Reactions of Co-ordinated Ligands. Part 29.[1] The Formation of a 1,3-Diene at a Molybdenum Centre by linking of But-2-yne with an Alkene; *X*-Ray Crystal Structures of $[Mo(\eta^2\text{-}o\text{-}Ph_2PC_6H_4CH{=}CH_2)(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)]\text{-}[BF_4]$ and $[Mo(NCMe)(\eta^4\text{-}o\text{-}MeCH{=}CMe\text{-}CH{=}CHC_6H_4PPh_2)(\eta\text{-}C_5H_5)]\text{-}[BF_4]$ †

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Reaction of $[Mo(CO)(\eta^2\text{-}RC_2R')_2(\eta\text{-}C_5H_5)][BF_4]$ (R = R′ = Me; R = H, R′ = Bu^t) with *o*-diphenylphosphinostyrene (dpps) in CH_2Cl_2 affords the alkyne–alkene complex $[Mo(dpps)(\eta^2\text{-}RC_2R')(\eta\text{-}C_5H_5)][BF_4]$. The structure of $[Mo(\eta^2\text{-}dpps)(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$ was established by *X*-ray crystallography. Crystals are orthorhombic, space group $Pna2_1$ with $Z = 4$ in a unit cell of dimensions $a = 22.324(5)$, $b = 9.249(3)$, $c = 14.566(3)$ Å. The structure has been refined to $R = 0.040$ ($R' = 0.041$) for 2 228 reflections at 293 K. The molybdenum atom is bonded to an $\eta\text{-}C_5H_5$, an η^2-bonded but-2-yne, and chelating *o*-diphenylphosphinostyrene ligands, where the C–C vectors of the co-ordinated alkyne and alkene lie essentially parallel to the Mo–P axis. In refluxing acetonitrile the but-2-yne cation is transformed *via* C–C bond formation and a 1,3-H shift into a 1,3-diene complex $[Mo(NCMe)(\eta^4\text{-}MeCH{=}CMe\text{-}CH{=}CHC_6H_4PPh_2\text{-}o)(\eta\text{-}C_5H_5)][BF_4]$ identified by *X*-ray crystallography. Crystals are monoclinic, space group $P2_1/c$ with $Z = 4$ in a unit cell of dimensions $a = 10.836(2)$, $b = 8.551(2)$, $c = 30.896(6)$ Å, and $\beta = 94.80(2)°$. The structure has been refined to $R = 0.029$ ($R' = 0.030$) for 3 828 reflections at 293 K. The cation contains a molybdenum atom bound to an $\eta\text{-}C_5H_5$ ligand, an N-bonded acetonitrile, and a ligand formally derived from but-2-yne and *o*-diphenylphosphinostyrene, which is η^4-bonded to the Mo *via* a 1,3-diene moiety. The co-ordinated acetonitrile is displaced by Bu^tCN, CO, and $P(OMe)_3$ to form the cations $[Mo(L)(\eta^4\text{-}MeCH{=}CMe\text{-}CH{=}CHC_6H_4PPh_2\text{-}o)(\eta\text{-}C_5H_5)][BF_4]$ [L = Bu^tCN, CO, or $P(OMe)_3$]. The nitrile-substituted cations exist in solution as a mixture of two conformational isomers, whereas the CO- and $P(OMe)_3$-substituted cations are present in only one isomeric form. The conformations of these species are discussed in terms of frontier molecular orbitals, and the nature of the 1,3-H shift process has been examined using deuterium-labelled *o*-diphenylphosphinostyrene.

The formation of metallacyclopent-2-enes by oxidative coupling of co-ordinated alkynes and alkenes has been implicated in the cobalt-,[2] rhodium-,[3] and palladium-promoted[4] cyclocotrimerisation of alkynes and alkenes. It has also been reported[5] that the benzyne complex $[TaMe_2(\eta^2\text{-}C_6H_4)(\eta\text{-}C_5H_5)]$ reacts with ethylene to form a tantalaindane complex. In exploring the chemistry of the cationic molybdenum bis(alkyne) complexes $[Mo(CO)(\eta^2\text{-}RC_2R')_2(\eta\text{-}C_5H_5)][BF_4]$[6,7] (R = R′ = Me; R = H, R′ = Bu^t) we became interested in the possibility of synthesising complexes containing both a co-ordinated alkene and an alkyne in the belief that these might be induced to undergo a carbon–carbon coupling reaction.

Results and Discussion

Reactions of $[Mo(CO)(\eta^2\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)][BF_4]$ (1) with triphenylphosphine has been shown[7] to lead to displacement of one but-2-yne ligand and the formation of $[Mo(CO)(PPh_3)(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$. In contrast, in refluxing CH_2Cl_2 *o*-diphenylphosphinostyrene[8] (dpps) reacts with (1) to give a quantitative yield of the red crystalline complex (2), which on the basis of analysis, i.r. and n.m.r. spectroscopy, was assigned the molecular formula $[Mo(dpps)(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)][BF_4]$. A similar reaction between $[Mo(CO)(\eta^2\text{-}HC_2Bu^t)_2(\eta\text{-}C_5H_5)][BF_4]$ (3) and dpps gave the analogous purple crystalline compound $[Mo(dpps)(\eta^2\text{-}HC_2Bu^t)(\eta\text{-}C_5H_5)][BF_4]$ (4).

The signal in the ^1H n.m.r. spectrum of (2) assigned to the methyl groups of the MeC_2Me ligand was a singlet at room temperature. On cooling, this broadened, collapsed, and two new peaks grew on either side of the original resonance. This observation is interpreted in terms of ' propeller rotation '[7] of the co-ordinated but-2-yne about the metal–alkyne axis. In agreement, the $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum at −95 °C showed the alkyne contact carbons at 231.2 [t, *J*(CP) 4 Hz] and 216.3 p.p.m. [t, *J*(CP) 22 Hz] collapsing to a single peak at room temperature. The coalescence temperature was −60 °C giving $\Delta G_{T_c}^{\ddagger} = 40$ kJ mol^{-1} for but-2-yne rotation. The ^{13}C spectrum also showed resonances at 63.2 (CH=) and 35.3 p.p.m. (CH_2=) suggesting that the alkene present in the dpps ligand was co-ordinated to the molybdenum. In order to confirm this, and to establish the geometry of (2) a single-crystal *X*-ray study was undertaken.

