

Reactions of Co-ordinated Ligands. Part 33.¹ Mononuclear η^2 -Vinyl Complexes: Synthesis, Structure, and Reactivity*

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Treatment of the four-electron alkyne cation $[\text{Mo}(\eta^2\text{-PhC}_2\text{Ph})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ with $\text{K}[\text{BHBu}^s_3]$ affords the η^2 -vinyl or metallacyclopropene complex $[\text{Mo}\{\text{C}(\text{Ph})\text{CHPh}\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (2). The related complexes $[\text{Mo}\{\text{C}(\text{Bu}^t)\text{CHPh}\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (3), $[\text{Mo}\{\text{C}(\text{Bu}^t)\text{CH}(\text{C}_6\text{H}_4\text{Me-4})\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (4), $[\text{Mo}\{\text{C}(\text{Pr}^i)\text{CH}(\text{C}_6\text{H}_4\text{Me-4})\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (5), and $[\text{Mo}\{\text{C}(\text{Me})\text{CPh}_2\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (6) are obtained on reaction of the corresponding lithium diarylcuprate with the respective alkyne cation $[\text{Mo}(\eta^2\text{-R}^1\text{C}_2\text{R}^2)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ ($\text{R}^1 = \text{Bu}^t$, $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{Pr}^i$, $\text{R}^2 = \text{H}$; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{Ph}$). The structures of (2), (3), and (6) have been determined by single-crystal X-ray diffraction studies. The molecules show close similarities; each has a molybdenum atom to which a vinyl moiety is co-ordinated *via* one short and one long Mo–C bond. These molecules may be described either as $\eta^2(3e)$ -vinyl or metallacyclopropene complexes. The orientation of the C_2 vinyl group relative to the $\text{Mo}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)$ fragment is discussed in terms of the torsion angles. In (2) and (3), C_α of the vinyl group lies closer to the plane of the $\eta\text{-C}_5\text{H}_5$ ligand than does C_β , whereas in (6) the reverse orientation is observed. The solution n.m.r. spectra of (2) and (3) have distinct ^{31}P environments, whereas in (6) the phosphorus environments are equivalent. This is discussed in terms of a rotational movement, an extended Hückel molecular orbital analysis suggesting that the orientation and fluxional behaviour of the η^2 -vinyl ligands parallel those of the related alkyne complexes. Reaction of $[\text{Mo}(\eta^2\text{-PhC}_2\text{CH}_2\text{Ph})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ with $\text{K}[\text{BHBu}^s_3]$ affords a separable mixture of isomeric complexes $[\text{Mo}\{\text{C}(\text{CH}_2\text{Ph})\text{CHPh}\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$, which differ only in the orientation of the η^2 -vinyl moiety. The complex (6) slowly rearranges in solution to an η^3 -allylic complex this being explained in terms of an η^2 to σ change in the bonding mode of the vinyl ligand. A similar transformation is suggested to explain the formation of η^3 -allylic complexes on reaction of $[\text{Mo}(\eta^2\text{-RC}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ ($\text{R} = \text{Bu}^t$ or Pr^i) with LiCuMe_2 . Extension of the dimethyl- or diphenyl-cuprate reactions to the cations $[\text{Mo}(\eta^2\text{-R}^1\text{C}_2\text{R}^2)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ provides evidence for competing reaction pathways involving either direct attack on the metal centre or on a co-ordinated alkyne carbon. The regioselectivity of the latter reaction is discussed in terms of steric and electronic effects.

Although species containing transition-metal vinyl complexes have been implicated in alkyne trimerisation,²⁻⁸ alkene-alkyne cyclocotrimerisation,⁹⁻¹² and also in alkyne linking reactions at palladium,¹³ dinickel,¹⁴ and dimolybdenum centres,^{15,16} their chemistry is still poorly understood. The more familiar role of the vinyl group is as a σ -bound (one-electron) ligand; however, in exploring the reactions of nucleophiles with cationic alkyne complexes of molybdenum,¹⁷⁻¹⁹ in which the alkyne functions as a four-electron donor,²⁰⁻²² we have discovered²³ a route to an unusual group of molecules where the C_2 fragment of the vinyl group adopts an alternative bonding mode as an $\eta^2(3e)$ system. An important implication of this observation is that when a $\sigma(1e)$ vinyl group is bonded to a co-ordinatively unsaturated metal centre then there is the possibility that the vinyl group can change [$\sigma(1e)$ to $\eta^2(3e)$] its bonding mode in order to accommodate the unsaturation, the α -carbon of the C_2 vinyl fragment assuming carbenoid- or alkylidene-like character. In a sense this process has a parallel in the generation of η^2 -acyl groups at unsaturated zirconium²⁴

and thorium centres.²⁵ This paper extends our preliminary work²³ with these systems and describes synthetic, structural, and reactivity studies.

Results and Discussion

Reaction of $[\text{Mo}(\eta^2\text{-PhC}_2\text{Ph})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]^+$ (1)²² with $\text{K}[\text{BHBu}^s_3]$ in tetrahydrofuran (thf) at -78°C afforded on column chromatography a green crystalline complex (2). Examination of the analytical data, ^1H , $^{13}\text{C}\{-^1\text{H}\}$, and $^{31}\text{P}\{-^1\text{H}\}$ n.m.r. spectra (see Experimental section) indicated the unusual molecular formula of $[\text{Mo}\{\text{C}(\text{Ph})\text{CH}(\text{Ph})\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ for (2). The structurally related (by n.m.r.) complexes $[\text{Mo}\{\text{C}(\text{Bu}^t)\text{CHPh}\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (3), $[\text{Mo}\{\text{C}(\text{Bu}^t)\text{CH}(\text{C}_6\text{H}_4\text{Me-4})\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (4), $[\text{Mo}\{\text{C}(\text{Pr}^i)\text{CH}(\text{C}_6\text{H}_4\text{Me-4})\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (5), and $[\text{Mo}\{\text{C}(\text{Me})\text{CPh}_2\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ (6), were obtained as red crystalline materials by reaction (-78°C , thf) of lithium diarylcuprates with $[\text{Mo}(\eta^2\text{-Bu}^t\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]^+$, $[\text{Mo}(\eta^2\text{-Pr}^i\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]^+$, or $[\text{Mo}(\eta^2\text{-PhC}_2\text{-Me})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]^+$ ²² respectively. The $^{13}\text{C}\{-^1\text{H}\}$ spectra of the complexes showed resonances associated with the contact carbons of the $\text{CR}^1\text{CR}^2\text{R}^3$ fragment in the range 286.9–237.4 and 30.0–26.1 p.p.m., which on the basis of off-

* Supplementary data available (No. SUP 56105, 8 pp.): anisotropic vibrational parameters, H-atom co-ordinates for (2), (3), and (6). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii–xix. Structure factors are available from the editorial office.

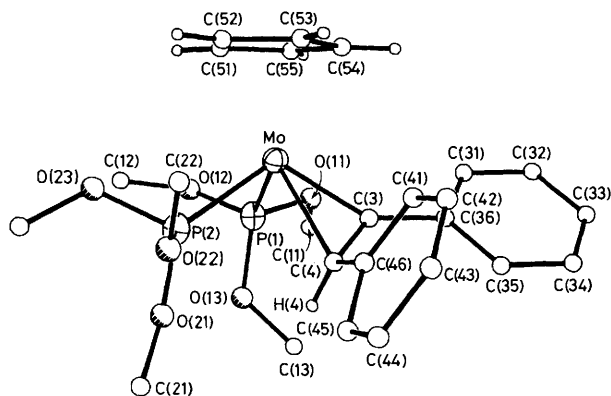


Figure 1. Molecular structure of (2)

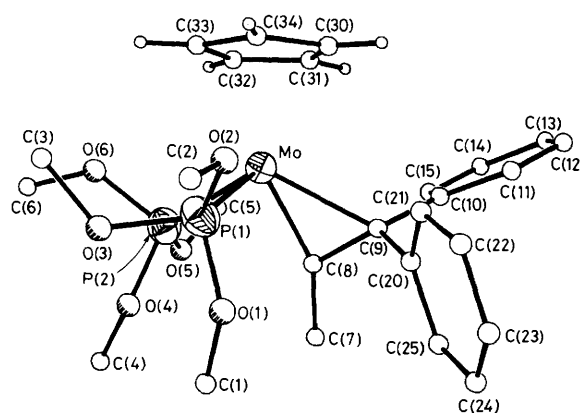


Figure 3. Molecular structure of (6)

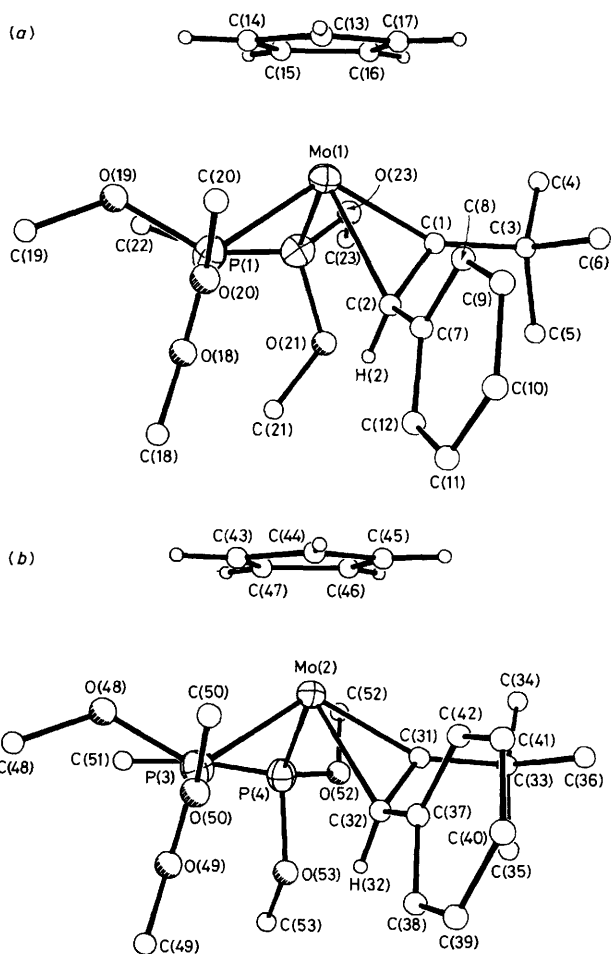


Figure 2. Molecular structure of the two crystallographically independent molecules of (3), (a) and (b)

resonance ^1H -decoupled spectra, are assigned respectively to the α - and β -carbons of the $\text{MoC(R)CR}^1\text{R}^2$ vinyl group. Of particular interest was the low-field signal characteristic of an alkylidene type carbon implying the presence of a molybdenum to carbon multiple bond. A further notable feature of these molecules was the observation that the ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra of the complexes (2)–(5) showed inequivalent trimethyl phosphite ligand environments, whereas, the corresponding

spectrum of (6), which carries two phenyl substituents on the β -carbon, exhibited only one ^{31}P signal down to a temperature of -90°C . Whilst it was possible that the two phosphorus nuclei in (6) are accidentally equivalent the appearance of the alkylidene signal $\text{Mo}=\text{C}(\text{Me})\text{CPh}_2$ in the ^{13}C - $\{^1\text{H}\}$ spectrum as a triplet [$J(\text{PC})$ 28 Hz] indicates equal $J(\text{PC})$ couplings, and hence, it is more likely that the molecule is fluxional with a time averaging of the ^{31}P environments.

In order to understand the bonding and molecular geometries of these species, single-crystal X -ray diffraction studies were carried out on (2), (3), and (6), the results being presented in Tables 1–3, which list the derived bond lengths and interbond angles. Details of structure determinations are given in the Experimental section. The molecular geometries of the complexes are illustrated in Figures 1, 2(a), and (b) (for the two crystallographically independent molecules), and 3. Aspects of these molecular geometries and that of the related blue crystalline complex $[\text{Mo}\{\text{C}(\text{SiMe}_3)\text{CH}_2\}\{\text{P}(\text{OMe})_3\}_2(\eta^5\text{-C}_9\text{H}_7)]$ (7), which has been described in a preliminary communication,²⁶ and will be discussed in detail in a following paper, are summarised in Table 4.

The molecules (2), (3), and (6) show close similarities; each has a molybdenum atom co-ordinated by an η^5 -bound cyclopentadienyl group, two phosphorus-bonded trimethyl phosphite ligands, and a vinyl moiety, co-ordinated *via* one short and one long Mo–C bond (*ca.* 1.95 and 2.3 Å respectively). These distances, which are typical dimensions for Mo–C bonds of order two and one, prompt description of these molecules as molybdenacyclopropenes. By way of comparison, lengths of formal Mo=C double bonds are in the range 1.83–2.06 Å as illustrated by the following complexes: *trans*- $[\text{MoCl}(\text{C}=\text{C}(\text{CN})_2)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ [1.833(6) Å],²⁷ *trans*- $[\text{MoI}(\text{C}=\text{CHBu}^t)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ [1.927(3) Å],²⁸ $[\text{Mo}\{\text{C}(\text{CH}_2\text{Bu}^t)\text{P}(\text{O})(\text{OMe})_2(\text{I})\}\{\text{P}(\text{OMe})_3\}(\eta\text{-C}_5\text{H}_5)]$ [2.006(4) Å],²⁹ and *trans*- $[\text{Mo}\{\text{C}(\text{OEt})\text{Ph}\}(\text{GePh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [2.062(11) Å].³⁰ Single Mo–C bond distances are usually in the range 2.2–2.4 Å: *e.g.* in $[\text{Mo}\{\sigma\text{-}(E)\text{-CH}=\text{CHBu}^t\}\{\text{P}(\text{OMe})_3\}_3(\eta\text{-C}_5\text{H}_5)]$ [2.243(2) Å]¹⁸ and $[\text{MoEt}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]$ [2.397(19) Å].³¹

To aid in discussion we adopt the nomenclature shown in Scheme 1. Thus, cp represents the centroid of the η^5 -cyclopentadienyl ligand, P represents the phosphorus atom of a trimethyl phosphite ligand, C_α the carbon atom doubly bonded to molybdenum, C_β that singly bonded, and R_α , R_β , and R_β' the substituent atoms at these carbons. The geometric parameters listed in Table 4 indicate the important features of the co-ordination stereochemistry of the vinyl ligands. In each complex the $\text{C}_\alpha\text{-C}_\beta$ vector is orientated so that there is one P–Mo– $\text{C}_\alpha\text{-C}_\beta$ torsion angle of *ca.* -90° ; in (2), (3), and (7) the other torsion

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

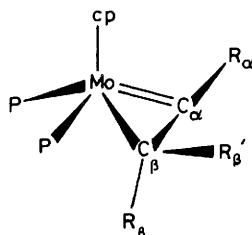
(a) Bond lengths (Å)

Mo-P(1)	2.340(1)	Mo-P(2)	2.326(1)	C(4)-C(46)	1.481(4)	C(31)-C(32)	1.385(5)
Mo-C(3)	1.951(3)	Mo-C(4)	2.301(3)	C(31)-C(36)	1.391(4)	C(32)-C(33)	1.366(6)
Mo-C(51)	2.345(4)	Mo-C(52)	2.388(3)	C(33)-C(34)	1.382(6)	C(34)-C(35)	1.391(5)
Mo-C(53)	2.376(3)	Mo-C(54)	2.344(4)	C(35)-C(36)	1.403(5)	C(41)-C(42)	1.391(5)
Mo-C(55)	2.338(4)			C(41)-C(46)	1.398(4)	C(42)-C(43)	1.356(5)
P(1)-O(12)	1.616(3)	P(1)-O(11)	1.603(2)	C(43)-C(44)	1.375(5)	C(44)-C(45)	1.387(5)
P(2)-O(21)	1.603(2)	P(1)-O(13)	1.594(2)	C(45)-C(46)	1.390(4)	C(51)-C(52)	1.384(7)
P(2)-O(23)	1.623(3)	P(2)-O(22)	1.620(2)	C(51)-C(55)	1.384(6)	C(52)-C(53)	1.390(6)
C(3)-C(36)	1.457(4)	C(3)-C(4)	1.433(4)	C(53)-C(54)	1.381(6)	C(54)-C(55)	1.381(6)
						C(4)-H(4)	0.861(24)

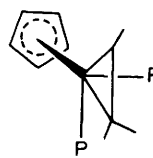
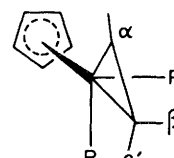
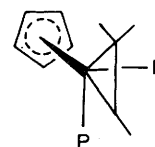
(b) Bond angles (°)

P(1)-Mo-P(2)	91.4(1)	P(1)-Mo-C(3)	87.2(1)	C(4)-Mo-C(54)	116.9(1)	C(51)-Mo-C(54)	57.1(2)
P(2)-Mo-C(3)	109.5(1)	P(1)-Mo-C(4)	99.4(1)	C(52)-Mo-C(54)	56.9(1)	C(53)-Mo-C(54)	34.0(1)
P(2)-Mo-C(4)	73.1(1)	C(3)-Mo-C(4)	38.3(1)	P(1)-Mo-C(55)	89.2(1)	P(2)-Mo-C(55)	139.1(1)
P(1)-Mo-C(51)	94.4(1)	P(2)-Mo-C(51)	104.9(1)	C(3)-Mo-C(55)	111.3(1)	C(4)-Mo-C(55)	146.8(1)
C(3)-Mo-C(51)	145.4(1)	C(4)-Mo-C(51)	166.0(1)	C(51)-Mo-C(55)	34.4(2)	C(52)-Mo-C(55)	56.7(1)
P(1)-Mo-C(52)	126.5(1)	P(2)-Mo-C(52)	91.6(1)	C(53)-Mo-C(55)	56.3(1)	C(54)-Mo-C(55)	34.3(1)
C(3)-Mo-C(52)	140.4(1)	C(4)-Mo-C(52)	132.2(1)			Mo-C(3)-C(4)	84.2(2)
C(51)-Mo-C(52)	34.0(2)	P(1)-Mo-C(53)	145.4(1)	Mo-C(3)-C(36)	143.9(2)	C(4)-C(3)-C(36)	129.8(3)
P(2)-Mo-C(53)	112.3(1)	C(3)-Mo-C(53)	106.6(1)	Mo-C(4)-C(3)	57.5(1)	Mo-C(4)-H(4)	113.8(19)
C(4)-Mo-C(53)	111.0(1)	C(51)-Mo-C(53)	56.4(2)	C(3)-C(4)-H(4)	121.2(17)	Mo-C(4)-C(46)	123.8(2)
C(52)-Mo-C(53)	33.9(2)	P(1)-Mo-C(54)	116.8(1)	C(3)-C(4)-C(46)	122.6(2)	H(4)-C(4)-C(46)	109.4(18)
P(2)-Mo-C(54)	146.0(1)	C(3)-Mo-C(54)	91.5(1)				

* Estimated standard deviations are given in parentheses here and throughout this paper.



