Vinylidene Complexes of the Molybdenum Auxiliary $Mo(Ph_2PCH_2CH_2PPh_2)(C_7H_7)$. Structural and Spectroscopic Investigations on Vinylidene Ligand Orientation†

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The new vinylidene complexes $[Mo\{C{=}C(H)R\}(L\text{-}L)(\eta\text{-}C_7H_7)]^+$ [L–L = $Ph_2PCH_2CH_2PPh_2$(dppe), R = Bu^t, Bu^n or H; L–L = $Ph_2PCH_2PPh_2$ (dppm), R = Bu^t; L–L = $Me_2PCH_2CH_2PMe_2$ (dmpe), R = Bu^t] have been synthesised by reaction of an excess of alk-1-yne, $RC{\equiv}CH$, either with $[Mo(Me_2CO)(L\text{-}L)(\eta\text{-}C_7H_7)]^+$ (L–L = dppe or dmpe) {formed *in situ* from $[Mo(\eta^6\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]^+$ and dppe or dmpe in acetone} or with $[MoCl(L\text{-}L)(\eta\text{-}C_7H_7)]$ (L–L = dppe or dppm) in methanol in the presence of $[NH_4][PF_6]$. The formation of $[Mo\{C{=}C(H)Bu^t\}(dmpe)(\eta\text{-}C_7H_7)]^+$ is accompanied by conversion of the excess of alkyne into polymeric $Bu^tC{\equiv}CH$ with respective M_n and M_w values of 29×10^3 and 63×10^3 as determined by gel permeation chromatography. Deprotonation of $[Mo\{C{=}C(H)Bu^n\}(dppe)(\eta\text{-}C_7H_7)]^+$ with $KOBu^t$ yields the alkynyl $[Mo(C{\equiv}CBu^n)(dppe)(\eta\text{-}C_7H_7)]$. The disubstituted vinylidenes $[Mo\{C{=}C(Me)R\}(dppe)(\eta\text{-}C_7H_7)]^+$ (R = Bu^t or Bu^n) were obtained by C_β methylation of $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]$ with MeI. One-electron oxidation of the alkynyls $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]$ (R = Bu^n or Ph) with $[Fe(\eta\text{-}C_5H_5)_2]^+$ yields the 17-electron radicals $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$ (R = Bu^n or Ph) which undergo coupling at C_β to yield dimeric, divinylidene-bridged $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4R_2)]^{2+}$ (R = Bu^n or Ph). The crystal structures of $[Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)][BF_4]$ and $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4Ph_2)][PF_6]_2$, have been determined. In the former the vinylidene substituents lie approximately in the pseudo-mirror plane of the $Mo(dppe)(\eta\text{-}C_7H_7)$ moiety (a vertical orientation) with the phenyl substituent directed 'up' towards the cycloheptatrienyl ring. In the latter centrosymmetric dimer the vinylidene ligand is rotated by 19.1° away from an exact vertical orientation and the phenyl substituents are located 'down' into a pocket enclosed by two phenyl groups of the dppe ligand. Variable-temperature ^1H NMR investigations on $[Mo(C{=}CH_2)(dppe)(\eta\text{-}C_7H_7)]^+$ are consistent with a preferred vertical orientation of the vinylidene ligand in solution at low temperature and the barrier to vinylidene rotation has been estimated as 51.9 ± 1 kJ mol^{-1}. The ^1H and ^{31}P NMR solution spectra of $[Mo\{C{=}C(R')Bu^n\}(dppe)(\eta\text{-}C_7H_7)]^+$ (R′ = H or Me) are also consistent with a vertically orientated vinylidene ligand and reveal the existence of two isomeric forms of each complex which differ in the location of the *n*-butyl substituent in the 'up' or 'down' position.

Vinylidene, $:C{=}CH_2$, is the simplest unsaturated carbene and is tautomeric with ethyne. Although the free molecule $:C{=}CH_2$ has been studied, either in a matrix or by suitable trapping reactions, the lifetime of vinylidene is extremely short as a result of a rapid 1,2-hydrogen shift to give ethyne. As with many other reactive organic molecules it is possible to stabilise vinylidenes $:C{=}CRR'$ (R = R′ = H, aryl or alkyl) as ligands in transition-metal complexes, allowing their behaviour as intermediates to be modelled and investigated. Such complexes have attracted considerable interest in the last decade.[1,2] They have been shown to be effective catalysts for alkyne polymerisation[3] or condensation reactions,[4] and surface-bonded vinylidene complexes are postulated as intermediates in the Fischer–Tropsch process ('McCandlish mechanism').[5] Several different methods have been used for the preparation of mononuclear vinylidene complexes but two of the commonest are the addition of electrophiles to metal alkynyl complexes and from the reaction of alk-1-ynes with certain transition-metal complexes *via* a formal 1,2-hydrogen shift. The latter method has found application in systems which promote alkyne–vinylidene rearrangement[2] which, as we have shown previously, include the $Mo(dppe)(\eta\text{-}C_7H_7)$ (dppe = $Ph_2PCH_2CH_2PPh_2$) auxiliary.[6,7] Thus reaction of $[Mo(solv)(dppe)(\eta\text{-}C_7H_7)]^+$ (solv = NCMe or acetone) with $PhC{\equiv}CH$ yields the vinylidene complex $[Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)]^+$ which has also been obtained from the reaction of $[MoCl(dppe)(\eta\text{-}C_7H_7)]$ with $PhC{\equiv}CH$ in methanol in the presence of $[NH_4][PF_6]$. This vinylidene complex is readily deprotonated to give the alkynyl complex $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)]$ and $[Mo(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_7H_7)]$ has also been prepared following a similar reaction sequence.[7] In a preliminary communication[8] we showed that the alkynyl radical cations $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$ (R = Bu^n or Ph) undergo coupling at C_β of the alkynyl ligand to afford the divinylidene-bridged, dimeric products $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4R_2)]^{2+}$. We now describe a series of synthetic, structural and spectroscopic studies on the vinylidene complexes $[Mo\{C{=}C(R')R\}(L\text{-}L)(\eta\text{-}C_7H_7)]^+$ which extend our enquiries to a range of vinylidene substituents R, R′ and chelate phosphines, L–L. Both structural and solution NMR investigations are consistent with a preferred vertical orientation of the vinylidene ligand when coordinated to the $Mo(L\text{-}L)(\eta\text{-}C_7H_7)$ auxiliary; this contrasts with the analogous complexes $[M\{C{=}C(R')R\}(L\text{-}L)(cp)]^+$ (M = Fe or Ru, cp = $\eta\text{-}C_5H_5$) for which a preferred horizontal vinylidene orientation is well established.

Results and Discussion

Synthetic Studies.—The initial objective of the work was to extend the series of monosubstituted vinylidene complexes of

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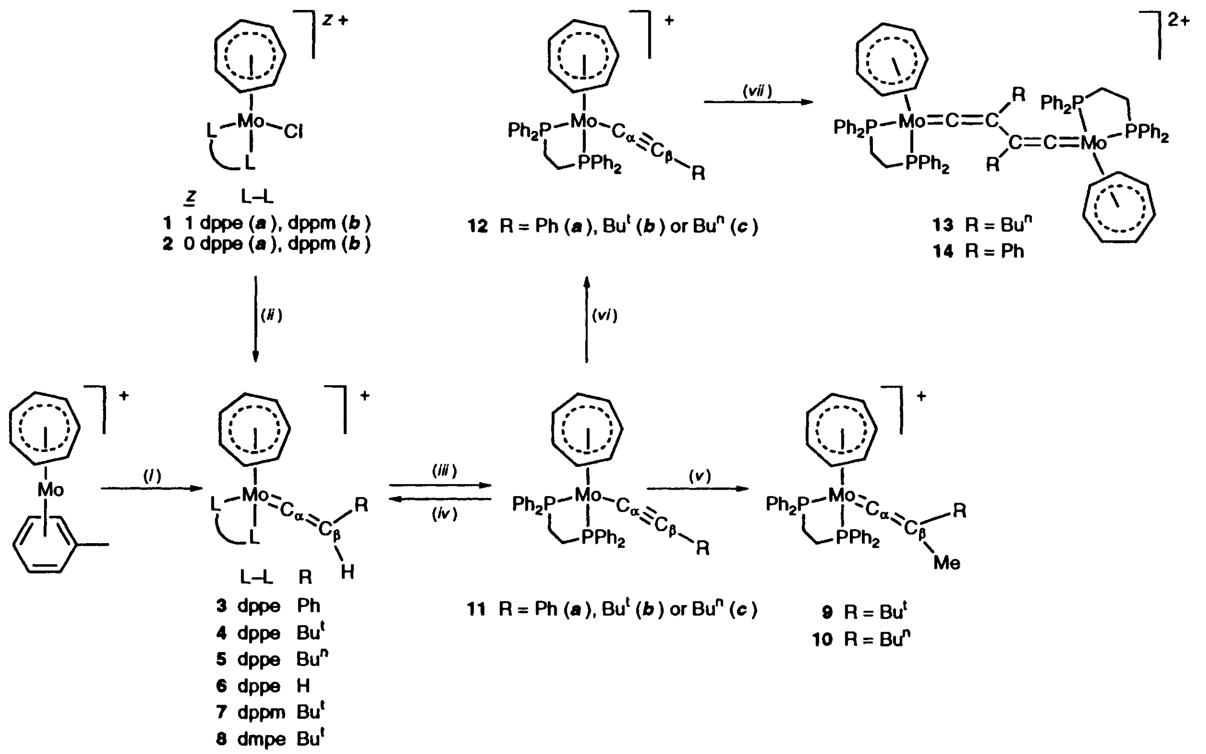
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.* 1995, Issue 1, pp. xxv–xxx



Scheme 1 (*i*) L–L = dppe, acetone, reflux 18 h, then RC≡CH (R = Ph, Bu^t, Bu^n, or SiMe$_3$), reflux 3–4 h; L–L = dmpe, acetone, reflux 20 min, stir at room temperature 90 min, then Bu^{t}C≡CH, reflux 4 h, (*ii*) L–L = dppe, *z* = 1. Zn, $[NH_4][PF_6]$, RC≡CH (R = Bu^n or SiMe$_3$), MeOH reflux; L–L = dppm, *z* = 0, $[NH_4][PF_6]$, Bu^{t}C≡CH, MeOH, reflux 3 h. (*iii*) L–L = dppe, R = Ph, Bu^t or Bu^n, KOBu^t in acetone, stir 1 h. (*iv*) R = Ph, Bu^t or Bu^n, $HBF_4 \cdot Et_2O$ in diethyl ether, 0 °C. (*v*) R = Bu^t or Bu^n, MeI in CH_2Cl_2, reflux 24 h. (*vi*) $[Fe(cp)_2][PF_6]$ in CH_2Cl_2. (*vii*) R = Bu^n, stir in CH_2Cl_2 15 min then precipitate with hexane; R = Ph, anhydrous thf, stir 24 h

the type $[Mo\{C=C(H)R\}(L-L)(\eta\text{-}C_7H_7)]^+$ by reaction of a range of terminal alkynes RC≡CH with sources of the $Mo(L-L)(\eta\text{-}C_7H_7)$ auxiliary. In addition to the known complex[7] $[Mo\{C=C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)]^+$ **3**, we now report the new derivatives $[Mo\{C=C(H)R\}(L-L)(\eta\text{-}C_7H_7)]^+$ [L–L = dppe, R = Bu^t **4**, Bu^n **5** or H **6**; L–L = dppm ($Ph_2PCH_2PPh_2$), R = Bu^t **7**; L–L = dmpe ($Me_2PCH_2CH_2PMe_2$), R = Bu^t **8**] (Scheme 1). The syntheses involve either (*i*) reaction of an excess of alk-1-yne with $[Mo(Me_2CO)(L-L)(\eta\text{-}C_7H_7)]^+$ (L–L = dppe or dmpe), formed *in situ* from reaction of the sandwich complex $[Mo(\eta^6\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]^+$ with acetone and dppe or dmpe or (*ii*) reaction of an excess of alk-1-yne with $[MoCl(L-L)(\eta\text{-}C_7H_7)]$ (L–L = dppe or dppm **2**) in methanol with $[NH_4][PF_6]$. {The 18-electron precursor complexes $[MoCl(L-L)(\eta\text{-}C_7H_7)]$ are conveniently prepared by *in situ* reduction of the more readily accessible 17-electron radicals $[MoCl(L-L)(\eta\text{-}C_7H_7)]^+$.} Details of the characterisation of complexes **4**–**8**, and of subsequently described, disubstituted vinylidenes $[Mo\{C=C(R')R\}(dppe)(\eta\text{-}C_7H_7)]^+$, **9**, **10**, **13** and **14** are given in the Experimental section (microanalytical and mass spectroscopic data) and in Tables 1–3 (^1H, ^{13}C, and ^{31}P NMR data respectively). A full consideration of the NMR data is reserved for discussion in relation to structural aspects of these complexes.