The molecular structure of the cation together with the atom numbering scheme is illustrated in Figure 1 and the bond lengths and bond angles listed in Tables 1 and 2, respectively. As expected from the n.m.r. data the molybdenum atom is bonded to an $\eta\text{-}C_5H_5$ ring and an η^2-but-2-yne ligand. In addition the *o*-diphenylphosphinostyrene is seen to be acting as a bidentate ligand, bonding to the metal through both the phosphorus atom and the *o*-vinyl substituent, co-ordinated as an η^2-alkene.

The but-2-yne shows the typical bending back of its methyl groups in a *cisoid* manner, the mean C–C–Me angle being

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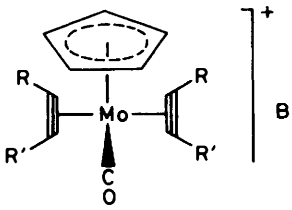
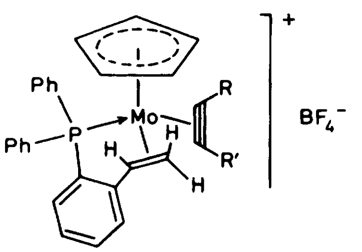
† (η^2-But-2-yne)(η-cyclopentadienyl)(α-β-η-*o*-diphenylphosphinostyrene-*P*)molybdenum(II) tetrafluoroborate and acetonitrile(η-cyclopentadienyl){1′—4′-η-[*o*-(3′-methylpenta-2′,4′-dienyl)phenyl]-diphenylphosphine-*P*}molybdenum(II) tetrafluoroborate.

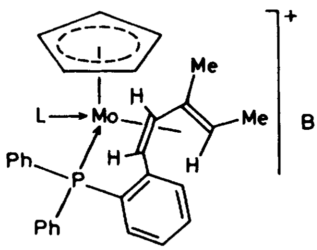
Supplementary data available (No. SUP 23792, 44 pp.): observed and calculated structure factors, thermal parameters. See Instructions for Authors *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.



(1) R = R′ = Me
(3) R = H, R′ = Bu^t



(2) R = R′ = Me
(4) R = H, R′ = Bu^t



(5) L = MeCN
(6) L = Bu^{t}CN
(7) L = CO
(8) L = P(OMe)$_3$

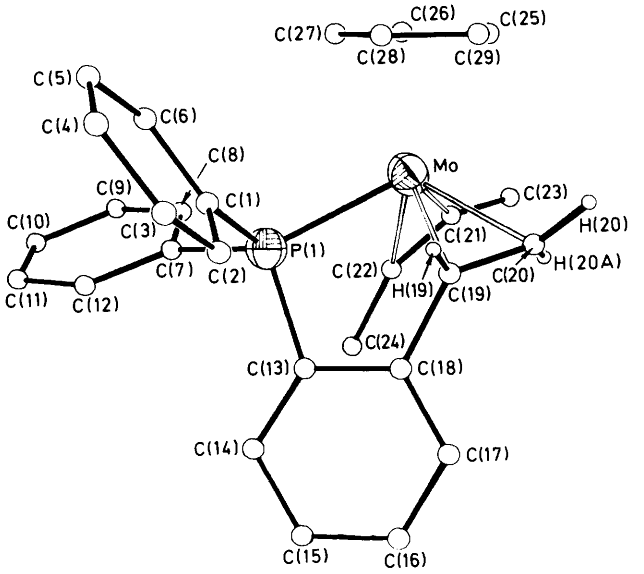


Figure 1. Molecular structure of the cation in (2)

Table 1. Bond lengths (Å) for (2) *

Mo–P(1)	2.442(2)	Mo–C(19)	2.266(7)
Mo–C(20)	2.265(8)	Mo–C(21)	1.996(8)
Mo–C(22)	2.037(7)	Mo–C(25)	2.384(7)
Mo–C(26)	2.321(8)	Mo–C(27)	2.303(7)
Mo–C(28)	2.355(9)	Mo–C(29)	2.416(8)
P(1)–C(1)	1.829(7)	P(1)–C(7)	1.805(6)
P(1)–C(13)	1.830(7)	C(1)–C(2)	1.384(10)
C(1)–C(6)	1.395(10)	C(2)–C(3)	1.394(11)
C(3)–C(4)	1.353(10)	C(4)–C(5)	1.370(12)
C(5)–C(6)	1.408(12)	C(7)–C(8)	1.401(10)
C(7)–C(12)	1.412(10)	C(8)–C(9)	1.354(11)
C(9)–C(10)	1.392(13)	C(10)–C(11)	1.348(14)
C(11)–C(12)	1.393(12)	C(13)–C(14)	1.375(10)
C(13)–C(18)	1.390(10)	C(14)–C(15)	1.422(12)
C(15)–C(16)	1.385(13)	C(16)–C(17)	1.377(12)
C(17)–C(18)	1.370(11)	C(18)–C(19)	1.499(11)
C(19)–H(19)	0.910(58)	C(19)–C(20)	1.425(11)
C(20)–H(20A)	1.157(61)	C(21)–C(22)	1.293(10)
C(21)–C(23)	1.495(13)	C(22)–C(24)	1.502(11)
C(25)–C(26)	1.405(14)	C(25)–C(29)	1.372(16)
C(26)–C(27)	1.386(13)	C(27)–C(28)	1.394(15)
C(28)–C(29)	1.366(13)	C(30)–Cl(1)	1.758(12)
C(30)–Cl(2)	1.693(13)	B–F(1)	1.342(18)
B–F(2)	1.353(23)	B–F(3)	1.271(20)
B–F(4)	1.208(21)		