Scheme 1.

 $\theta = 0^\circ$  $\theta = 45^\circ$  $\theta = 180^\circ$

Scheme 2.

angle (θ) is *ca.* 0° . In (6), however, the second P-Mo-C $_{\alpha}$ -C $_{\beta}$ torsion angle, designated θ , is *ca.* 180° . A consequence of this is that in (2), (3), and (7), C $_{\alpha}$ lies closer to the plane of the η^5 -cyclopentadienyl ligand than does C $_{\beta}$, whereas, in (6) this sequence is reversed (Scheme 2). In the $\theta \approx 0^\circ$ orientation the substituents R $_{\beta}$ and R $_{\beta}'$ can be classified as axial and equatorial in that R $_{\beta}$ lies approximately on the extension of the Mo-cp vector and the C $_{\beta}$ -R $_{\beta}'$ vector is roughly orthogonal to this axis. Thus, R $_{\beta}$ (pseudo-axial) is projected into the region below the molybdenum atom, close to methoxy groups of the phosphite ligands, while R $_{\beta}'$ (pseudo-equatorial) is projected away from other ligand atoms. It is noticeable that in (2) and (3) it is the sterically least demanding substituent, H, which occupies the axial site on C $_{\beta}$, and in the case where R $_{\beta}$ = R $_{\beta}'$ = Ph, *i.e.* complex (6), that the $\theta \approx 180^\circ$ orientation is preferred. In this latter geometry both R $_{\beta}$ and R $_{\beta}'$ are relatively remote from the phosphite ligands, and it is R $_{\alpha}$, *i.e.* R $_{\alpha}$ = Me for (6), which comes closest to occupying the sterically demanding axial site. Short contacts involving the axial site substituents are listed in Table 4. That geometries with $\theta \approx 0^\circ$ and bulky (Ph) substituents in the axial site are sterically untenable has been demonstrated by use of computer models.

In (2) and (3) both molybdenum and C $_{\beta}$ are chiral centres within the molecules, and clearly the preferred geometry observed in the solid state corresponds to a particular diastereomer. The crystal structures consist of racemic mixtures

of the illustrated isomers and their mirror images. The solution n.m.r. spectra of (2) and (3) have distinct phosphorus environments; this is a consequence of the chirality of C $_{\beta}$, which means that even if the vinyl moiety were to rotate, *i.e.* θ to vary between 0 and 360° , the phosphorus nuclei would not become equivalent on the n.m.r. time-scale. In contrast, the n.m.r. spectra of (6) and (7)²⁶ indicate that the phosphorus environments are equivalent, and not subject to the asymmetry seen in the solid state. Thus, the chirality of the molybdenum atom in (6) and (7) is lost on time averaging in solution indicating a fluxional process, which averages the phosphite ligand sites. The simplest such process is a 'windscreen-wiper' motion, which exchanges the R $_{\beta}$ and R $_{\beta}'$ sites by alteration of the torsion angle θ by *ca.* 90° . Further discussion of the energetics of this process is postponed for the moment.

Several geometric features of the vinyl ligand are worthy of note. Firstly, the MoC $_{\alpha}$ C $_{\beta}$ R $_{\alpha}$ and C $_{\beta}$ R $_{\beta}$ R $_{\beta}'$ planes are approximately orthogonal to one another as shown by the R $_{\alpha}$ -C $_{\alpha}$ -C $_{\beta}$ -R $_{\beta}$ torsion angles listed in Table 4. This is in marked contrast to conventional, σ -bonded vinyl ligands where these planes would be approximately coincident, *i.e.* R $_{\alpha}$ -C $_{\alpha}$ -C $_{\beta}$ -R $_{\beta}$ torsion angles $\sim 0^\circ$ and $\sim 180^\circ$. The C-C-R bond angles at C $_{\alpha}$ and C-C-R and R-C-R bond angles at C $_{\beta}$ indicate that their hybridisation states are closest to sp^2 and sp^3 respectively, as is required by the metallacyclopentene formalism. Taken with the C $_{\alpha}$ -C $_{\beta}$ distance, which is constant for the $\theta \approx 0^\circ$ orientation at

Table 2. Selected bond lengths and angles for (3)

(a) Bond lengths (Å)

Mo(1)–P(1)	2.341(1)	Mo(1)–P(2)	2.342(1)	P(4)–O(52)	1.621(3)	P(4)–O(53)	1.612(2)
Mo(1)–C(1)	1.943(4)	Mo(1)–C(2)	2.290(3)	C(1)–C(2)	1.436(5)	C(1)–C(3)	1.521(6)
Mo(1)–C(13)	2.366(4)	Mo(1)–C(14)	2.391(5)	C(2)–H(2)	0.921(27)	C(2)–C(7)	1.492(5)
Mo(1)–C(15)	2.384(4)	Mo(1)–C(16)	2.365(4)	C(3)–C(4)	1.526(6)	C(3)–C(5)	1.509(7)
Mo(1)–C(17)	2.359(4)	Mo(2)–P(3)	2.347(1)	C(3)–C(6)	1.509(8)	C(13)–C(14)	1.403(6)
Mo(2)–P(4)	2.345(1)	Mo(2)–C(31)	1.940(3)	C(13)–C(17)	1.392(7)	C(14)–C(15)	1.387(7)
Mo(2)–C(32)	2.278(3)	Mo(2)–C(43)	2.385(5)	C(15)–C(16)	1.399(8)	C(16)–C(17)	1.411(6)
Mo(2)–C(44)	2.368(5)	Mo(2)–C(45)	2.356(4)	C(31)–C(32)	1.438(5)	C(31)–C(33)	1.525(5)
Mo(2)–C(46)	2.360(4)	Mo(2)–C(47)	2.380(4)	C(32)–H(32)	0.920(31)	C(32)–C(37)	1.485(6)
P(1)–O(18)	1.610(2)	P(1)–O(19)	1.630(3)	C(33)–C(34)	1.531(5)	C(33)–C(35)	1.526(6)
P(1)–O(20)	1.616(3)	P(2)–O(21)	1.600(3)	C(33)–C(36)	1.517(7)	C(43)–C(44)	1.378(8)
P(2)–O(22)	1.603(4)	P(2)–O(23)	1.617(3)	C(43)–C(47)	1.388(8)	C(44)–C(45)	1.366(6)
P(3)–O(48)	1.634(3)	P(3)–O(49)	1.608(3)	C(45)–C(46)	1.362(7)	C(46)–C(47)	1.388(7)
P(3)–O(50)	1.604(3)	P(4)–O(51)	1.623(3)				

(b) Bond angles (°)

P(1)–Mo(1)–P(2)	92.7(1)	P(1)–Mo(1)–C(1)	112.1(1)	C(31)–Mo(2)–C(44)	114.9(2)	C(32)–Mo(2)–C(44)	116.6(2)
P(2)–Mo(1)–C(1)	85.4(1)	P(1)–Mo(1)–C(2)	73.6(1)	C(43)–Mo(2)–C(44)	33.7(2)	P(3)–Mo(2)–C(45)	133.6(1)
P(2)–Mo(1)–C(2)	89.7(1)	C(1)–Mo(1)–C(2)	38.6(1)	P(4)–Mo(2)–C(45)	132.7(1)	C(31)–Mo(2)–C(45)	92.4(1)
P(1)–Mo(1)–C(13)	99.4(1)	P(2)–Mo(1)–C(13)	147.2(1)	C(32)–Mo(2)–C(45)	114.7(1)	C(43)–Mo(2)–C(45)	55.9(2)
C(1)–Mo(1)–C(13)	117.2(2)	C(2)–Mo(1)–C(13)	122.9(1)	C(44)–Mo(2)–C(45)	33.6(2)	P(3)–Mo(2)–C(46)	144.4(1)
P(1)–Mo(1)–C(14)	90.2(1)	P(2)–Mo(1)–C(14)	116.1(1)	C(31)–Mo(2)–C(46)	101.4(1)	C(31)–Mo(2)–C(46)	102.7(1)
C(1)–Mo(1)–C(14)	148.9(1)	C(2)–Mo(1)–C(14)	150.5(1)	C(32)–Mo(2)–C(46)	138.4(1)	C(43)–Mo(2)–C(46)	56.2(2)
C(13)–Mo(1)–C(14)	34.3(2)	P(1)–Mo(1)–C(15)	114.4(1)	C(44)–Mo(2)–C(46)	56.0(2)	C(45)–Mo(2)–C(46)	33.6(2)
P(2)–Mo(1)–C(15)	90.5(1)	C(1)–Mo(1)–C(15)	133.4(2)	P(3)–Mo(2)–C(47)	112.0(1)	P(4)–Mo(2)–C(47)	95.7(2)
C(2)–Mo(1)–C(15)	171.9(2)	C(13)–Mo(1)–C(15)	56.7(1)	C(31)–Mo(2)–C(47)	136.1(2)	C(32)–Mo(2)–C(47)	170.8(2)
C(14)–Mo(1)–C(15)	33.8(2)	P(1)–Mo(1)–C(16)	146.7(1)	C(43)–Mo(2)–C(47)	33.9(2)	C(44)–Mo(2)–C(47)	56.1(2)
P(2)–Mo(1)–C(16)	97.3(1)	C(1)–Mo(1)–C(16)	100.3(2)	C(45)–Mo(2)–C(47)	56.1(2)	C(46)–Mo(2)–C(47)	34.0(2)
C(2)–Mo(1)–C(16)	137.8(2)	C(13)–Mo(1)–C(16)	57.3(2)	Mo(1)–C(1)–C(2)	83.9(3)	Mo(1)–C(1)–C(3)	148.0(2)
C(14)–Mo(1)–C(16)	56.9(2)	C(15)–Mo(1)–C(16)	34.3(2)	C(2)–C(1)–C(3)	128.1(3)	Mo(1)–C(2)–C(1)	57.5(2)
P(1)–Mo(1)–C(17)	132.7(1)	P(2)–Mo(1)–C(17)	130.7(1)	Mo(1)–C(2)–H(2)	115.0(19)	C(1)–C(2)–H(2)	119.0(19)
C(1)–Mo(1)–C(17)	92.1(2)	C(2)–Mo(1)–C(17)	117.5(1)	Mo(1)–C(2)–C(7)	126.8(2)	C(1)–C(2)–C(7)	123.1(3)
C(13)–Mo(1)–C(17)	34.3(2)	C(14)–Mo(1)–C(17)	56.9(2)	H(2)–C(2)–C(7)	108.1(18)	C(1)–C(3)–C(4)	112.6(4)
C(15)–Mo(1)–C(17)	57.0(2)	C(16)–Mo(1)–C(17)	34.8(1)	C(1)–C(3)–C(5)	107.7(4)	C(1)–C(3)–C(6)	111.8(4)
P(3)–Mo(2)–P(4)	90.0(1)	P(3)–Mo(2)–C(31)	112.0(1)	Mo(2)–C(31)–C(32)	83.4(2)	Mo(2)–C(31)–C(33)	147.9(2)
P(4)–Mo(2)–C(31)	84.3(1)	P(3)–Mo(2)–C(32)	73.8(1)	C(32)–C(31)–C(33)	128.6(3)	Mo(2)–C(32)–C(31)	57.8(2)
P(4)–Mo(2)–C(32)	91.4(1)	C(31)–Mo(2)–C(32)	32.8(1)	Mo(2)–C(32)–H(32)	117.2(19)	C(31)–C(32)–H(32)	117.4(20)
P(3)–Mo(2)–C(43)	89.1(1)	P(4)–Mo(2)–C(43)	121.8(2)	Mo(2)–C(32)–C(37)	124.5(2)	C(31)–C(32)–C(37)	122.0(3)
C(31)–Mo(2)–C(43)	147.3(2)	C(32)–Mo(2)–C(43)	143.0(2)	H(32)–C(32)–C(37)	109.6(20)	C(31)–C(33)–C(34)	111.9(3)
P(3)–Mo(2)–C(44)	100.4(1)	P(4)–Mo(2)–C(44)	151.8(1)	C(31)–C(33)–C(35)	106.4(3)	C(31)–C(33)–C(36)	112.5(3)

1.436(5) Å, and is 1.463(5) Å, for the $\theta \approx 180^\circ$ orientation seen in (6), these features indicate that the C_α – C_β bond order is close to unity in the η^2 -vinyl geometry: cf. a C=C bond order of two found for a σ -vinyl ligand in ref. 18. The most marked difference in the co-ordination geometry of η^2 -versus σ -vinyl ligands is the Mo – C_α – C_β angle, here ca. 83° , and in σ -vinyl complexes ca. 120° . To probe these geometric features and their origins in more detail we have carried out extended Hückel molecular orbital (EHMO) calculations on a model complex $[Mo(\eta^2-C_2H_3)\{P(OH)_3\}_2(\eta-C_5H_5)]$ (X) as described in the Experimental section, using a geometry derived from that of complex (7).

The analysis of a very low symmetry species such as (X) is not straightforward with the EHMO technique, nevertheless using fragment analysis several interesting points emerge. The frontier orbitals of the $ML_2(\eta-C_5H_5)$ fragment have been discussed at length by a number of authors.^{32,33} These consist of a well-hybridised, empty, acceptor orbital of σ symmetry, and at lower energy two orthogonal π -symmetry orbitals, and a poorly hybridised orbital of σ symmetry. For the case where the metal electron count is d^4 , as here, the set of three lower lying orbitals contain four electrons. The valence orbitals of the $CHCH_2^-$ moiety in the geometry related to that of (6) are less well known and are illustrated in Scheme 3.