In general, analytically pure samples of product were not obtained directly by route (*i*). In the case of complex **4** (and **3**), deprotonation of the crude products to give the alkynyl complexes $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]$ (which were purified by column chromatography) and subsequent reprotonation with $HBF_4 \cdot Et_2O$ afforded pure samples of the required vinylidene complexes. Microanalytical samples of the Bu^n derivative **5** are more conveniently prepared by route (*ii*). The synthesis of the parent, unsubstituted complex $[Mo(C=CH_2)(dppe)(\eta\text{-}C_7H_7)]^+$ **6**, was achieved using the alkyne $Me_3SiC{\equiv}CH$ analogous to the preparation of the related complex $[Ru(C=CH_2)(dppe)(cp)]^+$;[9] attempted deprotonation–protonation did not however reform **6**. The dppm complex **7** was not accessible by route (*i*) but was prepared by route (*ii*) starting from $[MoCl(dppm)(\eta\text{-}C_7H_7)]$ **2b**, Bu^{t}C≡CH and $[NH_4][PF_6]$; it was accompanied by formation of the known[10] complex $[Mo_2(\eta\text{-}C_7H_7)_2(\mu\text{-}OMe)_3]^+$ which was separated from **7** by fractional crystallisation. The preparation of **2b**, the precursor to **7**, from $[Mo(\eta^6\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]^+$ also produced significant quantities of the 17-electron radical $[MoCl(dppm)(\eta\text{-}C_7H_7)]^+$ **1b**; this was reduced chemically with $[Co(cp)_2]$ to give **2b**. [The formal redox potential for the one-electron, reversible oxidation of **2b** in CH_2Cl_2 is 0.00 V *versus* a saturated calomel electrode (SCE).]

The preparation of $[Mo\{C=C(H)Bu^t\}(dmpe)(\eta\text{-}C_7H_7)]^+$ **8** from $[Mo(\eta^6\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)]^+$, dmpe and Bu^{t}C≡CH was accompanied by the precipitation of a white solid side product which was identified as polymeric Bu^{t}C≡CH by comparison of infrared and NMR spectra with reported data.[11–14] Examination of the methyl resonances in the ^{13}C NMR spectrum revealed that the polymer formed in the current work consists mainly of the *cis* form although small quantities of the *trans* form are also present. Analysis by gel permeation chromatography showed the weight distribution to consist of two reasonably narrow bands which overlapped; the number average molecular weight (M_n) was 29 × 10^3 and the weight average molecular weight (M_w) was 63 × 10^3. The synthesis of high-molecular-weight polymers from alkynes in good yields is difficult, in contrast to the production of vinyl polymers. Although some poly(alkynes) can be produced by Ziegler catalysts, recently some Group 5 and 6 transition metal (Nb, Ta, Mo, W) catalysts have been exploited for the production of high-molecular-weight poly(alkynes). These polymerisations with Group 5 and 6 catalysts are thought to involve carbene complexes as the active species, but catalytically active vinylidene complexes have been proposed, such as $[W\{C=C(H)R\}(CO)_5]$, in the polymerisation of RC≡CH (R = H or Ph) by $W(CO)_6$.[3,14] The

Table 1 Proton NMR spectral data for the vinylidene complexes $[\mathrm{Mo\{C{=}C(R')R\}\{R''_2P(CH_2)_nPR''_2\}(\eta\text{-}C_7H_7)}]^{+\,a}$

		$\mathrm{R''_2P(CH_2)_nPR''_2}$			
Complex	$\mathrm{C_7H_7}$	R″	$\mathrm{(CH_2)_n}$	R	R′
4	5.25 (td,[b] 3)	7.96–7.35	2.70–2.52	$\mathrm{Bu^t}$, 0.55 (s)	H, 4.37 [m, J(H–P) 12]
5 (20 °C)	5.25 (br)	7.92–7.35	2.71–2.45	$\mathrm{Bu^n}$, 0.80 (br), 0.95 (br), 1.40 (br)	H, 4.45 (br)
Major form (−40 °C)	5.19 (t, 3.1)	7.95–7.24	2.86–2.31	0.76 [t, J(H–H) 5.9, $\mathrm{C^4H_3}$], 0.83 (m, $\mathrm{C^2H_2}$ and $\mathrm{C^3H_2}$), 1.35 (m, $\mathrm{C^1H_2}$)	4.36 (m)
Minor form (−40 °C)	5.08 (t, 3.0)	7.95–7.24	2.86–2.31	−0.09 (m, $\mathrm{C^2H_2}$), 0.19 (m, $\mathrm{C^1H_2}$), 0.48 (m, $\mathrm{C^4H_3}$), 0.53 (m, $\mathrm{C^3H_2}$)	5.2[c]
6 (20 °C)	5.23 (m, 3.3)	7.91–7.15	2.61–2.33	H, 4.43 (br)	H, 4.43 (br)
(−40 °C)	5.20 (m, 3.3)	7.85–7.19	2.61–2.26	4.67 [m, |J(H–H)| 16.6, J(H–P) 15.2]	4.03 [m, |J(H–H)| 16.6, J(H–P) 15.5]
7[d]	5.74 (td,[b] 3.6)	8.08–7.27	5.01 (m),[e] 3.96 (dt)[f]	$\mathrm{Bu^t}$, 0.74 (s)	H, 4.86 [m, J(H–P) 11.9]
8	5.36 (td,[b] 3.7)	1.69 [d, J(H–P) 10.2], 1.58 [d, J(H–P) 9.1]	1.62 (m), 1.57 (m)	$\mathrm{Bu^t}$, 1.12 (s)	H, 5.48 [t, J(H–P) 12.4]
9	5.04 (t, 3.5)	8.00–7.35	3.00–2.79	$\mathrm{Bu^t}$, 0.86(s)	Me, −0.21 [t, J(H–P) 4.3]
10 Major form	5.07 (t, 3.4)	7.88–7.25	2.93–2.47	$\mathrm{Bu^n}$, 0.93[t, J(H–H) 7.4, $\mathrm{C^4H_3}$], 1.09 (m, $\mathrm{C^2H_2}$), 1.23 (m, $\mathrm{C^3H_2}$), 1.51 (m, $\mathrm{C^1H_2}$)	Me, −0.25 [t, J(H–P) 4.5]
Minor form	5.06 (t, 3.3)	7.88–7.25	2.93–2.47	−0.12(m, $\mathrm{C^2H_2}$), 0.13 (m, $\mathrm{C^1H_2}$), 0.42 [t, J(H–H) 6.0, $\mathrm{C^4H_3}$], 0.47 (m, $\mathrm{C^3H_2}$)	1.16 [t, J(H–P) 4.6]
13	4.80 (br)	7.91–7.36	3.12, 2.84	$\mathrm{Bu^n}$, −0.10 (br), 0.26 (br), 0.84 (br)	
14	4.37 (t, 3)	8.04–7.20	2.65, 1.77	Ph, 7.29(m, 1 H), 7.0 (m, 2 H), 5.43 (m, 2 H)	

[a] 300 MHz Spectra except for complexes **5** and **10** (500 MHz), recorded at ambient temperature unless stated otherwise, chemical shifts downfield from $\mathrm{SiMe_4}$; s = singlet, t = triplet, dt = doublet of triplets, td = triplet of doublets, m = multiplet, br = broad signal; coupling constants (J/Hz) in parentheses: in $\mathrm{CD_3CN}$ unless stated otherwise; see Scheme 3 for numbering scheme for $\mathrm{Bu^n}$ substituent. [b] Additional coupling of approximately 1 Hz to $\mathrm{C_7H_7}$ protons; double-irradiation experiments on complex **4** demonstrate coupling of $\mathrm{C_7H_7}$ protons to vinylidene H. [c] Resonance obscured by $\mathrm{C_7H_7}$ resonance of major isomer, not observed directly but located by ^{1}H–^{1}H COSY. [d] In $\mathrm{(CD_3)_2CO}$. [e] J(H–P) 8.5, \|J(H–H)\| 16.1 Hz. [f] J(H–P) 11.9, \|J(H–H)\| 16.1 Hz.