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

139.4°. This bend-back angle is typical of 4e-donor alkyne ligands {*cf.* the angles in the related compounds [Mo(CO)(PEt$_3$)(η^2-MeC$_2$Me)(η^5-C$_9$H$_7$)][BF$_4$] (140.7°) and [Mo(PMe$_3$)$_2$(η^2-MeC$_2$Me)(η^5-C$_9$H$_7$)][BF$_4$] (136.2°)}.[7] The Mo–C distances of the alkyne show slight asymmetry, that carbon closer to the phosphorus atom showing the longer bond length [C(22)–Mo 2.037(7) *versus* C(21)–Mo 1.996(8) Å]. Similar asymmetry in a complex of the type [Mo(L)(η^2-L′)(η^2-L″)(η-C$_5$H$_5$)]$^+$ has been observed[9] previously (for L = CO, L′ = L″ = MeC$_2$Me). The olefinic Mo–C distances are markedly longer (by *ca.* 0.25 Å) and symmetric [Mo–C(19) 2.266(7), Mo–C(20) 2.265(8) Å]. These lengths are, however, much shorter than those observed[10] for the methyl-substituted phosphinostyrene complex [Mo(CO)$_4$(η^2-MeCH=CHC$_6$H$_4$PPh$_2$-*o*)] (mean Mo–C 2.48 Å) where the olefin moiety is *trans* to a strong π-acceptor carbonyl ligand. As in other [Mo(L)(η^2-L′)(η^2-L″)(η-C$_5$H$_5$)]$^+$ complexes[7,9] (*e.g.*, L′ = L″ = MeC$_2$Me, L = CO or NCMe) both the C–C vectors of L′ and L″ [C(21)–C(22) and C(19)–C(20)] lie essentially parallel to the Mo–L axis [*viz.* torsion angles C(19)–C(20)–Mo–P(1) −12.5, C(22)–C(21)–Mo–P(1) −10.4°]. This ligand orientation is illustrated in Figure 2 which shows a stereoscopic view of the cation in (2).

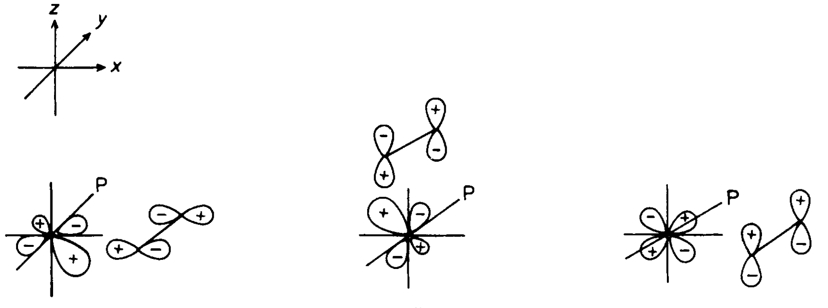
The electronic reasons for the orientation observed here are similar to those dominant in related complexes where an alkyne ligand acts as a net 3e or 4e donor.[9] The factors involved may be understood using an octahedral orbital framework, placing the phosphorus atom on the y axis, the alkyne centroid on the x axis, and the olefin centroid on the z axis; thus the Mo–cyclopentadienyl centroid vector lies between the $-x$, $-y$, and $-z$ directions. The important metal–olefin and -alkyne interactions are illustrated by the orbital interactions (I)—(III).

Interactions (I) and (II) correspond to stabilisation of filled metal atom orbitals by overlap with vacant π^* ligand orbitals. Interaction (III) allows the alkyne to act as a 4e donor enabling the metal to achieve an 18e count. Since the formal oxidation state of the molybdenum is +2, and it therefore has a d^4 configuration, these electrons occupy the d_{xy} and d_{yz} orbitals in (I) and (II). The observed ligand orientation allows these three interactions to be maximised.

When (2) was heated under reflux in acetonitrile solution for 24 h, an orange crystalline complex (5) was formed in high yield. Both elemental analysis and n.m.r. suggested that

Table 2. Bond angles (°) for (2)