They consist of two filled orbitals of σ and π (labelled π_\perp)

symmetry with respect to the Mo – C_2H_3 interaction, and a low-lying empty orbital of π (labelled $\pi_{||}$) symmetry. These orbitals resemble in symmetry those of acetylene in co-ordinated geometry, i.e. with H–C–C angles ca. 140° , and for comparison these are drawn alongside those of the $CHCH_2$ fragment in Scheme 3. In a theoretical analysis of the bonding of alkynes to $d^4 ML_5$ species, including $[MoL_2(\eta-C_5H_5)]^+$, Templeton *et al.*³⁴ concluded that the role of the π_\perp orbital was minimal, the principal interaction being via the $\pi_{||}$, σ , and π_\perp orbitals of the alkyne. These find suitable matches from the σ and π orbitals on the metal fragment leading to electron donation from the alkyne σ and π_\perp orbitals, and back donation into the $\pi_{||}$ orbital. Precisely the same interactions are clearly available to the η^2 -vinyl ligand. Both these interactions lead to a reduction of the C_α – C_β bond order towards unity, as they lead to occupancy of the σ and $\pi_{||}$ orbitals (which are C_α – C_β bonding and antibonding respectively) being reduced and increased respectively. The major difference between the alkyne and η^2 - $C_2H_3^-$ frontier orbitals lies in the energy and spatial nature of the π_\perp orbital. In the vinyl ligand this orbital is essentially pure $C_\alpha(p)$ in character, and therefore is both asymmetric with respect to the two contact carbons and at higher energy than the π_\perp orbital of the alkyne. Therefore, this orbital leads to better donor ability, on energetic grounds, of η^2 - $C_2H_3^-$ than C_2H_2 , and to a localised Mo – C_α double bond in accord with the

Table 3. Selected bond lengths and angles for (6)

(a) Bond lengths (Å)

Mo-P(1)	2.398(1)	Mo-P(2)	2.367(1)	P(2)-O(4)	1.591(4)	P(2)-O(5)	1.620(3)
Mo-C(8)	1.963(4)	Mo-C(9)	2.249(4)	P(2)-O(6)	1.611(4)	C(8)-C(7)	1.501(6)
Mo-C(30)	2.381(4)	Mo-C(31)	2.340(5)	C(8)-C(9)	1.463(5)	C(9)-C(10)	1.508(6)
Mo-C(32)	2.337(6)	Mo-C(33)	2.352(5)	C(9)-C(20)	1.520(6)	C(30)-C(31)	1.382(7)
Mo-C(34)	2.392(5)	P(1)-O(1)	1.619(4)	C(30)-C(34)	1.385(8)	C(31)-C(32)	1.379(8)
P(1)-O(2)	1.595(3)	P(1)-O(3)	1.604(4)	C(32)-C(33)	1.409(8)	C(33)-C(34)	1.402(8)

(b) Bond angles (°)

P(1)-Mo-P(2)	89.8(1)	P(1)-Mo-C(8)	95.8(1)	P(2)-Mo-C(33)	93.8(1)	C(8)-Mo-C(33)	167.9(2)
P(2)-Mo-C(8)	80.6(1)	P(1)-Mo-C(9)	95.5(1)	C(9)-Mo-C(33)	144.1(2)	C(30)-Mo-C(33)	56.6(2)
P(2)-Mo-C(9)	120.5(1)	C(8)-Mo-C(9)	39.9(1)	C(31)-Mo-C(33)	57.0(2)	C(32)-Mo-C(33)	35.0(2)
P(1)-Mo-C(30)	111.0(1)	P(2)-Mo-C(30)	143.9(1)	P(1)-Mo-C(34)	85.8(1)	P(2)-Mo-C(34)	126.8(1)
C(8)-Mo-C(30)	123.9(2)	C(9)-Mo-C(30)	87.6(2)	C(8)-Mo-C(34)	152.6(2)	C(9)-Mo-C(34)	112.7(2)
P(1)-Mo-C(31)	142.2(1)	P(2)-Mo-C(31)	114.5(1)	C(30)-Mo-C(34)	33.7(2)	C(31)-Mo-C(34)	56.7(2)
C(8)-Mo-C(31)	115.6(2)	C(9)-Mo-C(31)	95.9(2)	C(32)-Mo-C(34)	57.5(2)	C(33)-Mo-C(34)	34.4(2)
C(30)-Mo-C(31)	34.0(2)	P(1)-Mo-C(32)	129.1(1)	Mo-C(8)-C(9)	80.6(2)	Mo-C(8)-C(7)	153.3(3)
P(2)-Mo-C(32)	87.0(1)	C(8)-Mo-C(32)	133.4(2)	Mo-C(9)-C(8)	59.4(2)	C(7)-C(8)-C(9)	126.0(4)
C(9)-Mo-C(32)	129.1(2)	C(30)-Mo-C(32)	57.0(2)	C(8)-C(9)-C(10)	116.8(3)	Mo-C(9)-C(10)	116.0(3)
C(31)-Mo-C(32)	34.3(2)	P(1)-Mo-C(33)	94.9(2)	C(8)-C(9)-C(20)	121.4(4)	Mo-C(9)-C(20)	120.9(3)
						C(10)-C(9)-C(20)	112.6(3)

metallacyclopropene analogy. The orientation adopted by the η^2 -vinyl ligands of (2), (3), (6), and (7), *i.e.* $\theta \approx 0$ or 180° , is strongly reminiscent of those observed²² for the related $[\text{Mo}(\eta^2\text{-RC}_2\text{R}')\text{LL}'(\eta^5\text{-C}_5\text{H}_5)]^+$ cations [$\text{L} = \text{L}' = \text{PMe}_3$, $\text{R} = \text{R}' = \text{Me}$, $\theta = +171.7^\circ$; $\text{L} = \text{PEt}_3$, $\text{L}' = \text{CO}$, $\text{R} = \text{R}' = \text{Me}$, $\theta = -172^\circ$]. Likewise the fluxionality of the alkyne species²² is paralleled by that of the η^2 -vinyl ligands in those cases where it can be observed, *i.e.* (6) and (7).

The energetics of the 'windscreen-wiper' motion, which exchanges R_β and R'_β sites in η^2 -vinyl complexes, was investigated by the simple approximation of rotating the CHCH_2 moiety in (X) about an axis orthogonal to the MoP_2 plane through Mo, allowing no relaxation of geometry. This gave a barrier to $\text{R}_\beta/\text{R}'_\beta$ exchange *via* the process (A) \rightleftharpoons (C) [as in complex (7)] of *ca.* 20 kJ mol^{-1} or (B) \rightleftharpoons (D) [as in (6)] (see Scheme 4) of *ca.* 20 kJ mol^{-1} , and to full rotation, *i.e.* (A) \rightarrow (D) \rightarrow (A) or (B) \rightarrow (C) \rightarrow (B) of the η^2 -vinyl moiety of *ca.* 84 kJ mol^{-1} . Inspection of Table 4 reveals that this simple model is probably rather inadequate for the full rotation process since it assumes, for example, that the $\text{P}_{\parallel}\text{-Mo-C}_\beta$ angles at $\theta = 0$ and $\theta = 180^\circ$ sum to 180° , when they do not (sum of these from Table 4 $\approx 193^\circ$). These subtleties will, therefore, remain outside the scope of our analysis.

To return to the structural evidence it is clear that the factors governing the favoured orientation of the vinyl ligands allow some degree of rotational variation. Thus, with one molecule (3), even crystal packing forces can cause a 7° variation in θ with only minor effects on the remaining geometry. In total a range of *ca.* 30° in θ about the $\theta = 0^\circ$ position is observed in (2), (3), and (7) in accord with the calculated and experimentally measured facility of the 'windscreen-wiper' motion.

The geometry of the $\text{Mo}(\text{cp})\text{P}_2\text{C}_\alpha\text{C}_\beta$ unit in (2)–(7) may also be considered in the context of $[\text{ML}_4(\eta\text{-C}_5\text{H}_5)]$ complexes (see ref. 35 and refs. therein). Such complexes are typically of the 'four-legged piano stool' geometry with cp-Mo-L angles in the range $115\text{--}120^\circ$. In the highly distorted ($\text{C}_\alpha\text{-Mo-C}_\beta \sim 38^\circ$; *cf.* *cis-L-M-L* angles, usually $70\text{--}80^\circ$) geometry of (2)–(7) one cp-Mo-L angle deviates markedly from a value of $115\text{--}120^\circ$ towards 180° , a distortion which constitutes a step towards a 3:3:1 geometry (see ref. 35).

Finally, it is important to note that there exist other molecules closely related to (2)–(7). These were synthesised and structurally characterised by Davidson and co-workers,^{36–38}

and have similar geometric properties. For example, $[\text{Mo}(\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)\{\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)(\text{NC}_5\text{H}_4\text{S})\}(\eta\text{-C}_5\text{H}_5)]$ has Mo-C_α 1.914(4), Mo-C_β 2.210(3), $\text{C}_\alpha\text{-C}_\beta$ 1.390(5) Å; $[\text{W}(\text{CO})\{\text{C}(\text{CF}_3)\text{-C}(\text{CF}_3)\text{C}(\text{O})\text{SMe}\}(\eta\text{-C}_5\text{H}_5)]$ has W-C_α 1.96, W-C_β 2.19, $\text{C}_\alpha\text{-C}_\beta$ 1.44 Å; and $[\text{WCl}(\eta^2\text{-CF}_3\text{C}_2\text{CF}_3)\{\text{C}(\text{CF}_3)\text{C}(\text{CF}_3)\text{-}(\text{CNBu}^1)\}(\eta\text{-C}_5\text{H}_5)]$ has W-C_α 1.894(8), W-C_β 2.304(10), $\text{C}_\alpha\text{-C}_\beta$ 1.410(12) Å. Detailed comparison with these species is hampered by the very different substituents at the metals and at the C_α and C_β carbons as compared with (2)–(7).

Additional evidence for processes which exchange R_β and R'_β sites in a η^2 -vinyl complex was obtained from a study of the reaction of $[\text{Mo}(\eta^2\text{-PhC}_2\text{CH}_2\text{Ph})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ with $\text{K}[\text{BHBu}^1_3]$ in *thf* at -78°C . Column chromatography of the reaction mixture gave two isomeric complexes (8) and (9), which were obtained as orange and dark orange crystalline materials in yields of 30 and 42% respectively. Elemental analysis, and ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ spectroscopy (see Experimental section) indicated that both isomers were η^2 -vinyl complexes with the molecular formula $[\text{Mo}\{\text{C}(\text{CH}_2\text{Ph})\text{CHPh}\}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$. However, in the n.m.r. spectrum of complex (8) the CHPh ^1H resonance occurred at 2.91 p.p.m. (dd, X part of an ABX system), whereas, in isomer (9) the corresponding signal occurred at 3.65 p.p.m., a chemical shift similar to that observed at 3.83 p.p.m. in the ^1H spectrum of complex (2). Also, examination of the ^1H and $^{31}\text{P}\{^1\text{H}\}$ n.m.r. spectra of a solution of (9) in C_6D_6 showed that a clean isomerisation to (8) occurred over 24 h at room temperature.

An explanation for these observations is that the kinetically controlled product (9) has a molecular geometry analogous to that established for (2) in the solid state, *i.e.* conformation (A) in Scheme 4, and that in solution a slow intramolecular isomerisation occurs to give the thermodynamically controlled product (8). Examination of Scheme 4 suggests that isomerisation could involve a 90° rotation (Scheme 5) to give (8) with a geometry analogous to that established for complex (6) by X-ray crystallography, and where as previously discussed, the substituents on C_β are in a less crowded environment. In both of the other two possible conformations (C) and (D) (Scheme 4) the phenyl group on C_β would be in a sterically congested position.

An alternative, and rather interesting explanation for these observations is illustrated in Scheme 6, where it is postulated that the $\eta^2(3\text{e})$ -vinyl complex (9) transforms into a co-

Table 4. Summary of geometry of η^2 -vinyl complexes

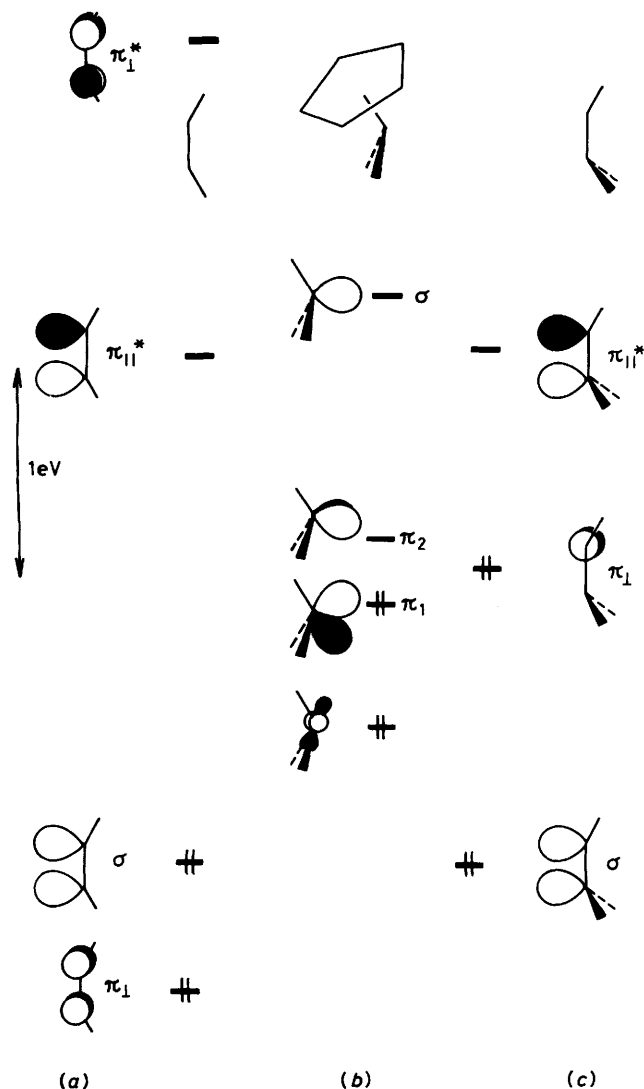
Vinyl ligand	(2) C(Ph)CHPh	(3) C(Bu ^t)CHPh		(6) C(Me)CPh ₂	(7) C(SiMe ₃)CH ₂
		Molecule (a)	Molecule (b)		
Distances from C _x H _y ring plane ^a (Å)					
Mo	2.043	2.053	2.060	2.041	2.048
C _α	3.052	3.022	3.045	3.644	3.132
C _β	3.806	3.943	3.833	3.049	4.058
P _⊥ ^b	3.046	3.186	3.347	3.071	2.920
P _∥	3.286	3.210	3.182	2.995	3.286
Bond lengths (Å)					
Mo-C _α	1.951(3)	1.943(4)	1.940(3)	1.963(4)	1.955(3)
Mo-C _β	2.301(3)	2.290(3)	2.278(3)	2.249(4)	2.258(1)
Mo-P _⊥	2.340(1)	2.342(1)	2.345(1)	2.398(1)	2.358(1)
Mo-P _∥	2.326(1)	2.341(1)	2.347(1)	2.367(1)	2.351(1)
C _α -C _β	1.433(4)	1.436(5)	1.438(5)	1.463(5)	1.437(6)
Bond angles (°)					
Mo-C _α -R _α	143.9(2)	148.0(2)	147.9(3)	153.3(3)	151.4(2)
Mo-C _β -R _β ^c	114(2)	115(2)	117(2)	116.0(3)	115(2)
Mo-C _β -R _β '	123.8(2)	126.8(2)	124.5(2)	120.9(3)	121(2)
P-Mo-P	91.4(1)	92.7(1)	90.0(1)	98.8(1)	91.8(1)
cp ^d -Mo-C _α	121.6(1)	120.9(1)	121.7(1)	145.0(1)	116.4(1)
cp-Mo-C _β	139.3(1)	146.5(1)	141.5(1)	115.8(1)	150.3(1)
cp-Mo-P _⊥	116.6(1)	118.5(1)	123.2	114.3(1)	116.4(1)
cp-Mo-P _∥	121.2(1)	118.9(1)	117.8	115.3(1)	121.4(1)
C _α -Mo-P _⊥	87.2(1)	85.4(1)	84.3(1)	95.8(1)	96.2(1)
C _α -Mo-P _∥	109.5(1)	112.1(1)	112.0(1)	80.6(1)	110.8(1)
C _β -Mo-P _⊥	99.4(1)	89.7(1)	91.4(1)	95.5(1)	88.8(1)
C _β -Mo-P _∥	73.1(1)	73.6(1)	73.8(1)	120.5(1)	72.8(1)
C _β -C _α -R _α	129.8(3)	128.1(3)	128.6(3)	126.0(4)	123.7(3)
C _α -C _β -R _β	121(2)	119(2)	117(2)	116.8(3)	117(2)
C _α -C _β -R _β '	122.6(2)	123.1(3)	122.0(3)	121.4(3)	115(3)
R _β -C _β -R _β '	109(2)	108(2)	110(2)	112.6(3)	117(3)
Mo-C _α -C _β	84.2(2)	83.9(3)	83.4(2)	80.6(2)	81.9(2)
Mo-C _β -C _α	57.5(1)	57.5(2)	57.8(2)	59.4(2)	59.0(2)
Torsion angles (°)					
P _⊥ -Mo-C _α -C _β	-109.6(2)	-95.4(2)	-99.3(2)	-91.6(2)	-80.5(2)
P _∥ -Mo-C _α -C _β (θ)	-18.6(2)	-4.4(2)	-116(2)	179.6(2)	13.8(2)
R _β -C _β -C _α -R _α	-93(2)	-79(2)	-76(2)	-71.3(1)	90(2)
R _β '-C _β -C _α -R _α	54.8(1)	62.9(1)	63.9(1)	73.1(1)	54(2)
Interplanar angles					
C _β R _β R _β '/R _α C _α C _β	106(2)	96(2)	94(2)	89.3(1)	74(2)
C _α C _β R _α /MoC _α C _β	13.1(1)	1.4(1)	2.7(1)	1.1(1)	13.9(1)
Intramolecular short contacts					
R _{ax}	H(4)	H(2)	H(32)	C(7)	H(7a)
Second atom	O(21)(2.64)	O(18)(2.77)	O(49)(2.88)	O(4)(3.39)	O(6)(2.55)
(distance; Å)	C(13)(3.01)	O(21)(2.75)	O(53)(2.73)	O(5)(3.32)	C(1)(2.85)

^a C_xH_y = C₅H₅ for (2), (3), and (6); and C₉H₇ for (7); distances given are perpendicular distances from the least-squares plane through the five bonded carbon atoms. ^b P_⊥ is the phosphorus for which the P-Mo-C_α-C_β torsion angle ≈ -90°, P_∥ is the other. ^c R_β is the axial substituent in (2), (3), and (7). ^d cp = centroid of C₅ rings of η⁵-C₅H₅ or η⁵-C₉H₇.

ordinatively unsaturated σ(1e)-vinyl system, which then undergoes rotation about the Mo-C single bond before collapsing back to a η²-vinyl complex, (8). However, it is thought unlikely that such a process is responsible for the isomerisation (9) → (8), because once a 16-electron σ-vinyl complex is formed it would be expected¹⁸ to undergo a β-hydrogen elimination reaction resulting in the formation of a η³-allyl complex. The availability of this reaction pathway is

illustrated by the thermal rearrangement of the η²-vinyl complex (6) (Scheme 7).