Table 2 Carbon-13 NMR spectral data for the vinylidene complexes $[\mathrm{Mo\{C{=}C(R')R\}(L\text{–}L)(\eta\text{-}C_7H_7)}]^{+\,a}$

Complex	$\mathrm{C_7H_7}$	$\mathrm{C_\alpha}$	$\mathrm{C_\beta}$	L–L	R	R′
4	91.3 (s)	368.0 (t, 31)	127.5 (t, 10)	136.6–128.0, 25.0 (vt), (J 41.0)	35.5 (t, J 6, *C*Me), 29.2 (s, C*Me*)	
5	92.4 (s)	369.7[b]	*c*	135.0–129.6, 27.0[d]	31.7, 26.6, 22.7, 14.0	
6	90.4 (s)	368.0 (t, 30.1)	97.1 (t, 9.0)	134.9–126.3, 24.3 (vt, J 41.6)		
7[e]	91.8 (s)	366.5 (t, 30.5)	*c*	135.6–128.8, 40.0 (t, J 26.1)	36.9 (t, J 6.4, *C*Me), 30.3 (s, C*Me*)	
8	91.0 (s)	365.0 (t, 31.5)	126.8 (t, 9.9)	27.5 (vt, J 41.6), 16.3 (m), 15.2 (m)	36.9 (t, J 6.4, *C*Me), 31.1 (s, C*Me*)	
9	92.2 (s)	373.9 (t, 28.5)	*c*	138.6–129.9, 28.0 (vt, J 38.8)	38.9 (t, J 4.9, *C*Me, 29.3 (s, C*Me*)	13.9 (t, J 6.2)
10 Major form	92.0 (s)	371.1 (t, 29.2)	123.2 (t, 8.7)	138.3–129.8, 28.2 (vt, J 40.9)	31.8 (t, $\mathrm{C^1}$, J 5.9), 29.7 (s, $\mathrm{C^2}$), 23.5 (s, $\mathrm{C^3}$), 14.4 (s, $\mathrm{C^4}$)	14.2[d]
Minor form	92.1 (s)	370.8 (t, 29.1)	123.5 (t, 8.7)	138.3–129.8, 28.7 (vt, J 42.0)	31.2 (t, $\mathrm{C^1}$, J 6.2), 28.0 (s, $\mathrm{C^2}$), 23.4 (s, $\mathrm{C^3}$), 13.8 (s, $\mathrm{C^4}$)	13.7[d]
13	91.7 (s)	375.9 (t, 25)	*c*	137.2–126.4, 26.6 (vt, J 37.8)	32.1, 29.9, 23.6, 13.6	
14	93.4 (s)	*f*	*c*	139.0–128.8, 28.3 (vt, J 35)	*c*	

[a] 75 MHz Spectra, chemical shifts downfield from $\mathrm{SiMe_4}$; vt = virtual triplet (AXX′), coupling constants (J/Hz) in parenthesis refer to J(C–P); in $\mathrm{CD_3CN}$ unless stated otherwise; see Scheme 3 for numbering scheme for $\mathrm{Bu^n}$ substituent. [b] Resonance too poorly resolved to determine J(P–C). [c] Signal in region of dppe Ph groups. [d] Signal partially obscured by resonance of $\mathrm{Bu^n}$ substituent. [e] In $\mathrm{CD_2Cl_2}$. [f] Signal not observed due to low solubility.

possibility of involvement of a vinylidene complex of the cycloheptatrienylmolybdenum auxiliary in alkyne-polymerisation catalysis is therefore under further investigation.

In addition to the syntheses of the monosubstituted vinylidene complexes $[\mathrm{Mo\{C{=}C(H)R\}(L\text{–}L)(\eta\text{-}C_7H_7)}]^+$ **4–8**, two routes to disubstituted derivatives $[\mathrm{Mo\{C{=}C(R')R\}(dppe)(\eta\text{-}C_7H_7)}]^+$ have been developed starting from the alkynyl complexes $[\mathrm{Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)}]$ (R = Ph, $\mathrm{Bu^t}$ or $\mathrm{Bu^n}$). The addition of electrophiles to $\mathrm{C_\beta}$ of alkynyl complexes is a well established reaction, exemplified by the protonation of $[\mathrm{Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)}]$ to form[7] the monosubstituted vinylidene complexes $[\mathrm{Mo\{C{=}C(H)R\}(dppe)(\eta\text{-}C_7H_7)}]^+$. In the chemistry of the $\mathrm{ML_2(cp)}$ auxiliary (M = Fe or Ru; L = phosphorus-donor ligand) the most convenient route to disubstituted vinylidene complexes involves the addition of suitable electrophiles to alkynyl complexes. For instance, reaction of $[\mathrm{Ru(C{\equiv}CMe)(PPh_3)_2(cp)}]$ with MeI produced $[\mathrm{Ru(C{=}CMe_2)(PPh_3)_2(cp)}]\mathrm{I}$.[15] Similar reaction of $[\mathrm{Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)}]$ (R = $\mathrm{Bu^t}$ or $\mathrm{Bu^n}$) with MeI in refluxing $\mathrm{CH_2Cl_2}$ yielded $[\mathrm{Mo\{C{=}C(Me)R\}(dppe)(\eta\text{-}C_7H_7)}]\mathrm{I}$ which were characterised as the $[\mathrm{PF_6}]^-$ salts **9** (R = $\mathrm{Bu^t}$) and **10** (R = $\mathrm{Bu^n}$) following anion exchange with $[\mathrm{NH_4}][\mathrm{PF_6}]$ in acetone.

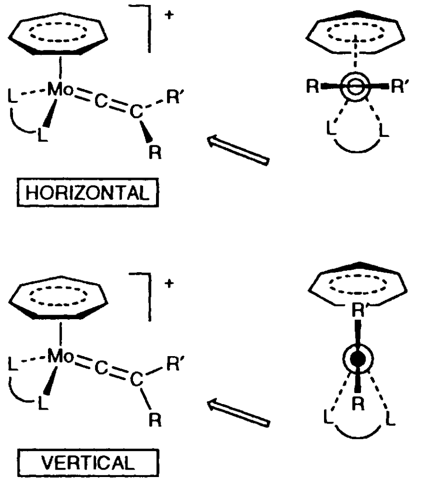
The second approach to disubstituted vinylidene complexes involves the redox-induced dimerisation of the alkynyls $[\mathrm{Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)}]$ (R = $\mathrm{Bu^n}$ or Ph) to give

Table 3 Phosphorus-31 NMR spectral data for vinylidene complexes[a]

	Low temperature data		Ambient/high-temperature data	
Complex	T/°C	δ	T/°C	δ
4[b]	−90	52.5	20	51.4
5[b–d]	−40	52.1 (major) 51.8 (minor)	20	51.7
6[e]	−40	53.8	20	53.4
7	−80	10.9	18	10.4
8	−80	24.1	20	22.9
9[b]	−80	49.1	40	49.5
10[e]	−30	57.9 (minor) 56.0 (major)	20	57.9 (minor) 55.9 (major)
			75	57.9 (minor) 56.0 (major)
13[b,c,f]	−90	48.7, 45.3	20	48.4
14[b]	−90	53.6	20	52.9[e]

[a] 122 MHz Spectra in $(CD_3)_2CO$ unless stated otherwise, chemical shifts downfield from H_3PO_4. [b] 32 MHz Spectrum. [c] In CD_2Cl_2. [d] Coalescence of ^{31}P resonances at approximately −10 °C. [e] In CD_3CN. [f] Coalescence of ^{31}P resonances at approximately −40 °C.

divinylidene-bridged $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4R_2)]^{2+}$ (R = Bu^n **13** or Ph **14**). As we have shown previously,[7] the alkynyl complexes $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]$ (R = Ph or Bu^t) undergo a reversible one-electron oxidation to yield the isolable 17-electron radical cations $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$. Similar behaviour is observed for $[Mo(C{\equiv}CBu^n)(dppe)(\eta\text{-}C_7H_7)]^+$ **11c**, which is formed by deprotonation of $[Mo\{C{=}C(H)Bu^n\}(dppe)(\eta\text{-}C_7H_7)]^+$ **5** with KOBu^t in acetone. Cyclic voltammetric investigations revealed that, over the scan rate range 50–500 mV s^{-1}, **11c** undergoes a diffusion-controlled, reversible, one-electron oxidation with $E° = -0.25$ V *versus* SCE in CH_2Cl_2. The ratio of peak currents was equal to unity over this scan rate range and the separations between the cathodic and anodic peaks were in good agreement with those measured for ferrocene under identical conditions. Chemical oxidation of a brown, CH_2Cl_2 solution of **11c** with $[Fe(cp)_2][PF_6]$ gave an orange solution which exhibited infrared [$\nu(C{\equiv}C)$ 2055 cm^{-1}] and ESR spectral data [$g_{av} = 1.995$, $A(^{31}P)$ 23 × 10^{-4} T, A(i) 4 × 10^{-4} T (due to coupling to protons of the cycloheptatrienyl ring or dppe phenyl protons)], consistent with the radical cation $[Mo(C{\equiv}CBu^n)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ **12c**. However, in contrast to $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$ (R = Ph or Bu^t), **12c** could not be isolated but rapidly reacted further to yield a deep purple, diamagnetic complex, subsequently identified as the dimer $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4Bu^n{}_2)][PF_6]_2$ **13**. The operation of a ligand-centred radical–radical coupling mechanism in the formation of **13** was demonstrated by investigations on the phenyl analogue $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4Ph_2)][PF_6]_2$ **14**, the dimeric, 2,3-diphenylbuta-1,3-diene-1,4-diylidene-bridged structure of which has been established by an X-ray crystallographic study (see below). When an isolated sample of the alkynyl radical $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ {prepared by chemical oxidation of $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)]$ with $[Fe(cp)_2][PF_6]$} was stirred in tetrahydrofuran (thf) for 24 h, the dimer **14** was formed as a deep red precipitate. By contrast, prolonged stirring of $[Mo(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ in thf results only in the formation of $[Mo\{C{=}C(H)Bu^t\}(dppe)(\eta\text{-}C_7H_7)][PF_6]$, presumably by hydrogen-radical abstraction from the solvent. It would appear that in this latter case dimerisation is sterically blocked. Some related divinylidene-bridged, dimeric compounds are known[16,17] including $[Fe_2(dppe)_2(\eta\text{-}C_5Me_5)_2(\mu\text{-}C_4H_2)]^{2+}$ which is accessible by an analogous redox-induced dimerisation of the alkynyl $[Fe(C{\equiv}CH)(dppe)(\eta\text{-}C_5Me_5)]$. However the chemistry of the cycloheptatrienylmolybdenum auxiliary remains unique in that the intermediate in the dimerisation process, the 17-electron radical $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$ (R = Bu^n or Ph), can be observed spectroscopically and, in the case R = Ph, isolated and crystallographically characterised.[18]



Scheme 2 Horizontal and vertical vinylidene ligand orientations in the complexes $[Mo\{C{=}C(R')R\}(L\text{–}L)(\eta\text{-}C_7H_7)]^+$

Crystal Structures of Compounds **3** *and* **14**.—A structural feature of recurrent interest in vinylidene complexes of the general half-sandwich type $[M\{C{=}C(R')R\}L_2(\eta\text{-}C_nH_n)]$ is the orientation of the vinylidene ligand substituents R, R′ with respect to the pseudo-mirror plane which bisects the $ML_2(\eta\text{-}C_nH_n)$ moiety. Taking the complexes $[Mo\{C{=}C(R')R\}(L\text{–}L)(\eta\text{-}C_7H_7)]^+$ as an example, Scheme 2 depicts the two extreme cases which are described as horizontal (where the vinylidene substituents are orthogonal to the pseudo-mirror plane) or vertical (where the substituents lie in this plane) although intermediate orientations may also be adopted. For mononuclear vinylidene complexes, of symmetrical moieties of the type $[M\{C{=}C(R')R\}L_2(cp)]^+$ (M = Fe or Ru; L = phosphorus-donor ligand), a preferred horizontal vinylidene orientation has been established by extensive crystallographic investigations.[19–25] Theoretical studies on these complexes conclude that, on electronic grounds only, the energetically most favourable orientation of the vinylidene ligand is in a horizontal conformation, with a vertical conformation being least favourable although the energy difference between the two extreme conformations on electronic grounds only is predicted to be small, namely *ca.* 15 kJ mol^{-1} for $[Fe(C{=}CH_2)(CO)_2(cp)]^+$ and less than 8.4 kJ mol^{-1} for $[Fe(C{=}CH_2)(PH_3)_2(cp)]^+$.[26,27] Steric effects must also be considered and molecular-modelling studies on the complex $[Ru\{C{=}C(H)Me\}(PMe_3)_2(cp)]^+$, taking into account electrostatic and van der Waals interactions, reveal that the preferred arrangement from steric factors is also virtually horizontal.[28] In complexes with small ancillary ligands, such as PMe_3, the electronic and steric factors reinforce each other, and a near-horizontal structure is observed, whilst in those complexes containing larger ligands such as dppe or PPh_3 the observed structure may be twisted away from a precise horizontal orientation depending on the extent of unfavourable steric interactions. Our preliminary communication on the crystal structure of $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4Ph_2)][PF_6]_2$ **14** revealed that the orientation of the divinylidene bridge approximates to a vertical arrangement.[8] This observation fostered additional structural investigations on vinylidene complexes of the cycloheptatrienylmolybdenum auxiliary with the objective of confirming that, in the solid state, the preferred