P(1)-Mo-C(19)	70.7(2)	P(1)-Mo-C(20)	106.6(2)	C(1)-C(6)-C(5)	119.8(7)	P(1)-C(7)-C(8)	120.8(5)
C(19)-Mo-C(20)	36.7(3)	P(1)-Mo-C(21)	117.6(2)	P(1)-C(7)-C(12)	120.0(6)	C(8)-C(7)-C(12)	119.0(7)
C(19)-Mo-C(21)	113.3(3)	C(20)-Mo-C(21)	90.0(3)	C(7)-C(8)-C(9)	120.9(7)	C(8)-C(9)-C(10)	119.8(8)
P(1)-Mo-C(22)	80.8(2)	C(19)-Mo-C(22)	96.7(3)	C(9)-C(10)-C(11)	120.6(8)	C(10)-C(11)-C(12)	121.4(8)
C(20)-Mo-C(22)	95.1(3)	C(21)-Mo-C(22)	37.4(3)	C(7)-C(12)-C(11)	118.3(9)	P(1)-C(13)-C(14)	127.9(6)
P(1)-Mo-C(25)	145.2(2)	C(19)-Mo-C(25)	119.4(4)	P(1)-C(13)-C(18)	109.6(5)	C(14)-C(13)-C(18)	122.5(7)
C(20)-Mo-C(25)	93.1(3)	C(21)-Mo-C(25)	90.0(4)	C(13)-C(14)-C(15)	116.7(7)	C(14)-C(15)-C(16)	120.7(7)
C(22)-Mo-C(25)	126.5(4)	P(1)-Mo-C(26)	120.3(2)	C(15)-C(16)-C(17)	120.4(8)	C(16)-C(17)-C(18)	120.0(8)
C(19)-Mo-C(26)	149.2(3)	C(20)-Mo-C(26)	127.8(3)	C(13)-C(18)-C(17)	119.7(7)	C(13)-C(18)-C(19)	117.6(6)
C(21)-Mo-C(26)	87.9(3)	C(22)-Mo-C(26)	113.0(3)	C(17)-C(18)-C(19)	122.7(6)	Mo-C(19)-C(18)	113.7(5)
C(25)-Mo-C(26)	34.7(3)	P(1)-Mo-C(27)	89.3(2)	Mo-C(19)-H(19)	111.2(35)	C(18)-C(19)-H(19)	105.3(34)
C(19)-Mo-C(27)	128.3(3)	C(20)-Mo-C(27)	136.8(3)	Mo-C(19)-C(20)	71.6(5)	C(18)-C(19)-C(20)	126.2(7)
C(21)-Mo-C(27)	118.2(4)	C(22)-Mo-C(27)	127.4(3)	H(19)-C(19)-C(20)	122.9(34)	Mo-C(20)-C(19)	71.7(4)
C(25)-Mo-C(27)	57.7(3)	C(26)-Mo-C(27)	34.9(3)	Mo-C(20)-H(20A)	120.6(30)	C(19)-C(20)-H(20A)	109.3(32)
P(1)-Mo-C(28)	90.9(2)	C(19)-Mo-C(28)	96.5(3)	Mo-C(21)-C(22)	73.0(5)	Mo-C(21)-C(23)	145.0(6)
C(20)-Mo-C(28)	103.6(3)	C(21)-Mo-C(28)	143.7(3)	C(22)-C(21)-C(23)	142.0(8)	Mo-C(22)-C(21)	69.6(5)
C(22)-Mo-C(28)	161.1(3)	C(25)-Mo-C(28)	56.2(4)	Mo-C(22)-C(24)	153.7(6)	C(21)-C(22)-C(24)	136.7(7)
C(26)-Mo-C(28)	57.1(3)	C(27)-Mo-C(28)	34.8(4)	Mo-C(25)-C(26)	70.2(4)	Mo-C(25)-C(29)	74.7(5)
P(1)-Mo-C(29)	121.0(2)	C(19)-Mo-C(29)	93.1(3)	C(26)-C(25)-C(29)	107.0(8)	Mo-C(26)-C(25)	75.1(5)
C(20)-Mo-C(29)	81.2(3)	C(21)-Mo-C(29)	120.7(3)	Mo-C(26)-C(27)	71.9(5)	C(25)-C(26)-C(27)	108.2(9)
C(22)-Mo-C(29)	158.1(3)	C(25)-Mo-C(29)	33.2(4)	Mo-C(27)-C(26)	73.3(5)	Mo-C(27)-C(28)	74.6(5)
C(26)-Mo-C(29)	56.2(3)	C(27)-Mo-C(29)	56.6(3)	C(26)-C(27)-C(28)	107.0(8)	Mo-C(28)-C(27)	70.6(5)
C(28)-Mo-C(29)	33.2(3)	Mo-P(1)-C(1)	117.2(2)	Mo-C(28)-C(29)	75.8(5)	C(27)-C(28)-C(29)	108.6(9)
Mo-P(1)-C(7)	118.8(2)	C(1)-P(1)-C(7)	101.4(3)	Mo-C(29)-C(25)	72.1(5)	Mo-C(29)-C(28)	70.9(5)
Mo-P(1)-C(13)	103.4(2)	C(1)-P(1)-C(13)	104.1(3)	C(25)-C(29)-C(28)	109.2(9)	Cl(1)-C(30)-Cl(2)	110.3(7)
C(7)-P(1)-C(13)	111.2(3)	P(1)-C(1)-C(2)	121.1(5)	F(1)-B-F(2)	100.1(13)	F(1)-B-F(3)	118.4(14)
P(1)-C(1)-C(6)	119.6(5)	C(2)-C(1)-C(6)	119.3(6)	F(2)-B-F(3)	98.7(14)	F(1)-B-F(4)	111.6(14)
C(1)-C(2)-C(3)	119.5(7)	C(2)-C(3)-C(4)	121.3(7)	F(2)-B-F(4)	106.7(16)	F(3)-B-F(4)	117.7(15)
C(3)-C(4)-C(5)	120.5(7)	C(4)-C(5)-C(6)	119.6(7)				



(I) $d_{xy}-\pi^*_{\parallel}$ alkyne (II) $d_{yz}-\pi^*$alkene (III) $d_{xz}-\pi_{\perp}$ alkyne

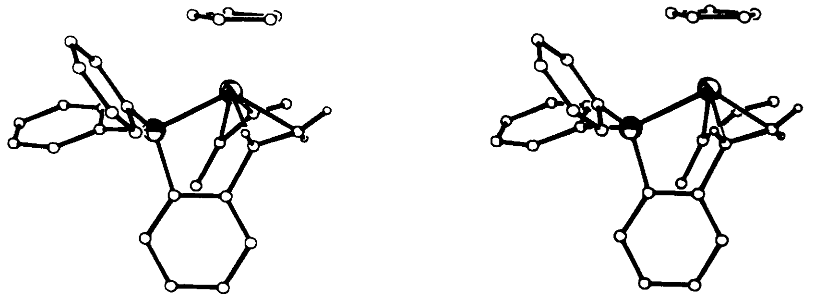


Figure 2. Stereoscopic view of the cation in (2)

(5) was a 1 : 1 adduct of MeCN and (2), existing in solution as a mixture of two isomers in the ratio 2 : 1. The presence in the ^1H spectrum of each isomer of two methyl signals, one a singlet and the other a doublet, suggested that an unusual rearrangement had occurred. The nature of this rearrangement was revealed by an *X*-ray diffraction study on (5). The results of this study, the bond lengths and angles, are listed in Tables 3 and 4, and the geometry of the molecular cation is illustrated in Figure 3.