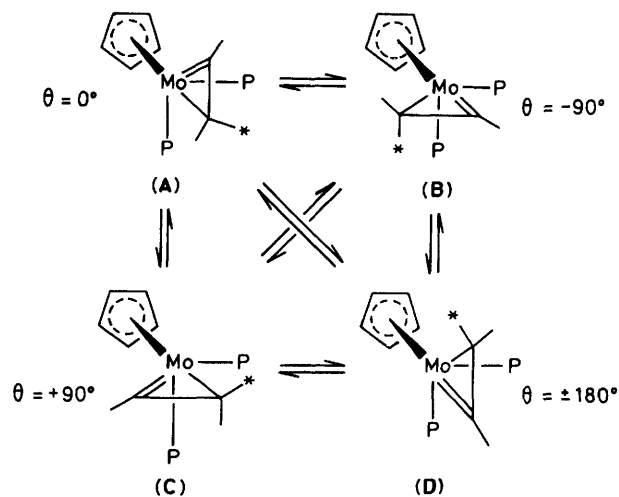
During 3 d at room temperature a toluene solution of (6) rearranged to an orange crystalline complex (10), isolated by column chromatography. Analysis, mass and n.m.r. spectroscopy showed that (10) was an η³-allyl complex isomeric with (6). This isomerisation reaction requires a hydrogen-shift process, and can be understood (see Scheme 7) in terms of an



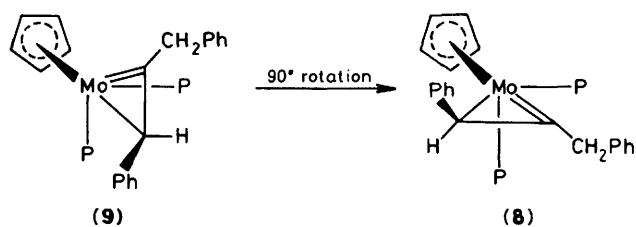
Scheme 3. Frontier molecular-orbital energies for HCCH (a), $[\text{Mo}\{\text{P}(\text{OH})_3\}_2(\eta\text{-C}_5\text{H}_5)]^+$ (b), and HCCH_2^- (c) fragments. Metal fragment to acetylene or vinyl bonding is achieved *via* interactions of σ and π symmetry; the latter can be viewed as occurring by overlap of linear combinations of π_1 and π_2 on the metal fragment with π_{11} and π_1 on the ligand as appropriate to the ligand orientation

initial $\eta^2 \rightarrow \sigma$ change in the bonding mode of the vinyl ligand followed by β -hydrogen transfer to the metal, rotation of the resultant 1,1-diphenylallene ligand, and migration of hydrogen from the molybdenum to the central carbon of the co-ordinated allene.¹⁸ Thus, it is suggested that whilst an $\eta^2(3e)$ -vinyl can switch to a $\sigma(1e)$ system this is not the explanation for the isomerisation process (9) \rightarrow (8), because if this was happening we would expect to see the formation of an η^3 -allylic complex.

Further insight into the behaviour of these systems was obtained from a study of the reaction of lithium dimethylcuprate with the cations $[\text{Mo}(\eta^2\text{-RC}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ ($\text{R} = \text{Bu}^i$ or Pr^i). A suspension of $[\text{Mo}(\eta^2\text{-Bu}^i\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ in thf reacted rapidly at -78°C with a solution of LiCuMe_2 to give on work-up an air-sensitive, low melting, yellow crystalline complex. Analytical data, mass and n.m.r. spectra for this material were consistent with the illustrated η^3 -allylic structure (11) (Scheme 8). The $^{31}\text{P}\text{-}\{^1\text{H}\}$ n.m.r. spectrum showed the phosphorus nuclei of the trimethyl



Scheme 4. $\text{P} = \text{P}(\text{OMe})_3$

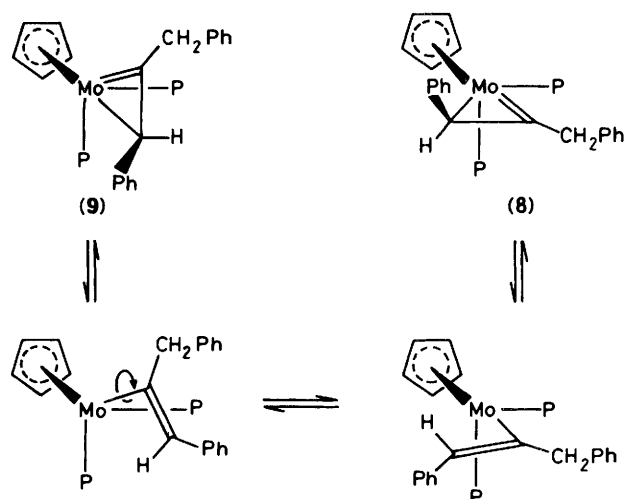
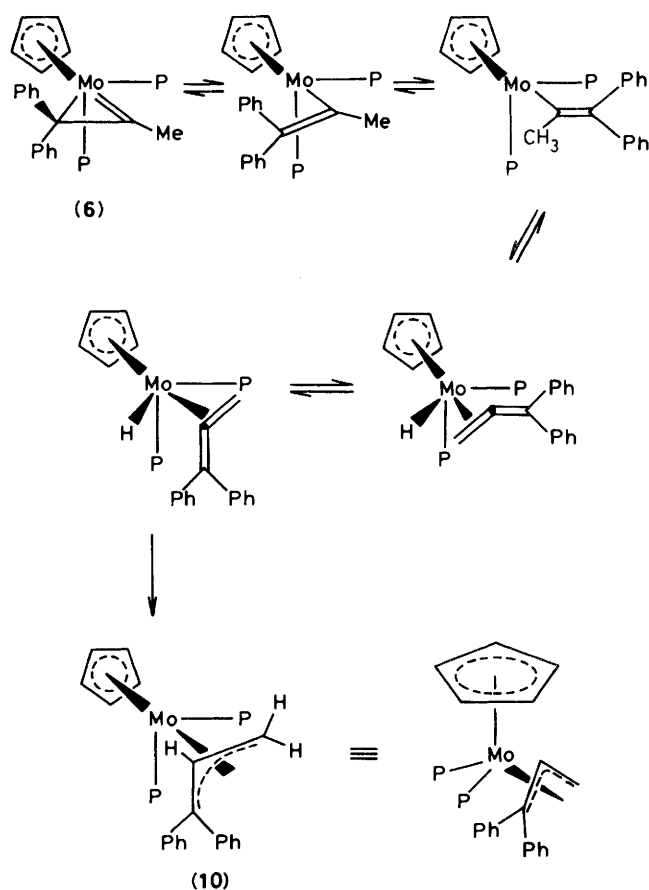


Scheme 5. $\text{P} = \text{P}(\text{OMe})_3$

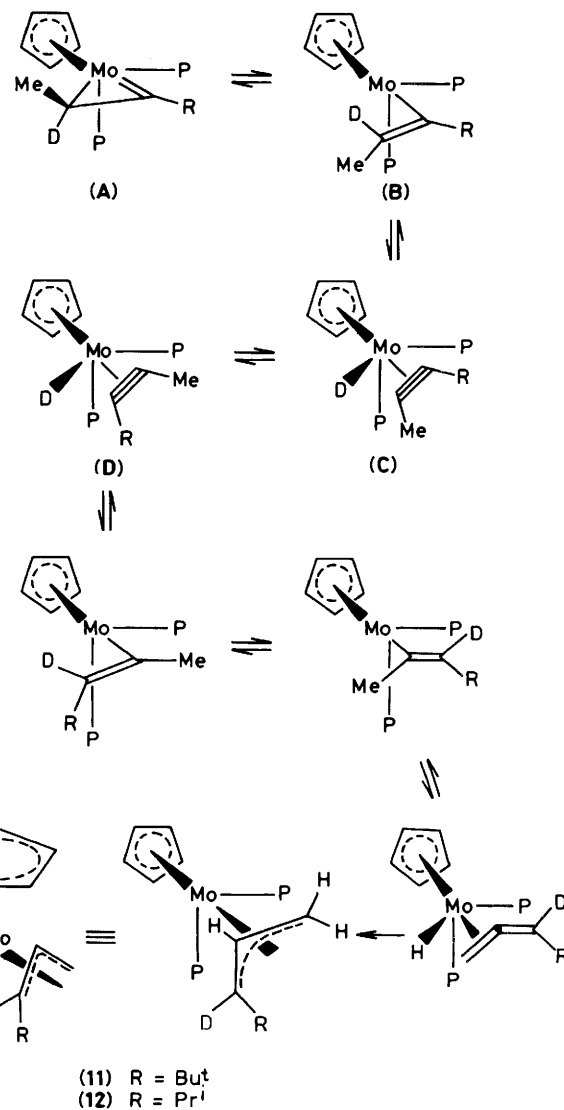
phosphite ligands to be inequivalent, and the $^{13}\text{C}\text{-}\{^1\text{H}\}$ n.m.r. spectra exhibited resonances at 71, 68, and 33 p.p.m. characteristic¹⁸ of the central, CHBu^i , and CH_2 carbons of an η^3 -allyl ligand. All four allylic protons were observed in the ^1H spectrum, and with broad-band ^{31}P decoupling the major $^1\text{H}\text{-}^1\text{H}$ coupling constants could be measured, and were used to assign the Bu^i group to an *anti* position. A similar reaction between LiCuMe_2 and $[\text{Mo}(\eta^2\text{-Pr}^i\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ afforded an analogous complex (12) exhibiting similar spectroscopic features. These reactions clearly involved a hydrogen-shift process, and therefore, the corresponding reactions of $[\text{Mo}(\eta^2\text{-RC}_2\text{D})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ ($\text{R} = \text{Bu}^i$ or Pr^i) were examined. In both cases the ^1H and $^{13}\text{C}\text{-}\{^1\text{H}\}$ spectra of the resultant η^3 -allylic complexes showed that the deuterium was located exclusively on the allylic carbon bearing the alkyl substituent.

These observations can be interpreted if it is assumed a methyl group is delivered by LiCuMe_2 directly to the unsubstituted carbon of the co-ordinated alkyne, with the same specificity as observed in the formation of (4) and (5) from lithium diarylcuprates. The resultant η^2 -vinyl complex (A) (Scheme 8) then opens reversibly to a σ -vinyl species (B), the equilibrium being displaced by a β -hydrogen shift. In principle the rotational movement involved in the $\eta^2(3e)$ to $\sigma(1e)$ transformation can place the hydrogen (deuterium) on the β -carbon either *cis* or *trans* to the molybdenum; however, only the *cis* isomer can undergo β -vinylic hydrogen elimination to form a hydrido-alkyne complex (C). Then by rotation of the alkyne and migration of the hydrogen (deuterium) back onto it, a co-ordinatively unsaturated σ -vinyl complex is formed, which carries a methyl group on the vinyl α -carbon atom. Rearrangement to the *anti*-substituted η^3 -allyl then follows *via* the previously discussed pathway.

In order to provide additional support for this reaction

Scheme 6. P = P(OMe)₃Scheme 7. P = P(OMe)₃

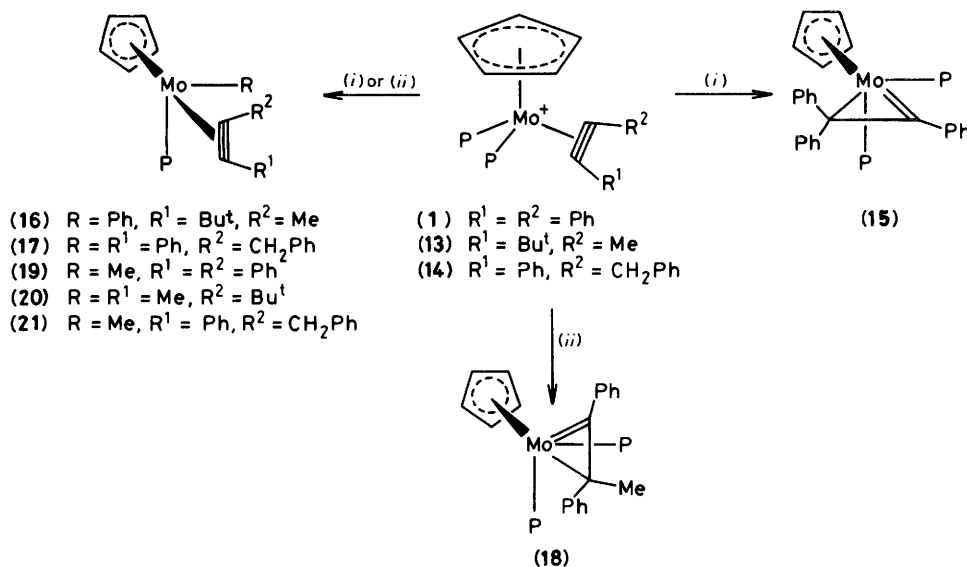
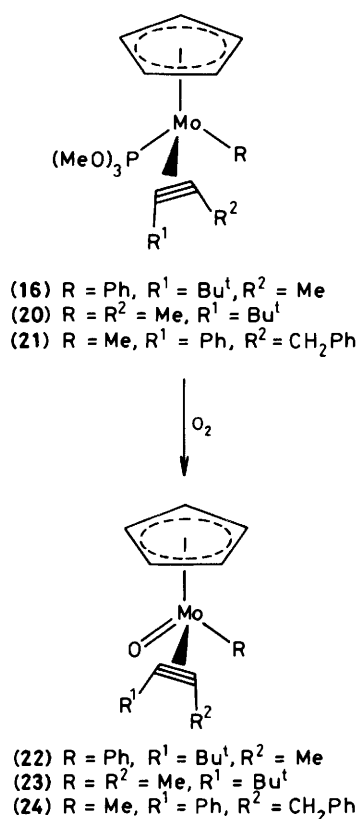
sequence the reaction of $K[BHBu^s_3]$ with $[Mo(\eta^2-Bu^tC_2Me)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ (13) was examined. The product of the reaction was isolated as an orange crystalline material, and identified by analysis, mass and n.m.r. spectroscopy as the η^3 -allylic complex (11), which had been previously obtained by reaction of $LiCuMe_2$ with $[Mo(\eta^2-Bu^tC_2H)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$. Thus, 'hydride' delivered by $BHBu^s_3$ attacks either* the molybdenum or an alkyne carbon of (13) to gain

Scheme 8. P = P(OMe)₃

access to the interconverting isomeric species (A), (B), (C), and (D) of Scheme 8 (R = Bu^t, D replaced by H).