Table 4 Important bond lengths (Å) and angles (°) for complexes **3** and **14**

3				**14**			
Mo–P(1)	2.526(4)	P(2)–C(21)	1.81(1)	Mo–P(2)	2.528(1)	P(5)–C(39)	1.832(5)
Mo–P(2)	2.529(3)	P(2)–C(27)	1.83(1)	Mo–P(5)	2.550(2)	P(5)–C(4)	1.824(6)
Mo–C(1)	1.93(1)	P(2)–C(34)	1.83(1)	Mo–C(13)	1.951(5)	C(13)–C(14)	1.353(7)
Mo–C(35)	2.29(2)	C(1)–C(2)	1.31(2)	Mo–C(6)	2.289(7)	C(14)–C(15)	1.498(7)
Mo–C(36)	2.26(2)	C(2)–C(3)	1.47(2)	Mo–C(7)	2.274(7)	C(3)–C(4)	1.525(8)
Mo–C(37)	2.33(1)	C(33)–C(34)	1.51(2)	Mo–C(8)	2.368(6)	C(6)–C(7)	1.411(12)
Mo–C(38)	2.31(1)	C(35)–C(36)	1.39(4)	Mo–C(9)	2.381(6)	C(6)–C(12)	1.406(12)
Mo–C(39)	2.29(2)	C(35)–C(41)	1.41(4)	Mo–C(10)	2.290(6)	C(7)–C(8)	1.417(11)
Mo–C(40)	2.27(2)	C(36)–C(37)	1.36(3)	Mo–C(11)	2.326(7)	C(8)–C(9)	1.367(11)
Mo–C(41)	2.27(2)	C(37)–C(38)	1.38(2)	Mo–C(12)	2.307(6)	C(9)–C(10)	1.373(11)
P(1)–C(9)	1.84(1)	C(38)–C(39)	1.37(3)	P(2)–C(21)	1.852(5)	C(10)–C(11)	1.357(10)
P(1)–C(15)	1.83(1)	C(39)–C(40)	1.28(3)	P(2)–C(27)	1.821(5)	C(11)–C(12)	1.376(11)
P(1)–C(33)	1.82(1)	C(40)–C(41)	1.37(4)	P(2)–C(3)	1.838(6)	C(14)–C(14*)	1.472(12)
				P(5)–C(33)	1.829(6)		
Ct–Mo–C(1)†	135	C(21)–P(2)–C(27)	103.9(5)	Ct–Mo–C(13)†	131	C(33)–P(5)–C(4)	103.8(2)
P(1)–Mo–P(2)	80.1(1)	C(21)–P(2)–C(34)	102.7(6)	P(2)–Mo–P(5)	79.1(1)	C(39)–P(5)–C(4)	104.8(3)
P(1)–Mo–C(1)	77.2(4)	C(27)–P(2)–C(34)	106.2(6)	P(2)–Mo–C(13)	87.3(2)	Mo–C(13)–C(14)	177.9(4)
P(2)–Mo–C(1)	84.2(4)	Mo–C(1)–C(2)	173(1)	P(5)–Mo–C(13)	87.4(2)	C(13)–C(14)–C(15)	116.7(5)
Mo–P(1)–C(9)	120.1(4)	C(1)–C(2)–C(3)	125(1)	Mo–P(2)–C(21)	118.9(2)	C(7)–C(6)–C(12)	126.0(5)
Mo–P(1)–C(15)	117.5(5)	C(36)–C(35)–C(41)	125(3)	Mo–P(2)–C(27)	121.0(2)	C(6)–C(7)–C(8)	127.8(7)
Mo–P(1)–C(33)	105.9(4)	C(35)–C(36)–C(37)	131(2)	Mo–P(2)–C(3)	107.3(2)	C(7)–C(8)–C(9)	128.9(4)
C(9)–P(1)–C(15)	102.6(6)	C(36)–C(37)–C(38)	126(2)	C(21)–P(2)–C(27)	100.9(2)	C(8)–C(9)–C(10)	128.2(4)
C(9)–P(1)–C(33)	104.3(6)	C(37)–C(38)–C(39)	130(2)	C(21)–P(2)–C(3)	101.7(3)	C(9)–C(10)–C(11)	129.7(4)
C(15)–P(1)–C(33)	104.8(6)	C(38)–C(39)–C(40)	127(2)	C(27)–P(2)–C(3)	104.6(2)	C(10)–C(11)–C(12)	128.3(4)
Mo–P(2)–C(21)	117.4(4)	C(39)–C(40)–C(41)	134(3)	Mo–P(5)–C(33)	117.9(3)	C(11)–C(12)–C(6)	130.1(5)
Mo–P(2)–C(27)	118.8(4)	C(35)–C(41)–C(40)	126(3)	Mo–P(5)–C(39)	117.9(2)	C(13)–C(14)–C(14*)	123.8(9)
Mo–P(2)–C(34)	106.3(4)			Mo–P(5)–C(4)	108.2(2)	C(14*)–C(14)–C(15)	119.3(5)
				C(33)–P(5)–C(39)	102.8(3)		

† Ct represents the centroid of the cycloheptatrienyl ring.

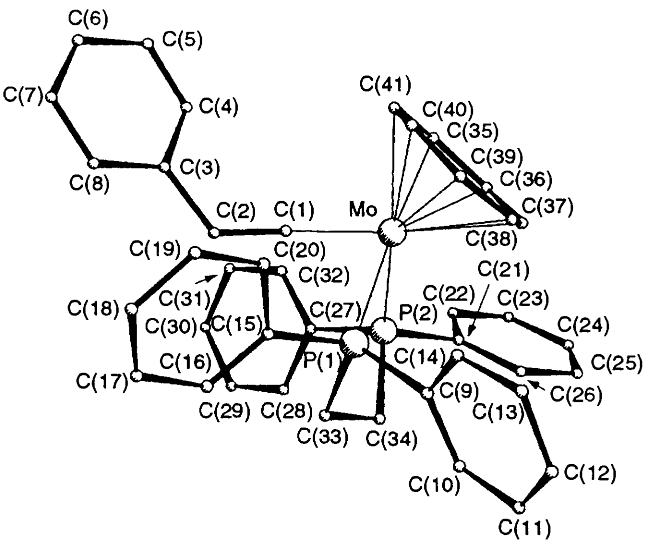


Fig. 1 Molecular structure of complex **3** showing the crystallographic numbering scheme (hydrogen atoms omitted for clarity)

vinylidene orientation in these complexes is vertical and the converse of that observed for $[M\{C{=}C(R')R\}L_2(cp)]^+$ (M = Fe or Ru).

The molecular configuration of $[Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)][BF_4]$ **3** (and the crystallographic numbering scheme adopted) is illustrated in Fig. 1 and important bond lengths and angles are presented in Table 4. The phenylvinylidene ligand in **3** exhibits typical structural parameters for a vinylidene ligand with an Mo–C(1) bond length of 1.93(1) Å {shorter than the corresponding Mo–C bond lengths in $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)]$ [2.138(5) Å] and $[Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)]^+$ [2.067(9) Å] which have formally single Mo–C bonds},[18] C(1)–C(2) 1.31(2) Å and a Mo–C(1)–C(2) bond angle of 173(1) °. However the salient structural feature of **3** is the unusual near-vertical orientation of the phenylvinylidene ligand; the dihedral angle between planes comprising Ct–Mo–C(1) and C(1)–C(2)–C(3) is 10.6° (Ct represents the cycloheptatrienyl ring centroid). The sterically more demanding phenyl substituent of the vinylidene ligand is located in the 'up' position pointing towards the cycloheptatrienyl ring and is directed away from the bulky dppe ligand, although there is a pocket between the phenyl rings of the dppe ligand into which vinylidene substituents could fit.

The crystal structure of the dimer $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4Ph_2)][PF_6]_2$ **14** and the atomic numbering scheme adopted are shown in Fig. 2; important bond lengths and angles are given in Table 4. This structure, first presented in a preliminary communication,[8] warrants further discussion here to accent comparisons with the molecular geometry of **3**. The molecule contains a centre of symmetry about the C(14)–C(14*) bond, in contrast to the structure of the related dimer $[Fe_2(dppe)_2(cp)_2(\mu\text{-}C_4Me_2)][BF_4]_2$.[16] In **14** the Mo–C(13) bond length is 1.951(5) Å consistent with a bond order of around two and the C(13)–C(14) bond length is 1.353(7) Å; both are similar to the corresponding distances in **3**. The bond angle Mo–C(13)–C(14) is 177.9(4)° indicating a more linear vinylidene than in **3**. However, the principal structural differences between the vinylidene units in **3** and **14** lie in the vinylidene ligand orientation and the arrangement of substituents at C_β. In **14** the dihedral angle between the planes comprising Ct–Mo(1)–C(13) and C(13)–C(14)–C(14*)–C(15) is 19.1°. Hence in the solid state the arrangement of the divinylidene bridge of **14** approximates to that of a vertical orientation but it is tilted further away from an exactly vertical orientation than found for **3**. By contrast in $[Fe_2(dppe)_2(cp)_2(\mu\text{-}C_4Me_2)][BF_4]_2$ the equivalent dihedral angles are 90 and 117.2 °; the latter corresponds to a tilting away from a preferred horizontal orientation. Thus it appears that, whilst the divinylidene-bridged dimers $[Fe_2(dppe)_2(cp)_2(\mu\text{-}$