The structure of (5) consists of isolated BF_4^- anions and complex cations. The cation contains a molybdenum atom bound to an η-C_5H_5 ligand, an N-bonded acetonitrile, and a ligand formally derived from condensation of the but-2-yne and phosphinostyrene ligands present in (2). This last ligand

Table 3. Bond lengths (A) for (5)

Mo(1)–P(1)	2.437(1)	C(2)–C(3)	1.400(4)	C(12)–P(1)	1.818(1)	C(14)–C(15)	1.385(5)
Mo(1)–N(1)	2.138(2)	C(3)–C(4)	1.519(4)	N(1)–C(30)	1.137(2)	C(15)–C(16)	1.378(5)
Mo(1)–C(2)	2.425(3)	C(3)–C(5)	1.415(4)	C(30)–C(31)	1.454(5)	C(16)–C(17)	1.387(5)
Mo(1)–C(3)	2.281(3)	C(5)–H(5)	0.97(3)	C(25)–C(26)	1.440(6)	C(17)–C(18)	1.397(5)
Mo(1)–C(5)	2.216(3)	C(5)–C(6)	1.430(4)	C(26)–C(27)	1.382(6)	C(18)–C(13)	1.386(5)
Mo(1)–C(6)	2.263(3)	C(6)–H(6)	0.89(3)	C(27)–C(28)	1.410(6)	C(13)–P(1)	1.836(3)
Mo(1)–C(25)	2.274(4)	C(6)–C(7)	1.499(4)	C(28)–C(29)	1.416(6)	C(19)–C(20)	1.401(4)
Mo(1)–C(26)	2.339(4)	C(7)–C(8)	1.394(4)	C(29)–C(25)	1.409(5)	C(20)–C(21)	1.378(5)
Mo(1)–C(27)	2.393(4)	C(8)–C(9)	1.380(5)	B(1)–F(1)	1.380(4)	C(21)–C(22)	1.385(5)
Mo(1)–C(28)	2.352(4)	C(9)–C(10)	1.390(5)	B(1)–F(2)	1.388(4)	C(22)–C(23)	1.380(6)
Mo(1)–C(29)	2.316(4)	C(10)–C(11)	1.371(4)	B(1)–F(3)	1.394(4)	C(23)–C(24)	1.382(5)
C(1)–C(2)	1.503(4)	C(11)–C(12)	1.399(3)	B(1)–F(4)	1.371(4)	C(24)–C(19)	1.393(5)
C(2)–H(2)	0.90(3)	C(12)–C(7)	1.400(3)	C(13)–C(14)	1.401(5)	C(19)–P(1)	1.836(3)

Table 4. Bond angles (°) for (5)

P(1)–Mo(1)–N(1)	84.1(1)	C(5)–Mo(1)–C(6)	37.2(1)	Mo(1)–P(1)–C(13)	116.4(1)	C(7)–C(6)–H(6)	110.6(1.8)
P(1)–Mo(1)–C(2)	75.0(1)	H(6)–C(6)–Mo(1)	112.8(1.7)	Mo(1)–P(1)–C(12)	106.4(1)	C(3)–C(2)–Mo(1)	67.1(2)
P(1)–Mo(1)–C(3)	117.0(1)	H(6)–C(6)–C(5)	111.6(1.8)	P(1)–C(12)–C(7)	112.7(1)	H(2)–C(2)–C(1)	109.9(1.6)
P(1)–Mo(1)–C(5)	108.1(1)	Mo(1)–C(6)–C(5)	69.6(2)	P(1)–C(12)–C(11)	126.8(1)	H(2)–C(2)–Mo(1)	105.7(1.7)
P(1)–Mo(1)–C(6)	75.2(1)	C(6)–C(5)–H(5)	119.6(1.7)	C(12)–C(11)–C(10)	120.2(3)	Mo(1)–C(2)–C(1)	125.2(2)
N(1)–Mo(1)–C(2)	75.0(1)	C(6)–C(5)–C(3)	122.4(3)	C(11)–C(10)–C(9)	119.8(3)	Mo(1)–N(1)–C(30)	175.4(2)
N(1)–Mo(1)–C(3)	96.1(1)	C(6)–C(5)–Mo(1)	73.2(2)	C(10)–C(9)–C(8)	120.6(3)	N(1)–C(30)–C(31)	178.0(1)
N(1)–Mo(1)–C(5)	132.7(1)	H(5)–C(5)–Mo(1)	117.3(1.8)	C(9)–C(8)–C(7)	120.4(3)	C(5)–C(3)–Mo(1)	69.2(2)
N(1)–Mo(1)–C(6)	144.3(1)	H(5)–C(5)–C(3)	117.3(1.7)	C(8)–C(7)–C(6)	121.8(3)	C(4)–C(3)–C(2)	122.7(3)
C(2)–Mo(1)–C(3)	34.4(1)	Mo(1)–C(5)–C(3)	74.2(2)	C(12)–C(7)–C(8)	118.7(2)	C(4)–C(3)–Mo(1)	123.8(2)
C(2)–Mo(1)–C(5)	62.1(1)	C(5)–C(3)–C(2)	117.0(3)	C(12)–C(7)–C(6)	119.3(2)	Mo(1)–C(3)–C(2)	78.4(2)
C(2)–Mo(1)–C(6)	73.9(1)	C(5)–C(3)–C(4)	120.2(3)	C(7)–C(6)–C(5)	128.5(3)	C(3)–C(2)–C(1)	121.0(3)
C(3)–Mo(1)–C(5)	36.6(1)	Mo(1)–P(1)–C(19)	119.6(1)	C(7)–C(6)–Mo(1)	117.6(2)	C(3)–C(2)–H(2)	121.6(1.5)
C(3)–Mo(1)–C(6)	66.5(1)						