The extension of the dimethyl- or diphenyl-cuprate reaction to the cations (1), (13), and (14) provided further insight into these reactions. Lithium diphenylcuprate in thf at $-78^\circ C$ reacted with (1) to afford a single green crystalline product (15), an η^2 -vinyl complex with the structure illustrated in Scheme 9. Although $LiCuPh_2$ reacted under similar conditions with (13) and (14), the green crystalline products (16) and (17) were identified by n.m.r. spectroscopy not as the expected η^2 -vinyls, but as four-electron η^2 -bonded alkyne complexes carrying only one trimethyl phosphite ligand and a σ -bonded phenyl group. The corresponding reactions with lithium dimethylcuprate were also revealing in a mechanistic sense. Reaction with (1) gave two products, (18) and (19), which were separated by column chromatography. The first complex (19) to be eluted from the column was obtained as bright green crystals, and was identified by analysis and n.m.r. as an analogue of (16) and (17), with a methyl ligand σ -bonded to a molybdenum atom, to which a single P(OMe)₃ ligand was also co-ordinated. The second

* As previously discussed¹⁸ it is at present not possible to distinguish between these two possible reaction pathways.

Scheme 9. P = P(OMe)₃; (i) LiCuPh₂, (ii) LiCuMe₂

Scheme 10.

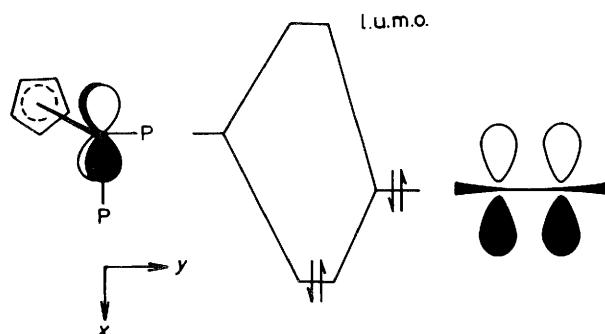
complex (18) isolated as dark green crystals was less soluble. Analysis and n.m.r. spectroscopy showed that the complex was an η²-vinyl species similar in structure to (2) with the phenyl group attached to the formally saturated carbon atom adopting a pseudo-equatorial position. Similar reactions between LiCuMe₂ and (13) and (14) afforded in each case only one product, the η²-alkyne species (20) and (21), there being no evidence for the formation of η²-vinyl complexes. Minor products were, however, formed in the reactions leading to the

formation of (16), (20), and (21), but these arose by reaction with traces of molecular oxygen resulting in replacement of the trimethyl phosphite ligand by an oxo-group. These complexes (22)—(24) were obtained as yellow crystalline materials and identified by the appearance of a Mo=O stretch in the i.r. spectrum, and by appropriate n.m.r. characteristics.

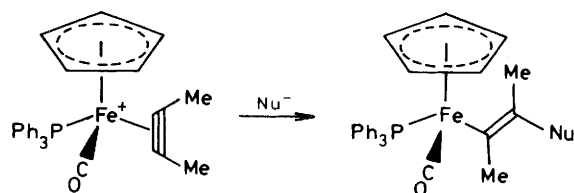
Although the *cis*-1,2-insertion of unactivated alkynes into metal-carbon σ bonds is relatively rare, as mentioned in the introduction such reactions have been implicated in alkyne oligomerisation reactions, and a careful study³⁹ of the reaction of methyl(pentane-2,4-dionato)(triphenylphosphine)nickel(II) with alkynes has firmly established this reaction pathway. Also, Katz and co-workers⁴⁰ have shown recently that in the Ziegler-Natta polymerisation of alkynes the *cis*-insertion pathway is followed rather than the metallacyclobutene mechanism.

It was, therefore, important to examine whether it was possible to effect the conversion of (19) into (18). Treatment of (19) with trimethyl phosphite under a variety of conditions resulted in the recovery of the unreacted η²-alkyne complex. Furthermore, attempts to convert (16), (17), (19), (20), and (21) into bis(trimethyl phosphite)η²-vinyl complexes analogous to (18) were unsuccessful. This could be related to the fact that the η²-bonded alkyne within these complexes functions as a four-electron donor, and that the co-ordination of a second phosphite ligand with a concomitant switch in the bonding mode of the alkyne is energetically unfavourable. Thus, these observations clearly suggest that in the reaction of diaryl- or dimethyl-cuprates with cationic molybdenum alkyne complexes competitive reactions are involved where aryl or methyl groups are delivered either directly to the molybdenum centre with loss of trimethyl phosphite or to an alkyne carbon atom leading to formation of an η²-vinyl species. Unlike the corresponding reaction with 'H⁻' where hydrogen migration from a metal to a co-ordinated alkyne is a facile process, the corresponding migration reaction with alkyl or aryl groups in these systems is apparently a higher energy process.

In order to probe further the idea of competing pathways in the reactions of the cuprates we have carried out a preliminary molecular orbital study using the extended Hückel method on the model cation [Mo(η²-HC₂H){P(OMe)₃}₂(η-C₅H₅)]⁺, using molecular parameters derived from the crystal structure of the cation [Mo(η²-Bu^tC₂H){P(OMe)₃}₂(η-C₅H₅)]⁺[BF₄]⁻.⁴¹ These calculations confirm that the lowest unoccupied molecular



Scheme 11.

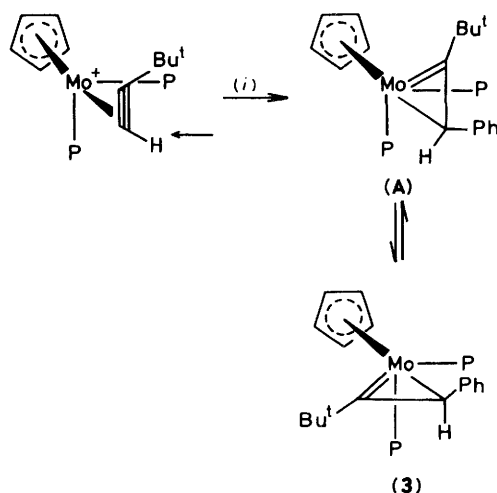
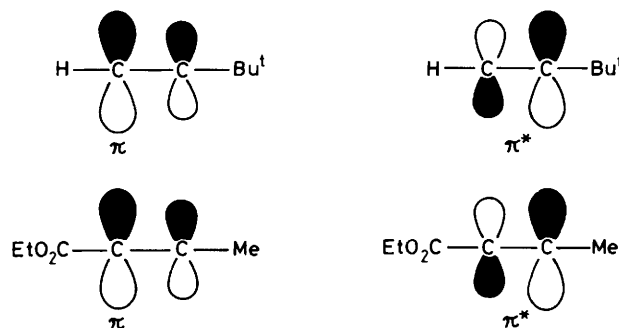


Scheme 12.

orbital (l.u.m.o.) of the molecular cation is due to the out-of-phase combination of ligand π_{\perp} and metal π -acceptor orbital, as illustrated in Scheme 11. This orbital is primarily made up ($\sim 70\%$ by our calculation) of the metal d_{xz} orbital, and is isolated in energy from the other unoccupied molecular orbitals. It might be expected then, that given the ground-state geometry, nucleophilic attack would proceed, under orbital control, at the metal atom. It is clear, however, that good orbital overlap between the incoming, filled, nucleophile orbital and the empty electrophile orbital is required for successful attack. Therefore, in this case the most spatially available portion of the l.u.m.o. might alternatively be attacked, *i.e.* the fraction located on the alkyne. Thus, this analysis is consistent with attack either at the metal or directly on the alkyne. In the case of the latter reaction pathway it is important to note that nucleophilic attack on a four-electron donor alkyne complex is on a ligand π_{\perp} orbital and *not* a ligand π^* orbital as must occur in the reactions of the d^6 iron cation $[\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^2\text{-MeC}_2\text{Me})(\eta\text{-C}_5\text{H}_5)]^+$.⁴² Here the alkyne is constrained to be a two-electron donor, and the l.u.m.o. is the antibonding combination of metal d_{xy} and the alkyne π_{\parallel}^* orbital. In this system the orbital is concentrated at the alkyne, and it is apparent that the incoming nucleophile would be expected to attack the π_{\parallel}^* orbital *trans* to the metal without perturbing the π_{\perp} orbital to give the σ -vinyl with the nucleophile (Nu) and the iron *trans* to each other. This is exactly what Reger and McElligott⁴² have observed (Scheme 12).

However, with an alkyne acting as a four-electron donor the orbital-controlled direction of attack by the nucleophile will not be *trans* to the metal, but perpendicular to the metal-alkyne bond affording an η^2 -vinyl complex. As shown, for example, in Scheme 13, where the reaction of $[\text{Mo}(\eta^2\text{-Bu}^t\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ with LiCuPh_2 to give complex (3) is depicted, such a reaction path delivers the incoming phenyl group to a pseudo-axial site affording the kinetic product (A). This rearranges *via* windscreen-wiper motion, *i.e.* a -90° rotation (see Scheme 4) to the isolated thermodynamically controlled product (3).

In this reaction selective attack occurs on the unsubstituted alkyne carbon atom, which is the opposite regioselectivity to that observed⁴³ in the reaction of organocuprates with uncoordinated alkynes. This selectivity could arise from both steric and electronic effects. An *X*-ray crystal structure determination

Scheme 13. P = P(OMe)₃; (i) LiCuPh₂, thf

Scheme 14.

of $[\text{Mo}(\eta^2\text{-Bu}^t\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ has established⁴¹ the molecular geometry shown, where the alkyne lies parallel to a Mo-P vector, the unsubstituted end of the alkyne being adjacent to a co-ordinated phosphite. In solution the same structure is adopted, but in addition there is a low-energy windscreen-wiper motion of the alkyne as evidenced by the ^{13}C - $\{^1\text{H}\}$ n.m.r. spectrum (CDCl_3), which shows the alkyne contact carbons at δ 244.9 [t, CBu^t , $^2J(\text{CP})$ 9.1 Hz] and 201.7 [t, CH, $^2J(\text{CP})$ 23.9 Hz]. Thus, the regioselectivity could arise from the preferred orientation of the alkyne.

Alternatively if we examine the relative coefficients of the π and π^* orbitals of an unsymmetrical alkyne carrying an electron-donor Bu^t group, it can be seen from Scheme 14 that nucleophilic attack would be facilitated at the unsubstituted carbon. This argument is reinforced by the report⁴⁴ that the iron cation $[\text{Fe}(\text{CO})(\text{PPh}_3)(\eta^2\text{-MeC}_2\text{CO}_2\text{Et})(\eta\text{-C}_5\text{H}_5)]^+$ reacts with LiCuMe_2 to afford the σ -vinyl complex $[\text{Fe}(\text{CO})(\text{PPh}_3)\{\sigma\text{-C}(\text{CO}_2\text{Et})\text{CMe}_2\}(\eta\text{-C}_5\text{H}_5)]$, which is consistent with attack on the π^* orbital of the co-ordinated alkyne, $\text{MeC}\equiv\text{CCO}_2\text{Et}$.

In this discussion, in order to simplify the argument it has been assumed that the reactions with cuprate anions involve a two-electron transfer process; however, it is not possible to exclude a two-step one-electron process. In fact this possibility is underlined by the observation⁴⁵ that the related cation $[\text{Mo}(\eta^2\text{-MeC}_2\text{Me})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ readily undergoes a reversible one-electron reduction (-1.28 V; calomel reference electrode, CH_2Cl_2 with $[\text{NBu}_4^+][\text{BF}_4^-]$), and it has been reported⁴⁶ that the oxidation potential of organocuprates is less than -2 V.

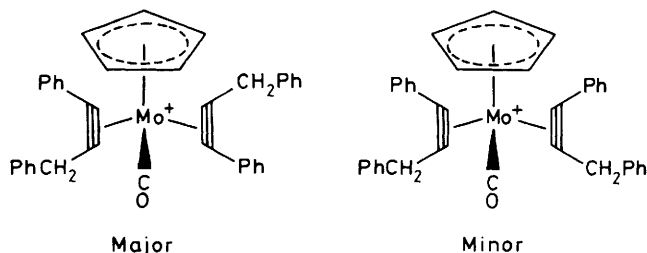
Clearly further work is required to clarify this question. Also from a theoretical standpoint it will be interesting to explore

whether nucleophilic attack on a co-ordinated four-electron alkyne is helped by a $\eta^2 \rightarrow \sigma$ slippage as found by Eisenstein and Hoffmann⁴⁷ in their important study of the reactions of nucleophiles with co-ordinated alkenes.

Experimental

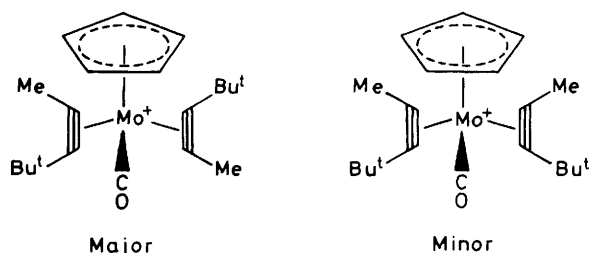
The ^1H , ^{13}C - $\{^1\text{H}\}$, and ^{31}P - $\{^1\text{H}\}$ n.m.r. spectra were recorded on JEOL FX 90Q or FX200 spectrometers, as appropriate. Data given are for room-temperature measurements unless otherwise indicated, and coupling constants are in Hz. Chemical shifts are positive to high frequency of the reference; SiMe_4 for ^{13}C and ^1H , and H_3PO_4 (85% external) for ^{31}P . I.r. spectra were recorded on a Perkin-Elmer 257 spectrophotometer. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Preparation of Starting Materials.—*Carbonyl(η -cyclopentadienyl)bis(1,3-diphenylprop-1-yne)molybdenum(II) tetrafluoroborate.* Silver tetrafluoroborate (5.2 g, 26.7 mmol) was added to a stirred solution of $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ (6.5 g, 13.3 mmol) and $\text{PhC}_2\text{CH}_2\text{Ph}$ (26.0 g, 132 mmol) in CH_2Cl_2 (100 cm^3) at room temperature. After 25 h the reaction mixture was filtered through Kieselguhr, the volume reduced *in vacuo* to 30 cm^3 , and diethyl ether (30 cm^3) added to give a yellow precipitate. This was recrystallised (0 $^\circ\text{C}$) from CH_2Cl_2 -Et₂O to give yellow crystals of $[\text{Mo}(\text{CO})(\eta^2\text{-PhC}_2\text{CH}_2\text{Ph})_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (14.0 g, 80%) (Found: C, 65.9; H, 4.4. $\text{C}_{36}\text{H}_{29}\text{BF}_4\text{MoO}$ requires C, 65.5; H, 4.4%). ν_{CO} (Nujol) 2 050 cm^{-1} . N.m.r.: ^1H (CDCl_3), major



isomer, δ 7.6–6.6 (m, 10 H, Ph), 5.90 (s, 5 H, C_5H_5), 5.10 [d, CHH', $J(\text{HH})$ 16.6], 5.09 [d, CHH, $J(\text{HH})$ 17.5], 4.72 [d, CHH', $J(\text{HH})$ 16.6], 4.71 [d, CHH, $J(\text{HH})$ 17.5] (two inequivalent CH_2 groups observed as AB systems); minor isomer, δ 7.6–6.6 (m, 10 H, Ph), 6.03 (s, 5 H, C_5H_5), 4.79 [d, (AB system) CHH', $J(\text{HH})$ 17.1], and 4.32 p.p.m. [d, (AB system) CHH', $J(\text{HH})$ 17.1]. The ratio of major to minor isomer is 1.46:1.

Carbonyl(η -cyclopentadienyl)bis(4,4-dimethylpent-2-yne)molybdenum(II) tetrafluoroborate. Similarly, reaction of AgBF_4 (5.1 g, 26.2 mmol), $[\text{Mo}_2(\text{CO})_6(\eta\text{-C}_5\text{H}_5)_2]$ (6.4 g, 13.1 mmol) and $\text{Bu}^t\text{C}_2\text{Me}$ (7.5 g, 78 mmol) in CH_2Cl_2 (100 cm^3) afforded yellow crystals of $[\text{Mo}(\text{CO})(\eta^2\text{-Bu}^t\text{C}_2\text{Me})_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (7.4 g, 60%) (Found: C, 51.3; H, 6.3. $\text{C}_{20}\text{H}_{29}\text{BF}_4\text{MoO}$ requires C, 51.3; H, 6.2%). ν_{CO} (Nujol) 2 055 cm^{-1} . N.m.r.: ^1H (CDCl_3), major isomer, δ 5.96 (s, 5 H, C_5H_5), 3.25 (s, 3 H, Me), 3.10 (s, 3 H, Me),



1.38 (s, 9 H, Bu^t), 1.36 (s, 9 H, Bu^t); minor isomer δ 5.80 (s, 5 H, C_5H_5), 2.93 (s, 6 H, Me), and 1.41 p.p.m. (s, 18 H, Bu^t). The ratio of major to minor isomer is 1.7:1.