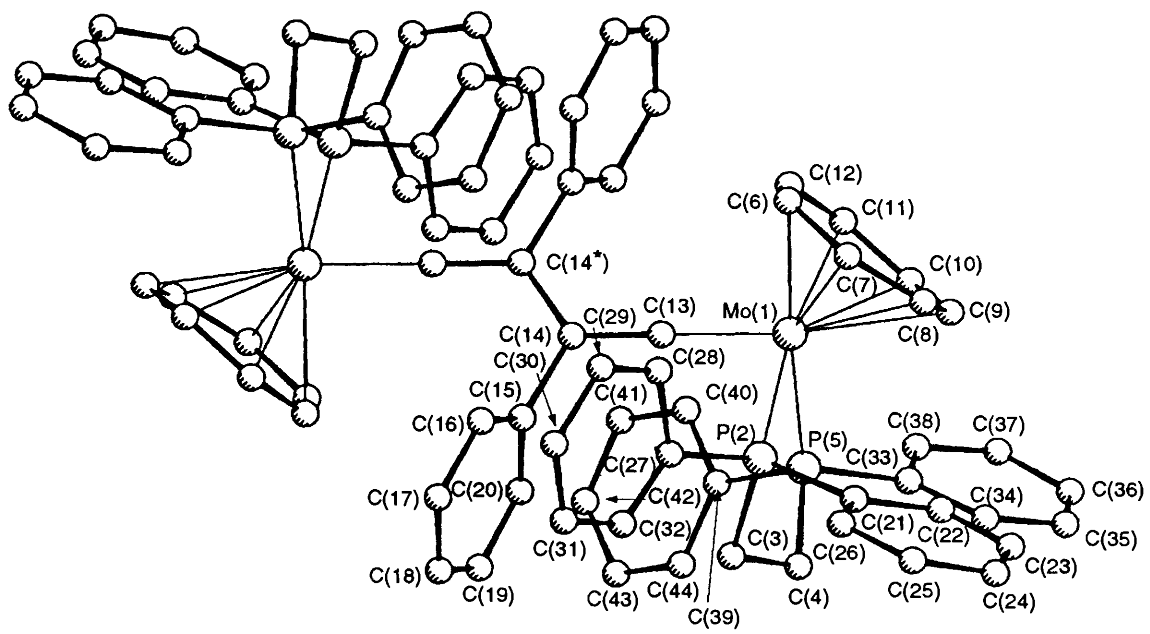
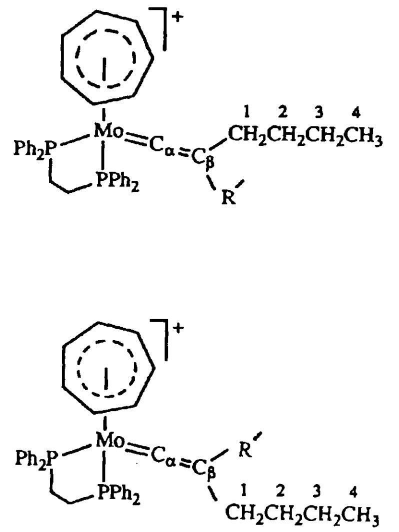


Fig. 2 Molecular structure of complex **14** showing the crystallographic numbering scheme (hydrogen atoms omitted for clarity)

$C_4Me_2)][BF_4]_2$ and $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4Ph_2)][PF_6]_2$ show some deviation of vinylidene orientation away from the preferred orientation of the corresponding mononuclear vinylidenes (possibly arising from steric effects), nevertheless the basic preference for a horizontal $ML_2(cp)$ (M = Fe or Ru) or vertical $MoL_2(\eta\text{-}C_7H_7)$ vinylidene orientation is retained. The second comparison of interest between **3** and **14** is in the arrangement of substituents at the C_β vinylidene carbon. In **3** the phenyl substituent points up towards the cycloheptatrienyl ligand and is directed away from the pocket enclosed by two phenyl groups of the dppe ligand. By contrast in **14** the vinylidene phenyl substituent is actually in this pocket, in the 'down' position. This difference may be rationalised on the basis that in each case the smaller vinylidene substituent is in the 'down' position; for **14** the second vinylidene substituent is effectively the other half of the dimer. These differing spatial orientations of the vinylidene phenyl substituents may be responsible for the large difference in angles at C_β [compare C(1)–C(2)–C(3) 125(1)° in **3** and C(13)–C(14)–C(15) 116.7(5)° in **14**].

Spectroscopic Investigations on Vinylidene Orientation.—Although there is a formal M=C double bond in vinylidene complexes, in solution rotation about this bond on the NMR time-scale has been observed for some cyclopentadienyliron and ruthenium vinylidene complexes. In favourable cases, at low temperature, this rotation can be frozen out and preferred carbene and vinylidene orientations have been successfully probed by ^1H and ^{31}P NMR studies.[19,29–32] The results of these spectroscopic studies are consistent with structural data from the solid state and, moreover, with suitable complexes, NMR data permit calculation of the activation energy to vinylidene rotation. In the current work variable-temperature NMR studies were carried out on vinylidene derivatives of cycloheptatrienylmolybdenum complexes to probe activation energies to vinylidene rotation and to establish that a vertical vinylidene orientation is also that preferred at low temperature in solution. The ^1H and ^{31}P NMR spectra of each of the mononuclear *tert*-butylvinylidene derivatives (**4**, **7**–**9**) were essentially temperature-independent and these data, taken apart from other studies, do not permit any structural inferences to be drawn. However NMR data for the unsubstituted vinylidene complex $[Mo(C{=}CH_2)(dppe)(\eta\text{-}C_7H_7)]^+$ **6** and the *n*-butyl-substituted derivatives, $[Mo\{C{=}C(H)Bu^n\}(dppe)(\eta\text{-}C_7H_7)]^+$ **5** and $[Mo\{C{=}C(Me)Bu^n\}(dppe)(\eta\text{-}C_7H_7)]^+$ **10**, proved to be more informative.

The ^1H NMR spectrum of the unsubstituted vinylidene complex $[Mo(C{=}CH_2)(dppe)(\eta\text{-}C_7H_7)][PF_6]$ **6** was temperature dependent. At room temperature it showed a single resonance for the two vinylidene protons but on cooling this broadened and then split into two resonances and a coalescence temperature of -5 ± 3 °C was determined in CD_3CN. These observations are consistent with rotation about the Mo=C bond on the NMR time-scale at 20 °C which at lower temperatures is frozen out. At low temperatures the two vinylidene protons are inequivalent, which is the case with the protons in any orientation except horizontal. A ^1H–^1H double-irradiation experiment, carried out at -40 °C, confirmed that the two vinylidene protons were coupled to each other ($|J|$ = 16.6 Hz). Removal of vinylidene–vinylidene proton coupling simplified each separate vinylidene proton signal to a triplet, this coupling originating from heteronuclear J(P–H) coupling to the phosphorus atoms of the dppe ligand. This is consistent with a very near-vertical orientation of the vinylidene ligand since a triplet resonance indicates that each vinylidene proton has very similar couplings to each phosphorus atom. Variable-temperature ^{31}P NMR spectroscopy shows a singlet resonance at both 20 and -40 °C, indicating that at temperatures at which vinylidene rotation does not occur on the NMR time-scale the two phosphorus atoms are chemically equivalent. For the phosphorus atoms to be chemically equivalent the vinylidene ligand must have a vertical or a horizontal conformation, but not any intermediate position. Consequently the ^1H and ^{31}P NMR spectra, taken together, indicate that at low temperature the vinylidene ligand of **6** adopts a preferred vertical orientation consistent with solid-state structural studies, as this is the only orientation which can rationalise the simultaneous inequivalence of the vinylidene protons but equivalence of the dppe phosphorus atoms. By an equivalent method to that employed for the vertically orientated carbene ligand in the complexes $[M(CH_2)(dppe)(cp)]^+$ (M = Fe[31] or Ru[32]), the variable-temperature ^1H NMR spectra of **6** and determination of the coalescence temperature for the vinylidene protons as -5 ± 3 °C permit estimation of the energy barrier to rotation about the Mo=C bond in **6** as $\Delta G^\ddagger = 51.9 \pm 1$ kJ mol^{-1} using the Eyring equation. This barrier is significantly higher than corresponding barriers in the related complexes $[M\{C{=}C(R')R\}(L\text{-}L)(cp)]^+$ [M = Fe, L–L = dppm, R' = H,



Scheme 3 Isomers of $[Mo\{C{=}C(R')Bu^n\}(dppe)(\eta\text{-}C_7H_7)]^+$ with a vertically orientated vinylidene ligand

R = CO_2Me, 31.8; R = Bu^t, 30.1; R = Ph, 41.0; R′ = Me, R = Ph, 35.1;[19] L–L = dppe, R′ = H, R = Ph; M = Fe, 39.3;[30] M = Ru, 38.1 kJ mol^{-1}[29]] and suggests that the $Mo(dppe)(\eta\text{-}C_7H_7)$ auxiliary exhibits an unusually high preference for a vertical vinylidene orientation.

Further evidence for the conclusions on the preferred solution orientation of the vinylidene ligand drawn from complex **6** is provided by NMR investigations on the *n*-butyl derivatives **5** and **10** in which the C_β vinylidene substituents are not equivalent. If a vertical vinylidene orientation is adopted, following cessation of vinylidene rotation on the NMR time-scale, then two isomeric forms (or rotamers) of each of these complexes, differing in the location of the Bu^n substituent in either the 'up' or 'down' position (directed respectively towards the cycloheptatrienyl ring or into the pocket enclosed by two dppe phenyl groups), might be expected (Scheme 3). The NMR data for **5** and **10** support this prediction.

The NMR spectra of the monosubstituted complex $[Mo\{C{=}C(H)Bu^n\}(dppe)(\eta\text{-}C_7H_7)][BF_4]$ **5** were also temperature dependent. In the ^1H NMR spectrum, at room temperature, broad resonances were observed which on cooling split and became well resolved at −20 °C. The low-temperature spectrum was consistent with the presence of two vertical vinylidene rotamers which coexist in the ratio 2.7:1. Two discrete sets of resonances were observed and assigned for each of the cycloheptatrienyl ring, the Bu^n group and the vinylidene hydrogen by double-irradiation experiments and a ^1H–^1H correlation spectroscopy (COSY) experiment. (The signal for the vinylidene H of the minor rotamer was not visible in the spectrum but was located by the COSY experiment under the signal for the cycloheptatrienyl ring protons of the major rotamer.) The ^{31}P NMR spectrum of **5** contained a single resonance at room temperature which on cooling split into two singlet signals; the lack of ^{31}P–^{31}P coupling suggested the two rotamers each to have a vertical arrangement. The NMR spectra of the disubstituted complex $[Mo\{C{=}C(Me)Bu^n\}(dppe)(\eta\text{-}C_7H_7)][PF_6]$ **10** were temperature independent over the range −40 to 75 °C. However they clearly indicate the presence of two isomeric forms which coexist in the ratio 2.4:1. The ^1H and ^{13}C NMR spectra, which were assigned with the aid of double-irradiation experiments, a ^1H–^1H COSY spectrum and a ^1H–^{13}C heteronuclear correlation (HETCOR) spectrum (the ^1H NMR spectrum was recorded at 500 MHz as at lower frequencies, such as 300 MHz, signals were overlapping) exhibited two distinct, fully assigned sets of signals for each of the cycloheptatrienyl ring, vinylidene C_α and C_β, the Bu^n and the Me groups. The ^{31}P NMR spectrum consisted of two singlet resonances, also in the ratio 2.4:1. As no ^{31}P–^{31}P coupling was observed in the ^{31}P NMR spectrum, the spectra are consistent with the presence of two rotamers of **10**, both having a vertically orientated vinylidene ligand, but differing in the orientation of the vinylidene Me and Bu^n substituents.

From the crystal structure of $[Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)][BF_4]$ **3** it may be envisaged that the major rotamer of **10** will be that with the larger substituent, the Bu^n group, in the 'up' position, directed towards the cycloheptatrienyl ring. As an attempt to confirm this, a series of NOE (nuclear Overhauser effect) difference spectra were run to investigate the position in space of the Me and CH_2 groups attached to C_β of each rotamer, relative to the cycloheptatrienyl ring. The results were consistent with the predicted structural assignment of the major rotamer but the interpretation was complicated by slow exchange between the two rotamers, observable on the much longer time-scale of the NOE experiment in relation to standard ^1H and ^{31}P NMR experiments. The methyl substituent protons of the major isomer of **10** are strongly shielded (δ −0.25) with respect to those of the minor isomer (δ 1.16), but *vice versa* for the Bu^n protons. A similar effect was noticed with complex **5** (vinylidene H: major isomer, δ 4.36; minor isomer, δ 5.2) suggesting that in both **5** and **10** the more sterically demanding Bu^n group is in the same position for the major isomeric form, most probably directed towards the cycloheptatrienyl ring in the 'up' position. A further inference is that the vinylidene substituent located in the 'down' position, between the dppe phenyl groups, experiences significant shielding of ^1H NMR resonances.

