)	7 387(1)
C(2)	2 428(4)	5 842(3)	4 470(2)	C(30)	4 120(3)	2 697(3)	8 985(2)
C(3)	1 693(4)	8 918(4)	3 937(2)	C(31)	4 588(3)	3 438(3)	9 541(2)
C(4)	59(3)	9 063(3)	7 230(2)	C(32)	5 023(3)	2 782(3)	10 093(2)
C(5)	3 167(4)	7 932(3)	7 911(2)	C(33)	4 805(3)	1 651(2)	9 886(2)
C(6)	2 329(4)	10 545(2)	5 958(2)	C(34)	4 273(3)	1 605(3)	9 206(2)
C(7)	11 228(3)	2 382(3)	10 141(2)	H(14a)	883(26)	5 671(20)	6 663(12)
C(8)	8 372(4)	621(3)	10 574(2)	H(14b)	1 105(39)	5 120(30)	5 974(19)
C(9)	8 149(3)	4 571(3)	10 537(2)	H(25a)	8 881(29)	4 977(23)	8 960(14)
C(10)	9 846(3)	1 654(2)	8 169(2)	H(25b)	9 430(31)	4 161(24)	8 312(15)

Table 5. Atomic co-ordinates (× 10^4) for (**11**)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	4 237(1)	1 201(1)	2 921(1)	C(7)	4 376(5)	1 002(4)	1 451(2)
P(1)	5 883(1)	3 847(1)	2 878(1)	C(8)	3 762(4)	−371(4)	1 761(2)
P(2)	1 824(1)	1 047(1)	2 487(1)	C(9)	5 532(4)	−1 673(4)	1 010(3)
Si	3 469(1)	−2 252(1)	1 116(1)	C(10)	2 582(4)	−3 893(4)	1 647(3)
O(1)	5 215(3)	4 611(3)	2 300(2)	C(11)	2 027(5)	−3 074(4)	−75(2)
O(2)	7 507(3)	4 457(3)	2 524(2)	C(12)	3 216(4)	319(4)	4 118(2)
O(3)	6 646(3)	5 219(3)	3 893(2)	C(13)	3 571(4)	−738(4)	3 679(2)
O(4)	1 472(3)	2 074(3)	3 225(2)	C(14)	5 302(4)	152(4)	3 854(2)
O(5)	83(3)	−624(3)	2 364(2)	C(15)	6 361(4)	−273(4)	3 630(2)
O(6)	1 471(3)	1 370(3)	1 533(2)	C(16)	8 019(4)	843(4)	3 956(3)
C(1)	4 984(5)	4 345(4)	1 326(2)	C(17)	8 721(4)	2 452(4)	4 523(3)
C(2)	8 475(4)	3 884(5)	2 706(3)	C(18)	7 768(4)	2 942(4)	4 722(2)
C(3)	7 688(5)	6 936(4)	4 013(3)	C(19)	6 025(4)	1 812(4)	4 394(2)
C(4)	2 588(5)	3 817(4)	3 584(3)	C(20)	4 702(4)	1 901(4)	4 532(2)
C(5)	−381(5)	−2 128(5)	1 754(3)	H(7a)	3 616(36)	1 036(33)	1 075(19)
C(6)	−36(5)	1 190(5)	1 161(3)	H(7b)	5 468(41)	1 434(37)	1 306(21)

An absorption correction, by the Gaussian quadrature method, was applied to the data for (**2**). Duplicate and symmetry-equivalent data were averaged to give unique data of which those with $I > 2\sigma(I)$ were considered observed and used in structure analysis.

Structure solution was by conventional heavy-atom (Patterson and difference Fourier) methods, all atoms being directly located in electron-density syntheses. In both structures methylene group hydrogens were refined without positional constraints, all other hydrogens being constrained to idealised geometry (C–H 0.96 Å). For (**2**) hydrogens and for (**11**) just methylene hydrogens had freely refined isotropic displacement parameters, other hydrogens having U_{iso} fixed at *ca.* $1.2U_{iso}$ for the attached carbon atom. Refinement was by blocked-cascade full-matrix least-squares methods with data assigned weights $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$ where $\sigma_c(F_o)$ is based on counting statistics alone. Final residuals are given in Table 3; the final positional parameters for all atoms freely refined for (**2**) and (**11**) are given in Tables 4 and 5 respectively.

All calculations were carried out with the SHELXTL program package[26] on a Nicolet R3m/E system, using complex neutral-atom scattering factors of ref. 27.

Crystal Data for (**2**).—$C_{17}H_{34}MoO_6P_2$, $M = 492.1$, triclinic, space group $P\bar{1}$, $a = 9.660(1)$, $b = 11.978(1)$, $c = 19.578(4)$ Å, $\alpha = 91.38(1)$, $\beta = 94.25(1)$, $\gamma = 93.48(1)°$, $U = 2\,253.9(5)$ Å^3, $Z = 4$, $D_c = 1.45$ g cm^{-3}, $F(000) = 1\,024$, μ(Mo-K_α) = 7.33 cm^{-1}. Crystal faces [distances from origin (mm)]: (100) [0.2], ($\bar{1}$00) [0.2], (010) [0.17], (0$\bar{1}$0) [0.25], (110) [0.25], ($\bar{1}\bar{1}$0) [0.20], (001) [0.055], (00$\bar{1}$) [0.055].

Crystal Data for (**11**).—$C_{20}H_{36}MoO_6P_2Si$, $M = 558.1$, triclinic, space group $P\bar{1}$, $a = 10.145(3)$, $b = 10.446(3)$, $c = 15.384(6)$ Å, $\alpha = 101.85(3)$, $\beta = 97.66(3)°$, $\gamma = 122.85(2)°$, $U =$

1 279.7(7) Å^3, $Z = 2$, $D_c = 1.45$ g cm^{-3}, $F(000) = 580$, μ(Mo-K_α) = 6.99 cm^{-1}.

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