is η^4-bound to the molybdenum atom *via* a 1,3-diene moiety, which is the *ortho* substituent on a phenyl ring attached to a diphenylphosphine unit P-bonded to the metal. The methyl groups of the but-2-yne ligand in (2) are mutually *cis* in (5); the phenyl ring linking the 1,3-diene and PPh_2 groups is an inner substituent on the diene. The diene moiety is in an *exo* conformation relative to the η-C_5H_5 ligand with the central C–C bond approximately orthogonal to the Mo–P axis [torsion angle P–Mo(1)–C(5)–C(3) −102.1°]. The Mo–C distances within this unit reflect some asymmetry in its binding [Mo(1)–C(2) 2.425(3), Mo(1)–C(3) 2.281(3), Mo(1)–C(5) 2.216(3), Mo(1)–C(6) 2.263(3) Å]. The C–C distances likewise show variation [C(2)–C(3) 1.400(4), C(3)–C(5) 1.415(4), C(5)–C(6) 1.430(4) Å] with the shortest C–C bond corresponding to the carbons more weakly bound to the metal. The shortness of the C(3)–C(5) bond indicates substantial occupancy of the l.u.m.o. π-acceptor function of the diene moiety. Of the substituents on the diene moiety only C(7) and H(2), the 'inner' substituents, lie substantially out of the C_4 plane [deviations are C(7) +0.84, C(4) −0.09, C(1) −0.09, H(2) +0.52, C(2) 0.01, C(3) −0.02, C(5) 0.02, H(5) −0.03, H(6) 0.18, and Mo −1.86 Å]. These deviations reflect both the rehybridisation of the carbon atoms of the diene and the ring strain imposed by the requirement of bonding the phosphorus to the metal. These features and the ligand orientations are clearly illustrated in Figure 4 which shows a stereoscopic view of the cation of (5).

The acetonitrile ligand present in (5) is labile, and reaction with Bu^tCN, CO, and $P(OMe)_3$ under mild conditions afforded the crystalline complexes (6), (7), and (8) characterised by analysis, i.r. and n.m.r. spectroscopy. The n.m.r. spectrum of (6) was very similar to that of (5) but (7) and (8) clearly existed in solution as single isomers corresponding (n.m.r.) to the minor isomers of (5) and (6). The ^1H spectra of (7) and (8) were readily assigned (see Experimental section).

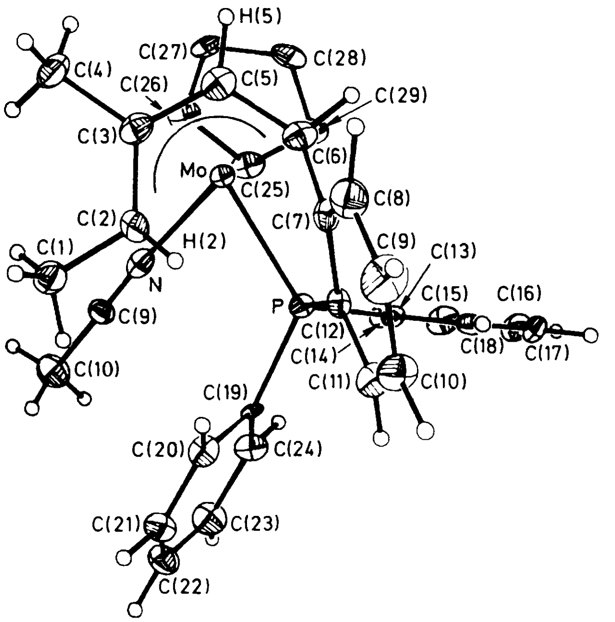


Figure 3. Molecular structure of the cation in (5)

In (7), H_a occurred close to the Me_a doublet and was an unresolved multiplet; however, ^{31}P decoupling gave the expected quartet. Me_b resonated as a singlet at lower field than Me_a, and H_b and H_c occurred as well separated doublets (an AX system) with a common J(HH) 9 Hz. When L = $P(OMe)_3$, *i.e.* complex (8), both H_b and H_c exhibited ^{31}P coupling, 4 Hz for H_b and 23 Hz for H_c. This large difference in ^{31}P coupling was used to assign the ^{13}C spectra of (7) and

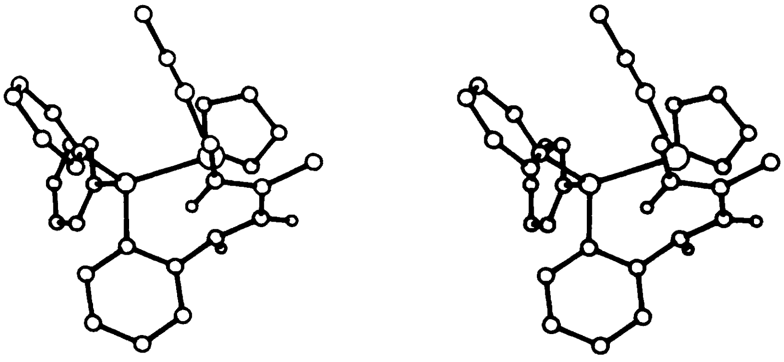


Figure 4. Stereoscopic view of the cation in (5)

(8). With these assignments a retrospective assignment of the signals in the ^1H spectra of both isomers of (5) and (6) was made (see Experimental section).