It is more difficult to draw structural conclusions from the temperature-independent NMR spectra of the mononuclear vinylidene complexes **4** and **7**–**9**. The chief difficulty lies in distinguishing between the possibilities of a single vertical isomer of a static (on the NMR time-scale) vinylidene ligand and the alternative of rapid vinylidene rotation, even at −80 °C, although, in view of the high barrier to vinylidene rotation observed for **6**, the latter seems unlikely. In the case of $[Mo\{C{=}C(Me)Bu^t\}(dppe)(\eta\text{-}C_7H_7)]^+$ **9** the observation of only one resonance for the vinylidene methyl substituent, with a high field shift (δ −0.21) closely comparable with that observed for the major isomer of **10**, suggests that **9** exists in solution as one form, most probably with the Bu^t substituent located in the 'up' position. Presumably, steric constraints associated with the Bu^t substituent preclude observation of a second isomer in which Bu^t would be in the 'down' position; such an arrangement appears to be restricted to the minor isomers of **5** and **10** which contain the less sterically demanding Bu^n substituent.

Although the NMR spectra of the ligand-bridged dimers $[Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4R_2)]^{2+}$ (R = Bu^n **13** or Ph **14**) cannot definitively establish vinylidene orientation, some points of interest arise. First, those of **14** are temperature independent but those of the *n*-butyl derivative present more complex behaviour. The room-temperature ^1H NMR spectrum exhibits broad signals for the cycloheptatrienyl and Bu^n resonances which show little change even on cooling to −80 °C. However the ^{31}P NMR spectrum of **13**, which is a singlet at room temperature, resolves into two singlet resonances of approximately equal intensity on cooling to −70 °C. Secondly, in the ^1H NMR spectrum of **13** the chemical shifts of the Bu^n resonances exhibit strong shielding, similar to those of the minor isomers of **5** and **10**; in **14** also, two protons of the vinylidene phenyl substituent display a remarkably high-field resonance at δ 5.43. These latter observations might be explained by location of the vinylidene Bu^n or Ph substituents in the 'down' position between the phenyl groups of the dppe ligand and in accord with the solid-state structure of **14**.

Conclusion

Vinylidene complexes of the type $[\mathrm{Mo\{C{=}C(R')R\}(L{-}L)(\eta\text{-}C_7H_7)}]^+$ are accessible for a range of vinylidene substituents, R, R′, and chelate phosphines L–L. X-Ray structural studies on $[\mathrm{Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)}][\mathrm{BF_4}]$ and $[\mathrm{Mo_2(dppe)_2(\eta\text{-}C_7H_7)_2(\mu\text{-}C_4Ph_2)}][\mathrm{PF_6}]_2$ reveal an essentially vertical orientation of the vinylidene ligand and low-temperature NMR studies suggest that this is also the preferred orientation in solution. The barrier to vinylidene rotation, determined for $[\mathrm{Mo(C{=}CH_2)(dppe)(\eta\text{-}C_7H_7)}]^+$, is significantly higher than that of the related vinylidenes $[\mathrm{M\{C{=}C(R')R\}(L{-}L)(cp)}]^+$ (M = Fe or Ru).

Experimental

General Procedures.—The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, distilled and deoxygenated before use. The complexes $[\mathrm{MoCl(dppe)(\eta\text{-}C_7H_7)}]$, $[\mathrm{MoCl(dppe)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$,[33] $[\mathrm{Mo(\eta^6\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$,[34] $[\mathrm{Mo\{C{=}C(H)Ph\}(dppe)(\eta\text{-}C_7H_7)}][\mathrm{BF_4}]$, $[\mathrm{Mo(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_7H_7)}]$, $[\mathrm{Mo(C{\equiv}CPh)(dppe)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$[7] and $[\mathrm{Fe(cp)_2}][\mathrm{PF_6}]$[35] were prepared by published procedures. Column chromatography was carried out on alumina (Brockmann activity II) and silica (230–400 mesh) supplied by Merck. The chemicals $[\mathrm{NH_4}][\mathrm{PF_6}]$, LiCl, dppe, dppm, dmpe, $\mathrm{HBF_4{\cdot}Et_2O}$, $\mathrm{PhC{\equiv}CH}$, $\mathrm{Bu^nC{\equiv}CH}$, $\mathrm{Me_3SiC{\equiv}CH}$, MeI and $[\mathrm{Co(cp)_2}]$ were supplied by Aldrich Chemical Co.; $\mathrm{Bu^tC{\equiv}CH}$ was obtained from Lancaster Synthesis and zinc powder from Fisons.

The 300 MHz ^{1}H and 75 MHz ^{13}C NMR spectra were recorded on Bruker AC 300 E or Varian Associates XL 300 spectrometers, the 500 MHz ^{1}H NMR spectra on a Varian Associates Unity 500 spectrometer, ^{31}P NMR spectra (^{1}H decoupled) on Varian Associates XL 300 (122 MHz) or Bruker WP80 (32.4 MHz) instruments, infrared spectra on a Perkin-Elmer FT 1710 spectrometer and X-band ESR spectra on a Varian Associates E4 spectrometer. The FAB mass spectra were recorded on a Kratos Concept 1S instrument; values are quoted for ^{98}Mo. The gel permeation chromatogram was obtained on a Waters 410 GPC apparatus with polystyrene standards. Cyclic voltammetric studies were carried out as described previously,[7] at a carbon working electrode using 0.2 mol dm^{-3} $[\mathrm{NBu^n{}_4}][\mathrm{BF_4}]$ as supporting electrolyte. All potentials are referenced to a saturated calomel electrode and, under these conditions, $E°$ for the ferrocene–ferrocenium couple is 0.56 V in $\mathrm{CH_2Cl_2}$. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Preparations.—$[\mathrm{MoCl(dppm)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$ **1b**. A green solution of $[\mathrm{Mo(\eta^6\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$ (0.988 g, 2.33 mmol) in AR acetone (50 cm^3) was refluxed for 20 min producing a red solution which was allowed to cool. The diphosphine dppm (0.895 g, 2.33 mmol) was added producing an immediate change to green and the reaction mixture was refluxed for 17 h. The solution was allowed to cool and a large excess of LiCl (2.0 g, 47.2 mmol) added; the solution turned yellow-green and was stirred for 4 h, before being reduced to dryness. The residue was dissolved in $\mathrm{CH_2Cl_2}$, filtered and the solvent removed *in vacuo*. Recrystallisation of the residue from $\mathrm{CH_2Cl_2}$–diethyl ether produced a mixture of $[\mathrm{MoCl(dppm)(\eta\text{-}C_7H_7)}]$ **2b**, together with **1b**. Complex **2b** was extracted from the mixture with toluene (1 × 60 cm^3, 4 × 20 cm^3) and the remaining residue recrystallised from $\mathrm{CH_2Cl_2}$–diethyl ether to give **1b** as a yellow solid; yield 0.52 g (30%) (Found: C, 51.4, H, 3.8. Calc. for $\mathrm{C_{32}H_{29}ClF_6MoP_3}$: C, 51.1; H, 3.9%). Mass spectrum (*m*/*z*): 608 (parent ion, M^+) and 573 ($[M - \mathrm{Cl}]^+$). Cyclic voltammetry: $E°$ ($\mathrm{CH_2Cl_2}$) = 0.00 V. ESR ($\mathrm{CH_2Cl_2}$): $g_{\mathrm{av}} = 1.988$, $A(^{31}\mathrm{P}) = 23 \times 10^{-4}$ T. The toluene extracts were combined, evaporated to dryness, and recrystallised from diethyl ether–hexane to give an impure sample of **2b**; yield 0.30 g.

$[\mathrm{MoCl(dppm)(\eta\text{-}C_7H_7)}]$ **2b**. To a stirred suspension of complex **1b** (0.91 g, 1.21 mmol) in toluene (50 cm^3) was added $[\mathrm{Co(cp)_2}]$ (0.27 g, 1.43 mmol). After 2 h the reaction mixture was filtered, evaporated to dryness and the residue recrystallised from toluene–hexane to give **2b** as a green solid; yield 0.52 g (71%) (Found: C, 63.7, H, 5.2. Calc. for $\mathrm{C_{32}H_{29}ClMoP_2}$: C, 63.3; H, 4.8%). Mass spectrum (*m*/*z*): 608 (M^+) and 573 ($[M - \mathrm{Cl}]^+$). Cyclic voltammetry: $E°$ ($\mathrm{CH_2Cl_2}$) = 0.00 V. NMR ($\mathrm{C_6D_6}$): ^{1}H, δ 7.75–7.08 (m, 20 H, Ph), 5.18 [t, 7 H, $\mathrm{C_7H_7}$, J(H–P) 2.0], 4.24 [dt, 1 H, PCHP, J(H–P) 9.2, $|J(\mathrm{H{-}H})|$ 14.4] and 3.69 [dt, 1 H, PCHP, J(H–P) 11.5, $|J(\mathrm{H{-}H})|$ 14.4]; ^{13}C, δ 138.3 [d, Ph, J(C–P) 27.5], 134.4–127.7 (Ph), 87.4 (s, $\mathrm{C_7H_7}$), and 43.3 [t, $\mathrm{CH_2}$, J(C–P) 17.9 Hz].

$[\mathrm{Mo\{C{=}C(H)Bu^t\}(dppe)(\eta\text{-}C_7H_7)}][\mathrm{BF_4}]$ **4**. A cooled (0 °C) solution of $[\mathrm{Mo(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_7H_7)}]$ (0.34 g, 0.51 mmol) in diethyl ether (50 cm^3) was treated with $\mathrm{HBF_4{\cdot}Et_2O}$ (0.42 g, 2.59 mmol) affording an immediate orange precipitate. Removal of the solvent and washing with diethyl ether to remove $\mathrm{HBF_4{\cdot}Et_2O}$, followed by three recrystallisations from acetone–diethyl ether gave complex **4** as a bright orange solid; yield 0.11 g (28%) (Found: C, 62.5, H, 5.6. Calc. for $\mathrm{C_{39}H_{41}BF_4MoP_2}$: C, 62.1; H, 5.4%). Mass spectrum (*m*/*z*): 669 (M^+) and 587 ($[M - \mathrm{C_2HBu^t}]^+$).

$[\mathrm{Mo\{C{=}C(H)Bu^n\}(dppe)(\eta\text{-}C_7H_7)}][\mathrm{BF_4}]$ **5**. *Method* (*a*). Complex **5** was obtained by reaction of $[\mathrm{Mo(C{\equiv}CBu^n)(dppe)(\eta\text{-}C_7H_7)}]$ **11c**, (0.17 g, 0.26 mmol) with $\mathrm{HBF_4{\cdot}Et_2O}$ in an identical procedure to the preparation of **4** from $[\mathrm{Mo(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_7H_7)}]$; yield 47 mg (24%) (Found: C, 62.2, H, 5.5. Calc. for $\mathrm{C_{39}H_{41}BF_4MoP_2}$: C, 62.1; H, 5.4%). Mass spectrum (*m*/*z*): 669 (M^+) and 587 ($[M - \mathrm{C_2HBu^n}]^+$).