(η -Cyclopentadienyl)(1,3-diphenylprop-1-yne)bis(trimethyl phosphite)molybdenum(II) tetrafluoroborate. Trimethyl phosphite (3.05 g, 24.4 mmol) was added dropwise to a stirred solution of $[\text{Mo}(\text{CO})(\eta^2\text{-PhC}_2\text{CH}_2\text{Ph})_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (7.7 g, 11.7 mmol) in CH_2Cl_2 (60 cm^3). An immediate colour change from yellow to purple occurred. After 1 h at room temperature, the reaction mixture was filtered, the volume reduced to 30 cm^3 , and diethyl ether (30 cm^3) added. The resultant precipitate was recrystallised from CH_2Cl_2 -Et₂O to give purple crystals of $[\text{Mo}(\eta^2\text{-PhC}_2\text{CH}_2\text{Ph})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (7.9 g, 98%) (Found: C, 45.6; H, 5.1. $\text{C}_{26}\text{H}_{35}\text{BF}_4\text{MoO}_6\text{P}_2$ requires C, 45.4; H, 5.1%). N.m.r.: ^1H (CDCl_3), δ 7.38–6.98 (m, 10 H, Ph), 5.57 [t, 5 H, C_5H_5 , $J(\text{HP})$ 1.4], 4.87 (s, 2 H, CH_2), 3.59 [apparent triplet, 18 H, POME, $J(\text{HP}) + J(\text{HP}')$ 11.1]; ^{13}C - $\{^1\text{H}\}$ (CDCl_3), 223.4 [t, CCH_2Ph , $J(\text{CP})$ 8.3], 222.0 [t, CPh, $J(\text{CP})$ 17.1], 139.4 (*i*-Ph), 138.5 (*i*-Ph), 129.3, 128.8, 128.6, 127.7, 127.1, 126.6 (Ph), 95.5 (C_5H_5), 53.6 [d, POME, $J(\text{CP})$ 7.3], 43.1 (CH_2); ^{31}P - $\{^1\text{H}\}$ (CDCl_3), δ 177.6 p.p.m.

(η -Cyclopentadienyl)(4,4-dimethylpent-2-yne)bis(trimethyl phosphite)molybdenum(II) tetrafluoroborate. A similar reaction between $[\text{Mo}(\text{CO})(\eta^2\text{-Bu}^t\text{C}_2\text{Me})_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (3.6 g, 7.7 mmol) and $\text{P}(\text{OMe})_3$ (2.0 g, 16 mmol) in CH_2Cl_2 (40 cm^3) afforded purple crystals of $[\text{Mo}(\eta^2\text{-Bu}^t\text{C}_2\text{Me})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (4.3 g, 95%) (Found: C, 36.1; H, 6.0. $\text{C}_{18}\text{H}_{35}\text{BF}_4\text{MoO}_6\text{P}_2$ requires C, 36.5; H, 6.0%). N.m.r.: ^1H (CDCl_3), δ 5.53 (s, 5 H, C_5H_5), 3.55 [apparent triplet, 18 H, POME, $J(\text{HP}) + J(\text{HP}')$ 11.1], 3.03 (s, 3 H, Me), 1.32 (s, 9 H, Bu^t); ^{13}C - $\{^1\text{H}\}$ (CDCl_3), δ 242.2 [t, CBu^t, $J(\text{CP})$ 4.95], 216.3 [apparent triplet, CMe, $J(\text{CP}) + J(\text{CP}')$ 41.2], 94.3 (C_5H_5), 53.3 [d, POME, $J(\text{CP})$ 7.3], 43.5 (CMe₃), 30.2 (CMe₃), 22.7 [t, Me, $J(\text{CP}) + J(\text{CP}')$ 11.5]; ^{31}P - $\{^1\text{H}\}$ (CDCl_3), δ 179.5 p.p.m.

Reaction of K[BHBu^s]₃ with $[\text{Mo}(\eta^2\text{-PhC}_2\text{Ph})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$.—A solution of 'potassium selectride'* (2.5 mmol in 2.5 cm^3 of thf) was added dropwise to a stirred (–78 $^\circ\text{C}$) suspension of $[\text{Mo}(\eta^2\text{-PhC}_2\text{Ph})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (1.5 g, 2.22 mmol) in thf (20 cm^3). An immediate colour change from purple to dark green was observed. After 2 h the solvent was removed *in vacuo*, and the residue extracted with diethyl ether (60 cm^3). This was filtered through alumina (20 mm), the volume of the solvent reduced to 10 cm^3 , and cooled (0 $^\circ\text{C}$) to give dark green crystals of (2) (0.9 g, 70%) (Found: C, 51.4; H, 6.1. $\text{C}_{25}\text{H}_{34}\text{MoO}_6\text{P}_2$ requires C, 51.0; H, 5.8%). N.m.r.: ^1H (CD_2Cl_2), δ 7.6–6.6 (m, 10 H, aromatic H), 5.24 (s, 5 H, C_5H_5), 3.83 [dd, X part of an ABX system, 1 H, CHPh, $^3J(\text{HP}) + ^3J(\text{HP}')$ 17, $^3J(\text{PH})$, 12, $^3J(\text{PH})$ 5], 3.34 [d, 9 H, POME, $J(\text{HP}) + J(\text{HP}')$ 11.5], 3.24 [d, 9 H, POME, $J(\text{HP}) + J(\text{HP}')$ 11.5]; ^{13}C - $\{^1\text{H}\}$ (CD_2Cl_2), δ 255.5 [d, Mo=C, $^2J(\text{CP})$ 40], 157.1, 143.9, 130.9, 128.2, 126.3, 121.1 (Ph); 91.4 (C_5H_5), 51.6 [d, POCH₃, $J(\text{CP}) + J(\text{CP}')$ 6], 51.4 [d, POCH₃, $J(\text{CP}) + J(\text{CP}')$ 12], 26.8 [MoCHPh , $J(\text{CP}) + J(\text{CP}')$ 17]; ^{31}P - $\{^1\text{H}\}$ (CD_2Cl_2), δ 164.7 [d, P(OMe)₃, $J(\text{AB})$ 77.5], and 158.1 p.p.m. [d, P(OMe)₃, $J(\text{AB})$ 77.5].

Reaction of Lithium Diphenylcuprate with $[\text{Mo}(\eta^2\text{-Bu}^t\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$.—A suspension of $[\text{Mo}(\eta^2\text{-Bu}^t\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)][\text{BF}_4]$ (1.1 g, 2 mmol) in thf (30 cm^3) was cooled to –78 $^\circ\text{C}$, and a freshly prepared solution of LiCuPh_2 (2 mmol) in thf (10 cm^3) added dropwise. The purple mixture immediately turned orange-red. The reaction vessel was removed from the cold bath, and the volatiles were removed *in vacuo*. The residue was dissolved in toluene and

* Registered trade name (Aldrich): K[BHBu^s]₃.

filtered through alumina (10 × 4 cm) affording an orange band that collected as a red solution. This was reduced *in vacuo* to an orange solid. The product was extracted into hexane and purified on a small alumina column (5 × 4 cm). Elution with 10% diethyl ether-hexane afforded an orange-red band, which was collected, the solvent removed, and crystallised (−78 °C) from pentane to give red crystals of (3) (0.65 g, 57%) (Found: C, 48.9; H, 6.9. C₂₃H₃₈MoO₆P₂ requires C, 48.6; H, 6.7%). N.m.r.: ¹H (C₆D₆), δ 7.6–6.2 (m, 5 H, aromatic H), 5.46 (br s, 5 H, C₅H₅), 3.78 [dd, 1 H, CHPh, |J(HP) + J(HP')| 11], 3.30 [d, 9 H, POMe, |J(HP) + J(HP')| 10], 3.22 [d, 9 H, POMe, |J(HP) + J(HP')| 10], 1.30 (s, 9 H, Bu^t); ¹³C-{¹H} (C₆D₆), δ 286.5 [dd, Mo=C(Bu^t), |J(CP) + J(CP')| 29], 157.3 (*i*-Ph), 127.9 (Ph), 126.6 (Ph), 121.3 (*p*-Ph), 89.7 (C₅H₅), 51.8 [d, POCH₃, |J(CP) + J(CP')| 5], 51.1 [d, POCH₃, |J(CP) + J(CP')| 5], 50.4 (CMe), 31.2 (CMe₃), 29.9 [dd, MoCHPh, |J(CP) + J(CP')| 22]; ³¹P-{¹H} (CDCl₃), δ 197.8 [d, P(OMe)₃, J(AB) 79.4], and 193.3 p.p.m. [d, P(OMe)₃, J(AB) 79.4].

Reactions of Lithium Di-*p*-tolylcuprate.—(a) With [Mo(η²-Bu^tC₂H)₂{P(OMe)₃}₂(η-C₅H₅)][BF₄]. Similarly, the reaction of LiCu(C₆H₄Me-*p*)₂ (2.0 mmol) with [Mo(η²-Bu^tC₂H)₂{P(OMe)₃}₂(η-C₅H₅)][BF₄] (1.1 g, 2 mmol) afforded red crystals of (4) (0.6 g, 52%) (Found: C, 49.2; H, 7.2%; M, 458. C₂₅H₄₂MoO₆P₂ requires C, 49.5; H, 6.9%; M, 458). N.m.r.: ¹H (C₆D₆), δ 7.8–7.2 (m, 4 H, aromatic H), 5.58 (br s, 5 H, C₅H₅), 3.84 [dd, 1 H, CH (*p*-tolyl), |J(HP) + J(HP')| 10], 3.50 [d, 9 H, POMe, |J(HP) + J(HP')| 10], 3.40 [d, 9 H, POMe, |J(HP) + J(HP')| 9], 2.37 (s, 3 H, C₆H₄Me-4), 1.40 (s, 9 H, Bu^t); ¹³C-{¹H} (C₆D₆), δ 286.9 [dd, Mo=C(Bu^t), |J(CP) + J(CP')| 27], 153.8 (*i*-C₆H₄), 129.7 (*p*-C₆H₄), 127.8 (C₆H₄), 127.2 (C₆H₄), 89.5 (C₅H₅), 51.7 [d, POCH₃, |J(CP) + J(CP')| 5], 51.0 [d, POCH₃, |J(CP) + J(CP')| 5], 50.2 (CMe₃), 31.1 (CMe₃), 29.3 [d, MoCH (*p*-tolyl), |J(CP) + J(CP')| 22], 20.9 (C₆H₄Me-4); ³¹P-{¹H} (C₆D₆), δ 198.2 [d, P(OMe)₃, J(AB) 80.6] and 193.0 p.p.m. [d, P(OMe)₃, J(AB) 80.6].

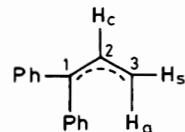
(b) With [Mo(η²-Pr^tC₂H)₂{P(OMe)₃}₂(η-C₅H₅)][BF₄].²² An analogous reaction gave yellow crystals of (5) (0.5 g, 44%) (Found: C, 48.9; H, 7.0. C₂₃H₃₈MoP₂O₆ requires C, 48.6; H, 6.7%). N.m.r.: ¹H (C₆D₆), δ 7.03 [d, 2 H, C₆H₄, J(AB) 8], 6.87 [d, 2 H, C₆H₄, J(AB) 8], 5.27 (s, 5 H, C₅H₅), 3.74 [septet, 1 H, CHMe₂, J(HH) 6.5], 3.65 [m, 1 H, CH (*p*-tolyl)], 3.48 [d, 9 H, POMe, |J(HP) + J(HP')| 8], 3.40 [d, 9 H, POMe, |J(HP) + J(HP')| 8], 2.35 (s, 3 H, C₆H₄Me-4), 1.46 [d, 3 H, CHMeMe', J(HH) 6.5], 1.27 [d, 3 H, CHMeMe', J(HH) 6.5]; ¹³C-{¹H} (C₆D₆), δ 276.2 [dd, Mo=CPr^t, |J(CP) + J(CP')| 37], 154.9 (*i*-C₆H₄), 129.5 (*p*-C₆H₄), 127.8 (C₆H₄), 126.6 (C₆H₄), 90.1 (C₅H₅), 51.3 [d, POMe, |J(CP) + J(CP')| 7], 45.0 [d, CHMeMe', |J(CP) + J(CP')| 8], 26.1 [d, MoCH (*p*-tolyl), |J(CP) + J(CP')| 15], 22.9 (CHMeMe'), 22.4 (CHMeMe'), 21.0 (C₆H₄Me-4); ³¹P-{¹H} (C₆D₆), δ 201.9 [d, P(OMe)₃, J(AB) 73.2], and 198.8 p.p.m. [d, P(OMe)₃, J(AB) 73.2].

Reaction of Lithium Diphenylcuprate with [Mo(η²-PhC₂Me)-{P(OMe)₃}₂(η-C₅H₅)][BF₄].—A suspension of [Mo(η²-PhC₂Me){P(OMe)₃}₂(η-C₅H₅)][BF₄]²² (1.0 g, 1.6 mmol) in thf (30 cm³) was cooled to −78 °C. To this was added a slight excess (2 mmol) of a freshly prepared solution of LiCuPh₂. The reaction mixture changed from deep blue to yellow-brown. The reaction vessel was removed from the cold bath and the volatiles were removed *in vacuo*. The residue was extracted into toluene and chromatographed on alumina (10 × 4 cm) giving one fast-moving red-brown band. This was collected, the toluene removed *in vacuo* giving a red solid, which was crystallised (−30 °C) from toluene-hexane to afford red crystals of (6) (0.5 g, 52%) (Found: C, 52.1; H, 6.2. C₂₆H₃₆MoO₆P₂ requires C, 51.8; H, 6.0%). N.m.r.: ¹H (CD₂Cl₂), δ 7.2–6.6 (m, 10 H, Ph), 4.68 (br s, 5 H, C₅H₅), 3.22 [apparent triplet, 18 H, POMe, |J(HP) +

J(HP')| 11], 2.88 [t, 3 H, Me, J(HP) 3]; ¹³C-{¹H} (CD₂Cl₂, −50 °C), δ 237.4 [t, Mo=CMe, J(CP) 28], 157.4 (*i*-Ph), 129.8 (*o*-Ph), 126.6 (*m*-Ph), 121.5 (*p*-Ph), 91.1 (C₅H₅), 51.5 (br s, POMe), 35.7 (MoCPh₂), 30.0 [t, Mo=CMe, J(CP) 9]; ³¹P-{¹H} (CD₂Cl₂, −50 °C), δ 200.7 p.p.m. [s, P(OMe)₃].

Reaction of K[BHBu^s]₃ with [Mo(η²-PhC₂CH₂Ph)-{P(OMe)₃}₂(η-C₅H₅)][BF₄].—A solution of potassium selectride (1.5 cm³ of a 1 mol dm^{−3} solution) in thf was added to a stirred (−78 °C) suspension of [Mo(η²-PhC₂CH₂Ph)-{P(OMe)₃}₂(η-C₅H₅)][BF₄] (1.0 g, 1.45 mmol) in thf (15 cm³). The reaction mixture was allowed to warm to room temperature, and after 1.5 h the solvent was removed *in vacuo*. The residue was extracted into hexane and chromatographed on alumina. Elution with hexane-diethyl ether (4:1) gave a yellow band which was collected and crystallised (−30 °C) from hexane affording low-melting pale orange crystals of (8) (0.26 g, 30%). N.m.r.: ¹H (C₆H₆), δ 7.44–6.86 (m, 10 H, Ph), 5.07 [d, H, CCH', J(HH) 14], 4.88 (s, 5 H, C₅H₅), 4.53 [d, H, CHH', J(HH) 14], 3.34 [d, 9 H, POMe, J(HP) 11], 3.18 [d, 9 H, POMe, J(HP) 10], 2.91 [t, 1 H, CH, |J(HP) + J(HP')| 10]; ¹³C-{¹H} (C₆D₆), δ 260.4 [dd, Mo=C, J(CP) 30.3, J(CP') 12.7], 140.4 (*i*-Ph), 137.9 (*i*-Ph), 128.7, 127.7, 126.5, 126.4, 126.1, 125.6 (Ph), 90.1 (C₅H₅), 51.0 [d, POMe, J(CP) 3.9], 39.6 (CH₂), 24.6 [d, MoCH(CH₂Ph), J(CP) 9.8]; ³¹P-{¹H} (C₆D₆), δ 205.4 and 202.7 p.p.m. [AB system, J(AB) 63.5]. Further elution with diethyl ether gave a dark orange band, which on recrystallisation (−30 °C) gave low-melting dark orange crystals of (9) (0.37 g, 42%). N.m.r.: ¹H (C₆D₆), δ 7.44–6.80 (10 H, m, Ph), 5.03 [d, 1 H, CHH', J(HH) 14], 4.86 (s, 5 H, C₅H₅), 4.42 [d, 1 H, CHH', J(HH) 14], 3.65 [t, 1 H, CH, |J(HP) + J(HP')| 11], 3.33 [d, 9 H, POMe, J(HP) 11], 3.16 [d, 9 H, POMe, J(HP) 10.5]; ¹³C-{¹H} (C₆D₆), δ 260.3 [dd, Mo=C, J(CP) 31.3, J(CP') 11.7], 158.0 (*i*-Ph), 141.4 (*i*-Ph), 129.7, 128.7, 127.7, 126.5, 126.0 (Ph), 90.1 (C₅H₅), 51.0 [d, POMe, J(CP) 3.9], 39.6 (CH₂), 24.6 [d, MoCH(CH₂Ph), J(CP) 9.8]; ³¹P-{¹H} (C₆D₆), δ 205.4 and 202.8 [AB system, J(AB) 62.3].