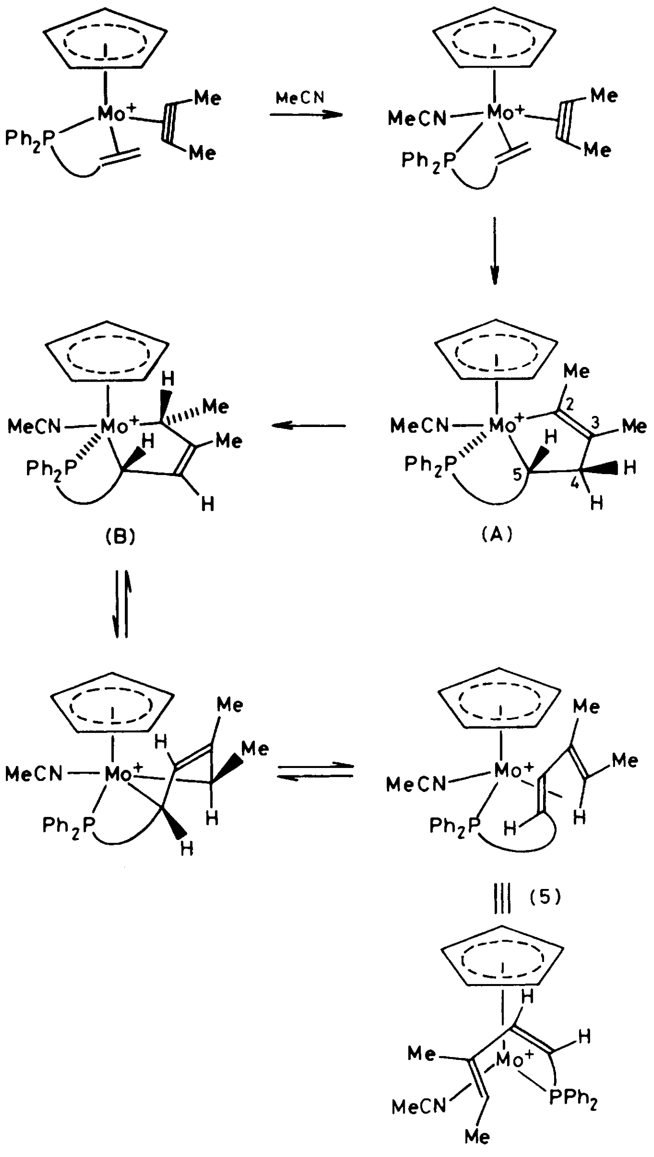
The existence of two isomers of the nitrile complexes (5) and (6), with an identical pattern of substituents on the diene as indicated by n.m.r. coupling constants, can be understood in terms of a conformational preference of the η^4-1,3-diene. A 1,3-diene has frontier π orbitals of the same symmetry as an alkyne (*i.e.* filled donor orbitals of σ and $\pi_\perp$ and empty acceptor orbitals of $\pi_\parallel$ and δ symmetry with respect to Mo–diene bonding).[11] As noted above, the orbital of $\pi_\parallel$ symmetry is substantially occupied in the solid-state structure of (5). These orbitals give similar conformational preferences to the diene and alkyne ligands bound to the MoLL′(η-C_5H_5) moiety, as previously discussed.[12,13]

It would be expected that in [Mo(CO)(PR_3)(η^4-1,3-diene)(η-C_5H_5)]$^+$ the central diene C–C bond would lie parallel to the Mo–P vector [conformation (A) in Scheme 1], so as to maximise orbital overlap in back-bonding to $\pi_\parallel$ of the η^4-diene. Although there is the complicating effect of strain in the chelating P–diene ring this same conformation (A) would be expected to be preferred in complexes (7) and (8); whereas, in (5) and (6), L = RCN, a strong σ donor and the alternative conformation (B) should now be slightly preferred.

Scheme 1.

In fact this is the conformation found in the solid state. In solution the major isomer also has conformation (B), whereas the minor isomer has the same conformation (A) as is adopted in the CO and $P(OMe)_3$ substituted cations (7) and (8). Comparison of the n.m.r. data confirms this conclusion.

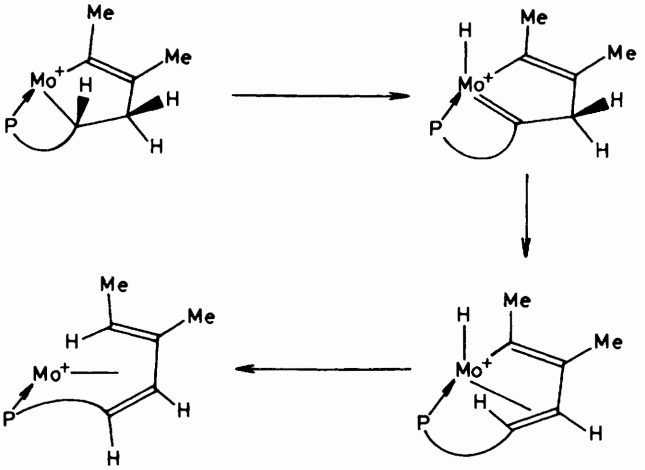
The formation of (5) on reaction of acetonitrile with the alkyne–alkene complex (2) is of particular interest in that it involves the formal addition of an alkenic carbon–hydrogen bond to an alkyne. A possible reaction pathway for the transformation of (2) into (5) is illustrated in Scheme 2.



Scheme 2. Counter anion is BF_4^- throughout

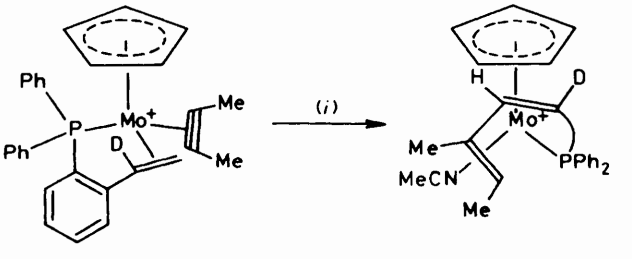
The initial step involves co-ordination of the good σ donor MeCN, this being accommodated by a concomitant ' switch ' (4e to 2e) in the bonding mode of the but-2-yne. This is followed by metallacyclopent-2-ene ring formation,[14] an oxidative reaction [Mo^{II} to Mo^{IV}] facilitated by donation of electron density to the metal centre by the co-ordinating nitrile. A 1,3-hydrogen-shift process generates an intermediate (B), of the type invoked by Faller and Rosan [15] to explain *cis–trans* isomerisation of co-ordinated penta-1,3-dienes, which then collapses to give (5). The hydrogen atom, which is part of the C*H*Me group present in the metallacyclopent-3-ene (B), is *cis* to the η-C_5H_5 ligand (see Scheme 2).