Method (*b*). To a stirred solution of $[\mathrm{MoCl(dppe)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$ (0.70 g, 0.92 mmol) in MeOH (50 cm^3) were added $[\mathrm{NH_4}][\mathrm{PF_6}]$ (0.30 g, 1.84 mmol) and zinc powder (0.12 g, 1.84 mmol) and stirred with gentle heating for 5 min to afford a green solution. The alkyne $\mathrm{Bu^nC{\equiv}CH}$ (0.6 cm^3) was then added and the solution refluxed for 20 min and evaporated to dryness. The residue was recrystallised from $\mathrm{CH_2Cl_2}$–diethyl ether to yield $[\mathrm{Mo\{C{=}C(H)Bu^n\}(dppe)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$ as an orange solid; yield 0.12 g (16%) (Found: C, 57.3; H, 5.0. Calc. for $\mathrm{C_{39}H_{41}F_6MoP_3}$: C, 57.6; H, 5.1%).

$[\mathrm{Mo(C{=}CH_2)(dppe)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$ **6**. *Method* (*a*). A mixture of $[\mathrm{MoCl(dppe)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$ (0.95 g, 1.24 mmol), zinc powder (0.17 g, 2.60 mmol) and $[\mathrm{NH_4}][\mathrm{PF_6}]$ (0.43 g, 2.64 mmol) was refluxed in methanol for 30 min, cooled, $\mathrm{Me_3SiC{\equiv}CH}$ (0.60 g, 6.12 mmol) added and reflux recommenced. After 3 h the reaction mixture was reduced to dryness *in vacuo*. The residue was washed with diethyl ether (2 × 30 cm^3), then recrystallised from $\mathrm{CH_2Cl_2}$–diethyl ether and acetone–diethyl ether, each time separating the initial oily residues, and complex **6** was isolated as an orange-yellow solid; yield 0.16 g (17%) (Found: C, 55.0, H, 4.4. Calc. for $\mathrm{C_{35}H_{33}F_6MoP_3}$: C, 55.6; H, 4.4%). Mass spectrum (*m*/*z*): 613 (M^+) and 587 ($[M - \mathrm{C_2H_2}]^+$).

Method (*b*). A green solution of $[\mathrm{Mo(\eta^6\text{-}C_6H_5Me)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$ (0.515 g, 1.21 mmol) in AR acetone (50 cm^3) was refluxed for 20 min turning red. The solution was cooled and dppe (0.484 g, 1.21 mmol) added, the solution immediately turning green, and reflux recommenced for 18 h. After cooling, $\mathrm{Me_3SiC{\equiv}CH}$ (0.62 g, 6.33 mmol) was added and the solution refluxed for 3 h, and the then orange solution evaporated to dryness. The residue was dissolved in $\mathrm{CH_2Cl_2}$ (10 cm^3) and dropped into stirring diethyl ether (150 cm^3) precipitating **6** as a yellow solid; yield 0.67 g (73%).

$[\mathrm{Mo\{C{=}C(H)Bu^t\}(dppm)(\eta\text{-}C_7H_7)}][\mathrm{PF_6}]$ **7**. A mixture of $[\mathrm{MoCl(dppm)(\eta\text{-}C_7H_7)}]$ **2b** (0.29 g, 0.48 mmol), $[\mathrm{NH_4}][\mathrm{PF_6}]$ (0.17 g, 1.04 mmol) and $\mathrm{Bu^tC{\equiv}CH}$ (0.20 g, 2.44 mmol) was refluxed in methanol (60 cm^3) for 3 h and then reduced to dryness. Two products were separated on recrystallisation from $\mathrm{CH_2Cl_2}$–diethyl ether, the first, green precipitate was $[\mathrm{Mo_2(\eta\text{-}C_7H_7)_2(\mu\text{-}OMe)_3}]^+$ which was followed by an orange

Table 5 Crystal and data collection parameters for complexes **3** and **14**[a]

	3	**14**
Formula	$C_{41}H_{37}BF_4MoP_2$	$C_{82}H_{72}F_{12}Mo_2P_6$
M	774.43	1663.2
Crystal colour, habit	Orange, plate	Dark red, tabular
a/Å	18.689(2)	16.399(4)
b/Å	10.897(2)	12.365(4)
c/Å	18.200(2)	20.577(6)
β/°	106.157(8)	122.21(2)
U/Å^3	3560(2)	3530.3
T/°C	22	21
Z	4	2
D/g cm^{-3}	1.445	1.56
F(000)	1584	1692
μ/cm^{-1}	43.47 (Cu-Kα)	6.1 (Mo-Kα)
Crystal dimensions/mm	0.02 × 0.15 × 0.15	0.06 × 0.11 × 0.27
Diffractometer	Rigaku AFC5R	Nonius CAD4
Radiation (λ/Å)	Cu-Kα (1.541 78)	Mo-Kα (0.710 69)
2θ range/°	6.0–120.2	1.0–50.0
Scan width/°	(1.15 + 0.30 tan θ)	(0.5 + 0.35 tan θ)
Total data	5836	6275
Unique data	5638	6275
'Observed' data [$I > 3\sigma(I)$], N_o	2456	3759
Least-squares variables, N_v	442	461
R	0.057	0.048
R'	0.073	0.045
Goodness of fit, S	2.12	1.054
Difference map features/e Å^{-3}	+0.44, −0.48	+0.4, −0.4

[a] Details in common: monoclinic, space group $P2_1/c$; ω–2θ scans; $R = \Sigma|\Delta|/\Sigma|F_o|$; $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$; $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$; $\Delta = F_o - F_c$.

Table 6 Atomic coordinates for complex **3**

Atom	x	y	z	Atom	x	y	z
Mo	0.203 72(6)	0.114 1(1)	0.112 32(6)	C(20)	0.342 5(8)	−0.062(1)	0.013 6(8)
P(1)	0.243 0(2)	−0.104 4(3)	0.098 2(2)	C(21)	0.106 6(7)	0.048(1)	0.261 1(7)
P(2)	0.193 4(2)	0.025 3(3)	0.237 3(2)	C(22)	0.101 7(7)	0.142(1)	0.314 0(7)
C(1)	0.309 1(7)	0.117(1)	0.163 2(7)	C(23)	0.034(1)	0.164(1)	0.330 3(8)
C(2)	0.381 8(7)	0.113(1)	0.190 6(7)	C(24)	−0.027 6(8)	0.101(2)	0.294 8(9)
C(3)	0.433 2(7)	0.211(1)	0.182 2(7)	C(25)	−0.024 6(7)	0.010(2)	0.241 6(9)
C(4)	0.414 1(8)	0.335(1)	0.183 6(8)	C(26)	0.042 5(7)	−0.011(1)	0.227 0(7)
C(5)	0.460(1)	0.426(1)	0.169 8(8)	C(27)	0.264 8(6)	0.065(1)	0.325 7(7)
C(6)	0.527(1)	0.393(2)	0.160(1)	C(28)	0.284 0(8)	−0.020(1)	0.384 9(8)
C(7)	0.550(1)	0.275(2)	0.160(1)	C(29)	0.337 2(9)	0.013(2)	0.451 8(8)
C(8)	0.502 2(8)	0.182(2)	0.170 6(7)	C(30)	0.370 3(7)	0.127(2)	0.459 0(7)
C(9)	0.178 7(7)	−0.211(1)	0.033 2(7)	C(31)	0.348 9(7)	0.206(1)	0.400 6(8)
C(10)	0.143 9(8)	−0.308(1)	0.058 4(8)	C(32)	0.297 3(6)	0.179(1)	0.332 4(7)
C(11)	0.092 8(9)	−0.382(2)	0.008(1)	C(33)	0.258 8(6)	−0.174(1)	0.192 4(7)
C(12)	0.078 5(8)	−0.366(2)	−0.068(1)	C(34)	0.197 2(7)	−0.142(1)	0.227 7(7)
C(13)	0.113 5(9)	−0.274(2)	−0.094 7(8)	C(35)	0.163(2)	0.311(2)	0.115(2)
C(14)	0.163 8(9)	−0.196(1)	−0.045 6(8)	C(36)	0.104(2)	0.231(3)	0.114(1)
C(15)	0.330 0(7)	−0.128(1)	0.072 9(7)	C(37)	0.075 1(8)	0.137(2)	0.067(1)
C(16)	0.382 4(8)	−0.210(1)	0.111 2(8)	C(38)	0.101(1)	0.094(1)	0.008(1)
C(17)	0.448 2(8)	−0.226(1)	0.089(1)	C(39)	0.159(1)	0.133(3)	−0.018(1)
C(18)	0.457 8(8)	−0.160(2)	0.028(1)	C(40)	0.201(1)	0.226(3)	0.007(2)
C(19)	0.406 6(9)	−0.078(2)	−0.008 9(8)	C(41)	0.209(2)	0.306(3)	0.066(2)

precipitate of complex **7**; yield 0.073 g (19%) (Found: C, 57.7; H, 5.4. Calc. for $C_{38}H_{39}F_6MoP_3$: C, 57.2; H, 4.9%). Mass spectrum (*m/z*): 655 (M^+) and 573 ([$M - C_2HBu^t$]$^+$).

[Mo{C=C(H)Bu^t}(dmpe)(η-C_7H_7)][PF_6] **8**. A green solution of [Mo(η^6-C_6H_5Me)(η-C_7H_7)][PF_6] (0.751 g, 1.77 mmol) in AR acetone (50 cm^3) was refluxed for 20 min turning red. The solution was cooled to −78 °C and dmpe (0.266 g, 1.77 mmol) added producing a green colour. The solution was allowed to warm to room temperature and after 90 min Bu^{t}C≡CH (0.67 g, 8.16 mmol) was added and the mixture refluxed for 4 h. During this time the solution turned orange and a white precipitate formed. The precipitate, (Bu^{t}C≡CH)$_n$, was collected, washed with acetone and dried; yield 0.49 g (93% based on excess of Bu^{t}C≡CH) [Found: C, 85.5; H, 12.8. Calc. for $(C_6H_{10})_n$: C, 87.8; H, 12.2%]. Infrared (CsI disc): 2965–2870, 1640–1615, 1480, 1391, 1361, 1260, 1237–1211, 1100, 900 and 800 cm^{-1}. NMR ($CDCl_3$): ^{1}H, δ 6.22 (s, CH_{cis}), 6.08 (br, CH_{trans}), and 1.17 (s, Me); ^{13}C, δ 149.9–119.5 (C=C), 38.2 (s, CMe_{trans}), 37.2 (s, CMe_{cis}), 32.5 (s, Me_{trans}), and 31.3 (s, Me_{cis}). The orange solution was reduced to dryness and the residue, dissolved in the minimum volume of CH_2Cl_2, was transferred to an alumina–hexane chromatography column. Elution with acetone produced an orange band which was collected and recrystallised from CH_2Cl_2–diethyl ether, acetone–diethyl ether twice, and finally acetonitrile–diethyl ether to give complex **8** as an orange solid; yield 13 mg (1.3%) (Found: C, 41.0, H, 6.2. Calc. for $C_{19}H_{33}F_6MoP_3$: C, 40.4; H, 5.9%). Mass spectrum (*m/z*): 421 (M^+) and 339 ([$M - C_2HBu^t$]$^+$).