Rearrangement of Complex (6).—A toluene solution of (6) (0.3 g, 0.5 mmol) was stirred under N₂ for 3 d. The solvent was removed *in vacuo*, the residue dissolved in hexane, and chromatographed on alumina. Elution with diethyl ether-hexane (1:5) afforded an orange band, which was collected. Recrystallisation (−78 °C) from pentane afforded orange-red crystals of (10) (0.2 g, 67%) (Found: C, 51.1; H, 6.9%; M, 602. C₂₆H₃₃MoO₆P₂ requires C, 51.8; H, 6.0%; M, 602). N.m.r.: ¹H (C₆H₆), δ 7.8–6.9 (m, 10 H, Ph), 4.58 (br s, 5 H, C₅H₅), 3.26 [d, 9 H, P(OMe)₃, |J(HP) + J(HP')| 10], 3.13 [d, 9 H, P(OMe)₃, |J(HP) + J(HP')| 10], 2.71 [t, 1 H, H_a, J(H_aH_c) ≈ J(HP) 7.5],



2.09 (m, 1 H, H_a); ¹³C-{¹H} (C₆D₆), δ 151.8 (Ph), 148.2 (Ph), 131.9 (Ph), 129.2 (Ph), 126.9 (Ph), 126.5 (Ph), 123.9 (Ph), 123.6 (Ph), 88.5 (C₅H₅), 77.0 [m, C¹], 72.9 [C²], 51.6 [d, POMe, |J(CP) + J(CP')| 5], 51.3 [d, POMe, |J(CP) + J(CP')| 3], 31.1 [t, C³, |J(CP) + J(CP')| 8]; ³¹P-{¹H} (C₆D₆), δ 202.7 [d, P(OMe)₃, J(PP) 95] and 197.5 p.p.m. [d, P(OMe)₃, J(PP) 97].

Reactions of Lithium Dimethylcuprate.—(a) With [Mo(η²-Bu^tC₂H)₂{P(OMe)₃}₂(η-C₅H₅)][BF₄]. Freshly prepared LiCuMe₂ (2.5 mmol) in thf (10 cm³) was added to a stirred suspension of [Mo(η²-Bu^tC₂H)₂{P(OMe)₃}₂(η-C₅H₅)][BF₄]

Table 5. Crystal data, collection, and refinement

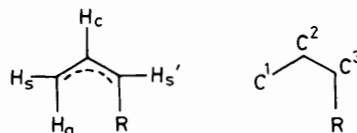
Complex	(2)	(3)	(6)
(a) Crystal data ^a			
Formula	C ₂₅ H ₃₄ MoO ₆ P ₂	C ₂₃ H ₃₈ MoO ₆ P ₂	C ₂₆ H ₃₆ MoO ₆ P ₂
<i>M</i>	588.1	568.1	602.1
Crystal system	monoclinic	triclinic	monoclinic
<i>a</i> /Å	12.258(3)	9.692(4)	13.499(7)
<i>b</i> /Å	13.123(2)	15.456(4)	10.452(3)
<i>c</i> /Å	17.000(4)	19.115(7)	19.623(9)
α /°	90	76.89(2)	90
β /°	103.26(2)	80.47(3)	97.72(4)
γ /°	90	75.44(2)	90
<i>U</i> /Å ³	2 661(1)	2 682(2)	2 744(2)
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>P</i> 1̄ (no. 2)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>D</i> _c /g cm ⁻³	1.47	1.40	1.45
Crystal colour	dark green	deep red	deep red
Shape	block	ground sphere	cleaved plate
Crystal size (mm)	0.5 × 0.4 × 0.3	0.48 (diameter)	0.5 × 0.3 × 0.1
μ (Mo- <i>K</i> _α)/cm ⁻¹	6.3	6.3	6.2
<i>F</i> (000)	1 216	1 184	1 248
(b) Data collection and processing ^b			
Scan widths (°)	2.0 + $\Delta_{\alpha_1\alpha_2}$	2.4 + $\Delta_{\alpha_1\alpha_2}$	2.4 + $\Delta_{\alpha_1\alpha_2}$
2 θ _{max.} /°	55	45	50
Absorption correction			
Method	Gaussian quadrature	—	—
Faces	{110}, {011}	—	—
Transmission range	0.75–0.87	—	—
No. of data	4 213	6 688	4 246
No. of unique data	3 966	5 823	3 546
No. used	3 844	5 390	2 994
(c) Structure analysis and refinement ^c			
Freely refined H atoms	H(4)	H(2), H(32)	none
Weighting scheme, <i>g</i> ^d	0.0001	0.000 05	0.0002
Final residuals ^e			
<i>R</i>	0.028	0.028	0.034
<i>R</i> '	0.029	0.028	0.032
<i>S</i>	2.12	1.69	1.32
Final difference density features (e Å ⁻³)	-0.6 to +0.7	-0.2 to +0.4	-0.3 to +0.6

^a Common data: Mo-*K*_α radiation (graphite-monochromated), $\lambda = 0.710 69 \text{ \AA}$; *Z* = 4. ^b Common data: *T* = 293 K; $\theta/2\theta$ scan; Nicolet *P3m* diffractometer; scan speed 3.0–29.3° min⁻¹; criterion for observed, $I > 2\sigma(I)$. ^c Common data: Patterson heavy-atom method; anisotropic atoms, Mo, P, O, C; isotropic atoms, H. ^d $w = [\sigma_c^2(F_o) + gF_o^2]^{-1}$. ^e $R = \Sigma|F_o - |F_c||/F_o$; $R' = \Sigma w^2|F_o - |F_c||/\Sigma w^2 F_o$; $S = [\Sigma w(F_o - |F_c|)^2]/(n.o. - n.v.)^{1/2}$.

(1.1 g, 2 mmol) in thf (30 cm³) at -78 °C. The purple suspension gradually dissolved and turned an orange colour. The solvent was removed *in vacuo*, the residue dissolved in diethyl ether and filtered through Kieselguhr. The diethyl ether was removed, the residue dissolved in hexane and chromatographed on alumina. Elution with diethyl ether-hexane (1:5) gave a primrose yellow band. This was collected, the solvent changed to pentane and the solution cooled (-78 °C) to yield the yellow low-melting solid (11) (0.6 g, 60%) (Found: C, 42.5; H, 7.1%; *M*, 507. C₁₈H₃₆MoO₆P₂ requires C, 42.6; H, 7.1%; *M*, 507). N.m.r.: ¹H-³¹P} (C₆D₆), δ 4.86 (s, 5 H, C₅H₅), 3.70 [ddd, 1 H, H_c, *J*(H_cH_a) 10, *J*(H_cH_s') 8, *J*(H_cH_a) 6], 3.39 (s, 9 H, POMe), 3.34 (s, 9 H, POMe), 3.23 [br d, 1 H, H_s', *J*(H_s'H_a) 8], 2.68 [d, 1 H, H_a, *J*(H_aH_c) 10], 2.03 [dd, 1 H, H_a, *J*(H_aH_s') 6, *J*(H_aH_s') 1.5], 1.17 (s, H, Bu¹); ¹³C-¹H} (C₆D₆), δ 83.6 (C₅H₅), 70.5 (C²), 68.1 [dd, C³, |*J*(CP) + *J*(CP')| 11], 50.9 (POMe), 39.2 (CMe₃), 34.2 (CMe₃), 33.2 [dd, C¹, |*J*(CP) + *J*(CP')| 11]; ³¹P-¹H} (C₆D₆), δ 203.1 [d, P(OMe)₃, *J*(PP) 88], and 202.3 p.p.m. [d, P(OMe)₃, *J*(PP) 88].

(b) With [Mo(η^2 -PrⁱC₂H)₂{P(OMe)₃}₂(η -C₅H₅)][BF₄]. A similar reaction between LiCuMe₂ and [Mo(η^2 -PrⁱC₂H)-

{P(OMe)₃}₂(η -C₅H₅)][BF₄] (1.0 g, 2 mmol) afforded yellow crystals of (12) (0.5 g, 65%) (Found: C, 41.9; H, 7.4%; *M*, 492.



C₁₇H₃₄MoO₆P₂ requires C, 41.5; H, 7.0%; *M*, 492). N.m.r.: ¹H-³¹P} (C₆D₆), δ 4.70 (s, 5 H, C₅H₅), 3.68 [dt, 1 H, H_c, *J*(H_cH_a) 9, *J*(H_cH_s) = *J*(H_cH_s') 6.5], 3.49 (s, 9 H, POMe), 3.37 (s, 9 H, POMe), 2.85 [d, 1 H, H_s', *J*(H_s'H_c) 7], 2.16 [dd, 1 H, H_a, *J*(H_aH_c) 6.5, *J*(H_aH_s') 2.0], 2.08 [d, 1 H, H_a, *J*(H_aH_c) 9], 1.30 (br s, 3 H, CHMeMe'), 1.02 (br s, 3 H, CHMeMe'); ¹³C-¹H} (C₆D₆), δ 85.1 (C₅H₅), 72.1 (C²), 63.6 [t, C³, |*J*(CP) + *J*(CP')| 11], 50.7 [d, POMe, |*J*(CP) + *J*(CP')| 3], 34.9 (CHMeMe'), 31.8 (CHMeMe'), 30.3 [t, C¹, |*J*(CP) + *J*(CP')| 11], 24.4 (CHMeMe'); ³¹P-¹H} (C₆D₆), δ 205 [d, P(OMe)₃, *J*(PP) 88], and 204 p.p.m. [d, P(OMe)₃, *J*(PP) 88].

Table 6. Atomic co-ordinates ($\times 10^4$) for (2)

Atom	x	y	z	Atom	x	y	z
Mo	2 303(1)	2 418(1)	2 017(1)	C(32)	2 730(3)	6 226(3)	1 400(2)
P(1)	418(1)	2 748(1)	1 423(1)	C(33)	3 318(3)	6 491(3)	839(3)
P(2)	2 162(1)	778(1)	1 482(1)	C(34)	3 679(3)	5 746(3)	384(2)
O(11)	103(2)	3 925(2)	1 494(1)	C(35)	3 468(3)	4 724(3)	507(2)
O(12)	-542(2)	2 304(2)	1 841(2)	C(36)	2 885(2)	4 438(2)	1 093(2)
O(13)	-183(2)	2 500(2)	508(1)	C(41)	5 099(3)	2 707(2)	1 448(2)
O(21)	1 369(2)	581(1)	605(1)	C(42)	6 201(3)	2 493(3)	1 420(2)
O(22)	3 238(2)	151(2)	1 340(1)	C(43)	6 451(3)	1 852(3)	861(2)
O(23)	1 668(2)	-16(2)	2 045(1)	C(44)	5 595(3)	1 406(3)	302(2)
C(11)	-992(3)	4 319(3)	1 116(3)	C(45)	4 491(3)	1 618(2)	313(2)
C(12)	-618(3)	1 303(2)	2 080(2)	C(46)	4 214(2)	2 261(2)	887(2)
C(13)	225(4)	2 900(4)	-126(2)	C(51)	2 008(4)	2 227(4)	3 324(2)
C(21)	1 568(4)	-55(3)	-33(3)	C(52)	3 042(4)	1 787(3)	3 350(2)
C(22)	4 231(3)	110(4)	1 974(3)	C(53)	3 750(3)	2 559(3)	3 211(2)
C(23)	1 399(4)	-1 047(3)	1 783(3)	C(54)	3 161(3)	3 464(3)	3 101(2)
C(3)	2 677(2)	3 369(2)	1 237(2)	C(55)	2 088(3)	3 260(3)	3 184(2)
C(4)	3 025(2)	2 471(2)	882(2)	H(4)	2 601(21)	2 191(19)	464(15)
C(31)	2 510(3)	5 211(2)	1 526(2)				

Table 7. Atomic co-ordinates ($\times 10^4$) for (3)

Atom	x	y	z	Atom	x	y	z
Mo(1)	2 699(1)	2 925(1)	5 953(1)	O(22)	5 506(3)	1 692(2)	4 907(2)
Mo(2)	2 363(1)	3 218(1)	1 299(1)	O(23)	5 915(3)	3 073(2)	5 171(2)
P(1)	2 033(1)	1 521(1)	6 232(1)	C(31)	1 811(3)	2 416(2)	2 183(2)
P(2)	5 059(1)	2 278(1)	5 534(1)	C(32)	2 934(4)	1 743(2)	1 892(2)
P(3)	4 529(1)	2 542(1)	685(1)	C(33)	795(4)	2 292(2)	2 880(2)
P(4)	3 647(1)	3 676(1)	2 034(1)	C(34)	-246(5)	3 189(3)	2 991(2)
C(1)	3 535(4)	3 135(2)	6 739(2)	C(35)	1 734(5)	1 972(3)	3 497(2)
C(2)	3 173(4)	2 292(2)	7 117(2)	C(36)	-71(5)	1 591(3)	2 905(3)
C(3)	4 228(4)	3 751(3)	7 018(2)	C(37)	2 631(4)	960(2)	1 662(2)
C(4)	4 621(7)	4 525(3)	6 426(3)	C(38)	3 593(4)	112(2)	1 757(2)
C(5)	5 576(6)	3 173(4)	7 325(4)	C(39)	3 340(5)	-630(3)	1 555(3)
C(6)	3 267(7)	4 166(4)	7 619(3)	C(40)	2 107(5)	-554(3)	1 255(3)
C(7)	2 105(4)	2 225(2)	7 775(2)	C(41)	1 152(5)	266(3)	1 151(2)
C(8)	878(4)	2 900(3)	7 879(2)	C(42)	1 408(4)	1 015(3)	1 346(2)
C(9)	-56(5)	2 828(3)	8 509(3)	C(43)	1 696(5)	4 149(4)	176(3)
C(10)	197(4)	2 066(3)	9 049(2)	C(44)	817(5)	3 538(3)	389(2)
C(11)	1 376(4)	1 372(3)	8 954(2)	C(45)	-17(4)	3 721(3)	1 011(2)
C(12)	2 313(4)	1 462(3)	8 329(2)	C(46)	327(5)	4 436(3)	1 196(2)
C(13)	474(4)	3 896(3)	5 664(2)	C(47)	1 395(5)	4 713(3)	678(3)
C(14)	1 048(5)	3 482(3)	5 066(2)	C(48)	6 286(5)	3 058(4)	-501(3)
C(15)	2 301(5)	3 769(3)	4 767(2)	C(49)	7 046(5)	1 459(3)	1 081(3)
C(16)	2 521(5)	4 363(3)	5 170(2)	C(50)	3 817(5)	1 590(4)	-118(3)
C(17)	1 369(5)	4 445(3)	5 727(2)	C(51)	5 491(5)	4 496(3)	1 083(2)
C(18)	3 050(6)	-173(3)	6 996(2)	C(52)	1 982(5)	4 968(3)	2 687(3)
C(19)	1 002(6)	526(3)	5 542(3)	C(53)	5 727(5)	3 030(3)	2 894(3)
C(20)	-602(4)	1 837(3)	6 905(3)	O(48)	4 977(3)	3 262(2)	-35(1)
C(21)	6 632(5)	738(3)	6 225(3)	O(49)	5 973(3)	2 234(2)	1 074(2)
C(22)	4 625(5)	1 388(4)	4 580(3)	O(50)	4 764(3)	1 638(2)	362(2)
C(23)	7 358(5)	2 908(4)	4 870(3)	O(51)	4 510(3)	4 482(2)	1 716(1)
O(18)	3 220(3)	596(2)	6 439(1)	O(52)	2 837(3)	4 085(2)	2 741(2)
O(19)	1 432(3)	1 343(2)	5 541(1)	O(53)	4 795(3)	2 873(2)	2 462(1)
O(20)	779(3)	1 268(2)	6 871(1)	H(2)	3 887(32)	1 769(20)	7 167(16)
O(21)	6 156(3)	1 678(2)	6 093(2)	H(32)	3 775(32)	1 558(20)	2 102(16)

Reaction of $K[BHBU_3]$ with $[Mo(\eta^2-Bu^iC_2Me)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$.—A solution of potassium selectride (1.4 cm³ of 1 mol dm⁻³ solution) in thf was added dropwise to a stirred suspension of $[Mo(\eta^2-Bu^iC_2Me)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ (0.8 g, 1.35 mmol) in thf (10 cm³) at -78 °C. The solution was allowed to warm to room temperature. After 30 min the solvent was removed *in vacuo*, the residue dissolved in hexane, and chromatographed on alumina. Elution with diethyl ether-hexane (1:4) gave a yellow band, which was collected. Recrystallisation (-78 °C) from hexane gave yellow crystals of (11) (0.22 g, 33%) identified by n.m.r. spectroscopy.