Table 7 Atomic coordinates for complex **14**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo(1)	0.2677(0)	0.0355(0)	0.0911(0)	C(23)	0.6094(4)	−0.0437(5)	0.3528(3)
P(2)	0.3125(1)	−0.0370(1)	0.2209(1)	C(24)	0.6295(4)	−0.0236(6)	0.4255(3)
C(3)	0.2966(4)	−0.1845(5)	0.2117(3)	C(25)	0.5570(5)	−0.0005(6)	0.4370(3)
C(4)	0.3416(4)	−0.2298(5)	0.1689(3)	C(26)	0.4615(4)	−0.0016(5)	0.3762(3)
P(5)	0.2934(1)	−0.1641(1)	0.0761(1)	C(27)	0.2479(4)	0.0059(5)	0.2661(3)
C(6)	0.2422(6)	0.2184(5)	0.0822(6)	C(28)	0.2245(4)	0.1147(6)	0.2639(4)
C(7)	0.3327(8)	0.1967(6)	0.1491(5)	C(29)	0.1895(5)	0.1515(6)	0.3082(4)
C(8)	0.4111(5)	0.1393(6)	0.1549(4)	C(30)	0.1767(5)	0.0791(7)	0.3536(4)
C(9)	0.4143(5)	0.0811(6)	0.0998(5)	C(31)	0.1973(5)	−0.0284(7)	0.3549(4)
C(10)	0.3417(6)	0.0646(6)	0.0247(4)	C(32)	0.2331(4)	−0.0657(5)	0.3108(4)
C(11)	0.2542(6)	0.1130(7)	−0.0172(4)	C(33)	0.3804(4)	−0.1985(5)	0.0495(3)
C(12)	0.2101(5)	0.1807(7)	0.0079(5)	C(34)	0.4783(5)	−0.2047(6)	0.1035(4)
C(13)	0.1344(4)	−0.0010(4)	0.0553(3)	C(35)	0.5443(5)	−0.2260(6)	0.0825(4)
C(14)	0.0426(4)	−0.0251(5)	0.0331(3)	C(36)	0.5126(5)	−0.2397(6)	0.0070(5)
C(15)	0.0294(4)	−0.1023(5)	0.0829(3)	C(37)	0.4166(5)	−0.2306(7)	−0.0482(4)
C(16)	0.0153(4)	−0.0639(6)	0.1393(3)	C(38)	0.3503(5)	−0.2117(6)	−0.0276(4)
C(17)	0.0068(5)	−0.1367(8)	0.1870(4)	C(39)	0.1878(4)	−0.2447(5)	0.0088(3)
C(18)	0.0161(5)	−0.2451(8)	0.1809(4)	C(40)	0.1198(4)	−0.1984(6)	−0.0610(3)
C(19)	0.0292(5)	−0.2838(6)	0.1250(5)	C(41)	0.0386(5)	−0.2569(7)	−0.1125(4)
C(20)	0.0350(4)	−0.2128(5)	0.0757(4)	C(42)	0.0252(5)	−0.3608(7)	−0.0950(5)
C(21)	0.4389(4)	−0.0248(5)	0.3025(3)	C(43)	0.0934(5)	−0.4065(6)	−0.0263(5)
C(22)	0.5148(4)	−0.0442(5)	0.2917(3)	C(44)	0.1740(4)	−0.3488(5)	0.0255(4)

[Mo{C=C(Me)Bu^t}(dppe)(η-C$_7$H$_7$)][PF$_6$] **9**. A solution of [Mo(C≡CBu^t)(dppe)(η-C$_7$H$_7$)] (0.38 g, 0.57 mmol) in CH$_2$Cl$_2$(40 cm^3) was treated with MeI (0.3 cm^3) and refluxed for 18 h. The reaction mixture was reduced to dryness and then dissolved in AR acetone (60 cm^3). The salt [NH$_4$][PF$_6$] (0.23 g, 1.20 mmol) was added, the reaction mixture stirred for 90 min, reduced to dryness *in vacuo* and the residue recrystallised from CH$_2$Cl$_2$–diethyl ether and then finally acetone-diethyl ether to give complex **9** as a bright orange solid; yield (72 mg, 15%) (Found: C, 58.6; H, 5.6. Calc. for C$_{40}$H$_{43}$F$_6$MoP$_3$: C, 58.1; H, 5.2%). Mass spectrum (*m*/*z*): 683 (M^+) and 587 ([M − C$_2$MeBu^t])$^+$.

[Mo{C=C(Me)Bu^n}(dppe)(η-C$_7$H$_7$)][PF$_6$] **10**. Complex **10** was prepared from [Mo(C≡CBu^n)(dppe)(η-C$_7$H$_7$)] **11c** (1.28 g, 1.92 mmol), MeI (2.5 cm^3) and [NH$_4$][PF$_6$] (0.53 g, 3.25 mmol) by an identical procedure to that described for **9** to give a bright orange solid; yield (1.13 g, 71%) (Found: C, 57.7; H, 5.4. Calc. for C$_{40}$H$_{43}$F$_6$MoP$_3$: C, 58.1; H, 5.2%). Mass spectrum (*m*/*z*): 683 (M^+) and 587 ([M − C$_2$MeBu^n]$^+$).

[Mo(C≡CBu^n)(dppe)(η-C$_7$H$_7$)] **11c**. A solution of [Mo(η^6-C$_6$H$_5$Me)(η-C$_7$H$_7$)][PF$_6$] (2.01 g, 4.74 mmol) in acetone (100 cm^3) was refluxed for 20 min to give a deep red solution which, on addition of dppe (1.90 g, 4.77 mmol), went green. After a further 18 h of reflux Bu^{n}C≡CH (2.5 cm^3) was added and the reflux continued for 4 h after which evaporation to dryness gave an oily residue. This was dissolved in CH$_2$Cl$_2$ and added dropwise to a large volume of vigorously stirred diethyl ether to yield crude [Mo{C=C(H)Bu^n}(dppe)(η-C$_7$H$_7$)][PF$_6$] **5** as an orange solid. Deprotonation of complex **5** was effected by dissolution in acetone (80 cm^3) and treatment with KOBu^t (1.06 g, 9.46 mmol) followed by 1 h of stirring and evaporation to dryness. The residue was dissolved in CH$_2$Cl$_2$ and transferred to an alumina–hexane chromatography column. Elution with hexane–acetone (1 : 1) gave a brown band which was collected and evaporated to dryness. The residue was recrystallised from diethyl ether–hexane to give **11c** as a dark brown solid; yield 1.48 g (47%) (Found: C, 70.7, H, 6.0. Calc. for C$_{39}$H$_{40}$MoP$_2$: C, 70.3; H, 6.0%). Mass spectrum (*m*/*z*): 668 (M^+). IR [ν(C≡C), (CH$_2$Cl$_2$)]: 2068 cm^{-1}. Cyclic voltammetry: $E°$ (CH$_2$Cl$_2$) = −0.25 V. ^{1}H NMR (C$_6$D$_6$): δ 7.78–7.36 (m, 20 H, Ph), 5.16 (br, 7 H, C$_7$H$_7$), 2.08 (br, CH$_2$CH$_2$), 0.75 (br, Bu^n) and 0.57 (br, Bu^n).

[Mo$_2$(dppe)$_2$(η-C$_7$H$_7$)$_2$(μ-C$_4$Bu$^n{}_2$)][PF$_6$]$_2$ **13**. A solution of [Mo(C≡CBu^n)(dppe)(η-C$_7$H$_7$)] (0.29 g, 0.44 mmol) in CH$_2$Cl$_2$ (10 cm^3) was treated with [Fe(cp)$_2$][PF$_6$] (0.14 g, 0.42 mmol) affording an immediate change from brown to orange. The orange solution was shown to contain [Mo(C≡CBu^n)(dppe)(η-C$_7$H$_7$)][PF$_6$] **12c**. After stirring for 15 min the reaction mixture was treated with hexane giving a purple precipitate which was isolated and recrystallised from acetonitrile–diethyl ether to give **13** as a purple-red solid; yield 0.15 g (43%) (Found: C, 57.3, H, 5.0. Calc. for C$_{78}$H$_{80}$F$_{12}$Mo$_2$P$_6$: C, 57.7; H, 4.9%).

[Mo$_2$(dppe)$_2$(η-C$_7$H$_7$)$_2$(μ-C$_4$Ph$_2$)][PF$_6$]$_2$ **14**. The stirring of [Mo(C≡CPh)(dppe)(η-C$_7$H$_7$)][PF$_6$] (0.48 g, 0.58 mmol) in anhydrous (< 0.005% water) thf (20 cm^3) resulted in the precipitation of a red solid from the red-purple mother-liquors. After 24 h the mother-liquors were removed and recrystallisation of the remaining precipitate from CH$_2$Cl$_2$–hexane afforded complex **14** as a deep red solid; yield 0.26 g (54%) (Found: C, 58.9; H, 4.3; F, 13.9; Mo, 11.1; P, 11.3. Calc. for C$_{82}$H$_{72}$F$_{12}$Mo$_2$P$_6$: C, 59.2; H, 4.3; F, 13.7; Mo, 11.5; P, 11.2%).

X-Ray Crystal Structure Analyses of Complexes **3** *and* **14**.—The majority of the details of the structure analyses of complexes **3** and **14** are given in Table 5; non-hydrogen atom positional parameters are listed in Tables 6 and 7 respectively. Neutral atom scattering factors were taken from ref. 36.

[Mo{C=C(H)Ph}(dppe)(η-C$_7$H$_7$)][BF$_4$] **3**. Orange crystals of complex **3** were grown by slow diffusion of a diethyl ether layer into a CH$_2$Cl$_2$ solution of the complex. The unit-cell dimensions were derived from the setting angles of 25 reflections in the range $40.5 < 2\theta < 56.3°$. An empirical absorption correction using the program DIFABS[37] was applied and the data corrected for Lorentz and polarisation effects. The intensities of three representative reflections, measured after every 150, declined by 1.40% and an appropriate linear correction factor was applied. The structure was solved by direct methods and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at idealised positions and assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. The weighting scheme was $w = 4F_o{}^2/\sigma^2(F_o{}^2)$ with a p factor of 0.03 to weight down intense reflections. All calculations were performed using the TEXSAN crystallographic software package.[38]

[Mo$_2$(dppe)$_2$(η-C$_7$H$_7$)$_2$(μ-C$_4$Ph$_2$)][PF$_6$]$_2$ **14**. Dark red, tabular crystals of complex **14** were grown by slow diffusion of a diethyl ether layer into an acetonitrile solution of the complex. The unit-cell dimensions were derived from the setting angles of 24 reflections in the range $20.0 < 2\theta < 22.0°$. No absorption correction was applied and the data were not corrected for extinction. No decay correction was necessary. The structure was solved by heavy-atom (Patterson and Fourier) methods and refined by full-matrix least squares. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at idealised positions and assigned an isotropic B value of 6 Å^2. The weighting scheme was $w = 1/(14.7 - 0.3F + 0.002F^2)^{\frac{1}{2}}$. Calculations were carried out using software designed and generously provided by Mr. O. S. Mills.

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

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