Reactions of $LiCuPh_2$.—(a) **With $[Mo(\eta^2-PhC_2Ph)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$.** A solution of $LiCuPh_2$ (1.5 mmol) in thf (10 cm³) was added dropwise to a stirred (-78 °C) suspension of $[Mo(\eta^2-PhC_2Ph)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ (1.0 g, 1.48 mmol) in thf (20 cm³). 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 hexane-diethyl ether (10:1) gave a dark green band, which was collected and recrystallised (-78 °C) from hexane-diethyl ether to give dark

Table 8. Atomic co-ordinates ($\times 10^4$) for (6)

Atom	x	y	z	Atom	x	y	z
Mo	2 186(1)	2 727(1)	6 019(1)	C(10)	1 919(3)	-305(4)	6 189(2)
P(1)	2 537(1)	3 547(1)	4 935(1)	C(11)	1 227(3)	-1 210(4)	5 900(2)
P(2)	3 538(1)	3 927(1)	6 586(1)	C(12)	792(3)	-2 085(4)	6 295(3)
O(1)	3 325(2)	2 857(4)	4 501(2)	C(13)	1 047(4)	-2 112(5)	7 001(3)
O(2)	1 583(2)	3 509(3)	4 360(2)	C(14)	1 748(4)	-1 256(5)	7 303(2)
O(3)	2 977(3)	4 956(4)	4 851(2)	C(15)	2 172(4)	-361(4)	6 907(2)
O(4)	4 504(2)	4 129(3)	6 215(2)	C(20)	2 357(3)	234(4)	5 013(2)
O(5)	4 134(2)	3 462(4)	7 316(2)	C(21)	1 552(3)	504(4)	4 512(2)
O(6)	3 168(3)	5 335(3)	6 768(2)	C(22)	1 508(4)	55(5)	3 843(2)
C(1)	4 342(4)	2 737(6)	4 734(3)	C(23)	2 272(4)	-657(5)	3 651(3)
C(2)	1 610(4)	3 951(7)	3 669(3)	C(24)	3 079(4)	-939(5)	4 132(3)
C(3)	2 464(5)	6 085(6)	5 044(4)	C(25)	3 124(3)	-516(4)	4 808(3)
C(4)	5 528(3)	4 293(5)	6 530(3)	C(30)	450(3)	2 288(5)	5 989(3)
C(5)	3 629(4)	2 996(6)	7 853(2)	C(31)	877(3)	2 386(5)	6 668(3)
C(6)	3 746(5)	6 374(6)	6 982(4)	C(32)	1 212(4)	3 620(6)	6 795(3)
C(7)	4 265(3)	915(5)	6 326(3)	C(33)	994(4)	4 304(5)	6 173(3)
C(8)	3 227(3)	1 403(4)	6 102(2)	C(34)	516(3)	3 468(6)	5 675(3)
C(9)	2 388(3)	658(4)	5 757(2)				

green crystals of (15) (0.15 g, 15%) (Found: C, 56.9; H, 4.3. $C_{31}H_{28}MoO_6P_2$ requires C, 56.9; H, 4.3%). N.m.r.: 1H (C_6D_6), δ 8.1–7.0 (m, 15 H, Ph), 5.05 [t, 5 H, C_5H_5 , $J(HP)$ 1.2], 3.13 [t, 18 H, POMe, $|J(HP) + J(HP')|$ 10.8]; ^{13}C - $\{^1H\}$ (C_6D_6), δ 230.0 [t, Mo=C, $J(CP)$ 23.8], 131.6, 130.9, 130.4, 130.2, 129.6, 122.2 (Ph), 93.4 (C_5H_5), 51.6 (m, POMe); ^{31}P - $\{^1H\}$ (C_6D_6), δ 195.6 (s) p.p.m.

(b) With $[Mo(\eta^2-Bu^tC_2Me)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ (13). Similarly, reaction ($-78^\circ C$) between $LiCuPh_2$ (1.50 mmol) and (13) (0.88 g, 1.48 mmol) gave on elution with hexane-diethyl ether (4:1) a blue band. This was crystallised from hexane at $-78^\circ C$ to give blue-purple crystals of (16) (0.45 g, 67%) (Found: C, 54.7; H, 6.6%; M, 458. $C_{21}H_{31}MoO_3P$ requires C, 55.0; H, 6.8%; M, 458). N.m.r.: 1H (C_6D_6), δ 7.24–6.78 (m, 5 H, Ph), 5.20 (s, 5 H, C_5H_5), 3.15 [d, 9 H, POMe, $J(HP)$ 11.0], 3.00 [d, 3 H, Me, $J(HP)$ 2.9], 1.40 (s, 9 H, Bu^t); ^{13}C - $\{^1H\}$ ($CD_3C_6D_5$, $-30^\circ C$), δ 218.3 ($\equiv CBu^t$), 142.1, 128.3, 125.7, 121.4 (Ph), 91.8 (C_5H_5), 51.4 (POMe), 37.1 (CMe_3), 30.9 (CMe_3); ^{31}P - $\{^1H\}$ ($CD_3C_6D_5$, $-30^\circ C$), δ 196.6 (s) p.p.m.

(c) With $[Mo(\eta^2-PhC_2CH_2Ph)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ (14). Reaction of $LiCuPh_2$ (0.90 mmol) with (14) (0.6 g, 0.87 mmol) in thf (25 cm^3) gave on chromatography and crystallisation from hexane-diethyl ether (4:1) a green unstable solid (17) (0.14 g, 29%). N.m.r.: 1H (C_6D_6), δ 7.16–6.83 (m, 15 H, Ph), 5.04 (s, 5 H, C_5H_5), 4.85 [d, 2 H, CH_2 , $J(HP)$ 4.4], 3.15 [d, 9 H, POMe, $J(HP)$ 11.4]; ^{31}P - $\{^1H\}$ (C_6D_6), δ 192.5 (s) p.p.m.

Reactions of Lithium Dimethylcuprate.—(a) With $[Mo(\eta^2-PhC_2Ph)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$. A solution of $LiCuMe_2$ (1.50 mmol) in thf (10 cm^3) was added to a stirred suspension of (1) (1.0 g, 1.48 mmol) in thf (20 cm^3) at $-78^\circ C$. An immediate change in colour to dark green was observed. The reaction mixture was allowed to warm to room temperature, the solvent removed *in vacuo*, and the residue chromatographed on alumina. Elution with hexane-diethyl ether (4:1) gave first a bright green band, which afforded green crystals of (18) (0.1 g, 21%) (Found: C, 51.7; H, 6.1. $C_{26}H_{36}MoO_6P_2$ requires C, 51.8; H, 6.0%). N.m.r.: 1H (C_6D_6), δ 7.9–7.1 (m, 10 H, Ph), 5.10 (s, 5 H, C_5H_5), 3.24 [d, 9 H, POMe, $|J(HP) + J(HP')|$ 12], 3.17 [d, 9 H, POMe, $|J(HP) + J(HP')|$ 12], 2.43 (s, 3 H, Me); ^{13}C - $\{^1H\}$ (C_6D_6), δ 259.4 [dd, Mo=C(Ph), $|J(CP) + J(CP')|$ 31.5], 161.5, 144.4, 129.0, 128.5, 127.9, 126.9, 126.5, 126.0, 120.5 (Ph), 92.0 (C_5H_5), 51.4 (m, POMe), 30.3 (Me), 29.7 [m, MoC(Me)Ph]; ^{31}P - $\{^1H\}$ (C_6D_6), δ 200.9 [d, P(OMe) $_3$, $J(AB)$ 71] and 199.8 p.p.m. [d, P(OMe) $_3$, $J(AB)$ 71].

Further elution with the same solvent mixture gave a dark green band, which crystallised ($-30^\circ C$) from hexane-diethyl ether to give dark green crystals of (19) (0.34 g, 39%) (Found: C, 57.7; H, 5.6. $C_{23}H_{27}MoO_3P$ requires C, 57.7; H, 5.6%). N.m.r.: 1H (C_6D_6), δ 7.8–7.3 (m, 10 H, Ph), 4.97 (s, 5 H, C_5H_5), 3.23 [d, 9 H, POMe, $J(HP)$ 11], 0.57 [d, 3 H, MoMe, $J(HP)$ 6]; ^{13}C - $\{^1H\}$ (C_6D_6), δ 91.4 (C_5H_5), 51.4 [d, POMe, $J(CP)$ 4.4], -9.2 [d, MoMe, $J(CP)$ 17.6]; ^{31}P - $\{^1H\}$ (C_6D_6), δ 191.4 p.p.m.

(b) With $[Mo(\eta^2-Bu^tC_2Me)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ (13). A similar reaction between $LiCuMe_2$ (0.9 mmol) and (13) (0.50 g, 0.84 mmol) in thf (30 cm^3) afforded on chromatography a purple band. Recrystallisation ($-30^\circ C$) from hexane afforded unstable purple crystals of (20) (0.25 g, 75%). N.m.r.: 1H ($CD_3C_6D_5$, $0^\circ C$), δ 4.96 (s, 5 H, C_5H_5), 3.32 [d, 9 H, POMe, $J(HP)$ 11.7], 2.95 [d, 3 H, CMe, $J(HP)$ 2.0], 1.37 (s, 9 H, Bu^t), 1.19 [d, 3 H, MoMe, $J(HP)$ 5.7]; ^{13}C - $\{^1H\}$ ($CD_3C_6D_5$, $-30^\circ C$), δ 214.5 ($\equiv CBu^t$), 194.1 [d, $\equiv CMe$, $J(CP)$ 39.1], 90.5 (C_5H_5), 50.9 (POMe), 41.4 (CMe_3), 32.2 (CMe_3), 20.7 [d, $\equiv CMe$, $J(CP)$ 12.2], -12.7 [d, MoMe, $J(CP)$ 17.1]; ^{31}P - $\{^1H\}$ ($CD_3C_6D_5$, $-30^\circ C$), δ 201.9 (s) p.p.m.

(c) With $[Mo(\eta^2-PhC_2CH_2Ph)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ (14). An analogous reaction between $LiCuMe_2$ (2.2 mmol) and (14) (1.5 g, 2.18 mmol) afforded from hexane ($-78^\circ C$) dark green crystals of (21) (0.66 g, 62%) (Found: C, 58.5; H, 5.9. $C_{24}H_{29}MoO_3P$ requires C, 58.5; H, 5.9%). N.m.r.: 1H (C_6D_6), δ 7.52–6.8 (m, 10 H, Ph), 4.89 (s, 5 H, C_5H_5), 4.67 [d, 2 H, CH_2 , $J(HP)$ 1.7], 3.35 [d, 9 H, POMe, $J(HP)$ 11.1], 0.38 [d, 3 H, MoMe, $J(HP)$ 6.3]; ^{13}C - $\{^1H\}$ (C_6D_6), δ 202.7 [d, $\equiv CPh$, $J(CP)$ 16.1], 200.2 [d, $\equiv CCH_2Ph$, $J(CP)$ 43.4], 141.1, 130.7, 130.0, 129.3, 128.6, 126.5, 126.0, 125.8, 125.2, 124.2 (Ph), 91.5 (C_5H_5), 51.2 [d, POMe, $J(CP)$ 3.9], 41.3 [d, CH_2 , $J(CP)$ 7.8], -9.2 [d, MoMe, $J(CP)$ 17.6]; ^{31}P - $\{^1H\}$ (C_6D_6), δ 197.6 (s) p.p.m.

Reaction of Molecular Oxygen with (16).—A solution of (16) (0.2 g, 0.44 mmol) in thf (10 cm^3) was exposed to air for 2 d. The colour changed from purple to brown. The solvent was removed *in vacuo*, the residue extracted with hexane, and chromatographed on alumina. Elution with diethyl ether gave a yellow band, which was crystallised from diethyl ether to give pale yellow crystals of (22) (0.03 g, 19%) (Found: C, 62.0; H, 6.6. $C_{18}H_{22}MoO$ requires C, 61.7; H, 6.3%), ν_{MoO} (Nujol) 920 cm^{-1} . N.m.r.: 1H (C_6D_6), δ 6.94–6.76 (m, 5 H, Ph), 5.60 (s, 5 H, C_5H_5), 2.14 (s, 3 H, Me), and 1.38 p.p.m. (s, 9 H, Bu^t).

Analogous reactions afforded pale yellow (23) (27%) (Found: C, 55.0; H, 7.5%; M, 288. $C_{13}H_{20}MoO$ requires C, 54.2; H, 7.0%;

M, 288); ν_{MoO} (Nujol) 925 cm^{-1} . N.m.r.: ^1H (C_6D_6), δ 5.36 (s, 5 H, C_5H_5), 2.21 (s, 3 H, $\equiv\text{CMe}$), 1.81 (s, 3 H, MoMe), 1.36 (s, 9 H, Bu t); ^{13}C - $\{^1\text{H}\}$ (C_6D_6), δ 137.1 ($\equiv\text{CBu}^t$), 130.7 ($\equiv\text{CMe}$), 103.5 (C_5H_5), 37.0 (CMe_3), 30.7 (CMe_3), 10.1 ($\equiv\text{CMe}$), and 7.9 p.p.m. (MoMe); and pale yellow (24) (22%) (Found: C, 64.5; H, 5.0. $\text{C}_{21}\text{H}_{20}\text{MoO}$ requires C, 65.6; H, 5.3%). ν_{MoO} (Nujol) 925 cm^{-1} . N.m.r.: ^1H (C_6D_6), δ 7.72–7.08 (m, 10 H, Ph), 5.43 (s, 5 H, C_5H_5), 4.27 (s, 2 H, CH_2), and 2.03 p.p.m. (s, 3 H, MoMe).

Crystal Structure Determinations and Structure Refinements.—Crystals of (2), (3), and (6) were grown at -30°C from diethyl ether, hexane, and toluene solution respectively. Details of the data collection procedures, structure solution, and refinements are given in Table 4. Data were collected for a unique volume of reciprocal space using graphite-monochromated X-radiation. The structures were refined by blocked-cascade full-matrix least squares to convergence at the residual indices listed in Table 4. All non-hydrogen atoms were assigned anisotropic vibrational parameters. All hydrogen atoms were located on difference electron density maps and those on C_β were allowed to refine without positional constraints, those on other carbon atoms were placed in idealised geometries with C–H 0.96 Å and isotropic vibrational parameters fixed at ca. 1.2 times that of the attached carbon atom. Final difference electron-density syntheses showed no features of chemical significance the largest features being within 1 Å of the metal atoms. In each case analysis of the variation of the sum of $w\Delta^2$ ($\Delta = |F_o| - |F_c|$) with respect to $|F_o|$ and $\sin\theta$ was satisfactory and was taken as an indication that the weighting scheme was satisfactory. The resultant positional parameters for all atoms freely refined are given in Tables 6, 7, and 8 for (2), (3), and (6) respectively. All atoms were assigned complex neutral-atom scattering factors taken from ref. 48. All calculations were carried out on a Nicolet R3m/E structure determination facility using programs of the SHELXTL package.⁴⁹

EHMO Calculations.—Hückel parameters for all calculations⁵⁰ were taken from ref. 51 and refs. therein. The calculations were made on the model molecules $[\text{Mo}(\eta^2\text{-HCCH})\{\text{P}(\text{OH})_3\}_2(\eta\text{-C}_5\text{H}_5)]^+$ and $[\text{Mo}(\eta^2\text{-CHCH}_2)\{\text{P}(\text{OH})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ using non-hydrogen atom geometries from the structures of $[\text{Mo}(\eta^2\text{-Bu}^t\text{C}_2\text{H})\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ [BF $_{4^-}$]⁴¹ and $[\text{Mo}(\eta^2\text{-C}(\text{SiMe}_3)\text{CH}_2)\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]$ ²⁶ with O–H distances = 0.96 Å, and C–H = 1.08 Å. For each molecule (and each orientation of the $\eta^2\text{-CHCH}_2$ ligand in the latter case) the molecular orbitals for the full molecule and its constituent fragments $[\text{Mo}\{\text{P}(\text{OMe})_3\}_2(\eta\text{-C}_5\text{H}_5)]^+$, CHCH_2^- , and CHCH were calculated.

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