It was clearly important to establish how the 1,3-hydrogen-shift process occurred, which is presumed to be involved in the step (A) $\longrightarrow$ (B). An intermolecular elimination sequence involving loss of a proton (H^+) from C^4 of the metallacycle (A) followed by protolysis of the Mo–C^2 bond was thought unlikely when it was observed that the reaction still occurred in high yield in the presence of an excess of the base, anhydrous Na_2CO_3, an irreversible proton trap. Attention was then turned to the possibility that the presence in the intermediate (A) of a 16e molybdenum centre might promote an α-hydrogen elimination reaction followed by a 1,2-H shift of the kind which has been observed [16,17] with cationic iron carbene complexes (Scheme 3), a reductive elimination step completing the formation of the 1,3-diene cation.



Scheme 3. Other ligands omitted for clarity

In order to clarify this point, dpps specifically labelled with deuterium on the α-carbon atom was synthesised from α-[^{2}H]-*o*-bromostyrene, which was available by dehydration (230 °C/$KHSO_4$) of α-[^{2}H]-*o*-(bromophenyl)ethanol formed from *o*-bromoacetophenone and $LiAlD_4$. Reaction of α-[^{2}H]-*o*-diphenylphosphinostyrene with [Mo(CO)(η^2-$MeC_2Me)_2$(η-C_5H_5)][BF_4] afforded (2) with the deuterium incorporated onto the α-carbon atom of the co-ordinated alkene. In refluxing MeCN this labelled cation transformed cleanly into (5), in which the deuterium was specifically (n.m.r.) placed on the diene carbon shown in Scheme 4. Thus, an α-elimination reaction is not involved in the transformation of (2) to (5).



(2) (5)

Scheme 4. (*i*) Refluxing MeCN

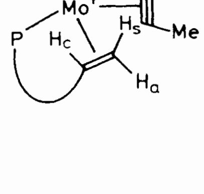
Examination of a molecular model of the intermediate (A) (Scheme 2) clearly showed that it was impossible for either of the two β-hydrogens bonded to C^4 to interact with the molybdenum, and therefore, unless the chelating phosphine dissociated from the metal, a β-hydrogen elimination process followed by a reductive elimination reaction seemed an unlikely pathway to (B). Since such an opening of a chelate ring is unlikely, we were led to consider one other interesting 1,3-H shift pathway, which does not involve transfer of the migrating hydrogen to the metal.

This alternative pathway is a metal-assisted suprafacial 1,3-H shift. In the intermediate (A) (Scheme 2) there is a molybdenum-substituted allyl fragment encompassing carbon atoms C^2, C^3, and C^4. The suprafacial migration of a hydrogen from C^4 to C^2 would be expected [18] to be a forbidden reaction; however, if it is assumed that the molybdenum donates electrons to the π^* orbital of the vinyl group C^2–C^3, then this could become sufficiently populated to facilitate a suprafacial 1,3-H shift. In this system once the intermediate (B) (Scheme 2) is formed it would be captured by collapsing to a 1,3-diene. Such a driving force is not available to the more common metal vinyl complexes, and for this reason it is possible their isomerisation to metal allyl species would not be observed.

Experimental

The ^{1}H, ^{13}C-{^{1}H}, and ^{31}P-{^{1}H} n.m.r. spectra were recorded on JEOL FX 90Q, or FX 200 spectrometers, as appropriate. Data given are for room-temperature measurements unless otherwise indicated and coupling constants are in Hz. Carbon-13 chemical shifts are relative to $SiMe_4$ with positive values to high frequency of the reference. Tris(acetylacetonato)-chromium(III) was added to reduce ^{13}C relaxation times. 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.

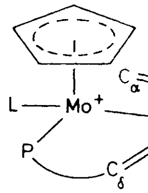
Reaction of o-*Diphenylphosphinostyrene with Bis(but-2-yne)-carbonyl(η-cyclopentadienyl)molybdenum*(II) *Tetrafluoroborate.*—A solution of dpps (0.6 g, 2 mmol) and [Mo(CO)$(MeC_2Me)_2$(η-C_5H_5)][BF_4] (1) (0.8 g, 2 mmol) in methylene chloride (40 cm^3) was heated under reflux for 48 h. The resultant red solution was filtered through Kieselguhr, the volume of the filtrate reduced *in vacuo*, and diethyl ether added giving red *crystals* of (2) (1.2 g, 90%) (Found: C, 53.6; H, 4.9. $C_{29}H_{28}BF_4MoP\cdot0.5CH_2Cl_2$ requires C, 53.4; H, 4.5%). N.m.r.: ^{1}H ([$^2H_6$]acetone), δ 7.9—7.2 (m, 14 H, aromatic H), 5.68 [d, 5 H, C_5H_5, ^3J(HP) 1.5], 5.56 (s, 2 H, CH_2Cl_2), 4.44 [ddd, 1 H, H_c, $J(H_cH_a)$ 14, $J(H_cH_s)$ 10.8, $J(H_cP)$ 2.8], 2.50 [dd, 1 H, H_s, $J(H_sH_c)$ 10.8, $J(H_sH_a)$ 3.2], 2.42 (s, 6 H, MeC≡), 0.88 [dd, 1 H, H_a, $J(H_aH_c)$ 14.0, $J(H_aH_s)$ 3.2]; ^{13}C-{^{1}H} (CD_3NO_2), δ 228.9 [d, Me*C*≡C, *J*(CP) 14.6], 153.2, 152.1, 147.6, 145.0, 140.5, 138.7, 137.7, 137.2, 134.0, 133.8, 133.4, 133.0, 132.5, 131.4, 131.1, 131.0, 130.7, 130.5, 130.1, 129.7, 129.5, 129.4, 102.5 (s, C_5H_5), 63.2 (*C*H=CH_2), 55.7 (CH_2Cl_2), 35.3 (CH=*C*H_2), 21.7 p.p.m. [d, *Me*C≡C, *J*(CP) 2.9]. On cooling to −90 °C the ^{1}H signal at 2.42 p.p.m. broadens then collapses, and at −90 °C two broad peaks appear at 3.42 and 1.44

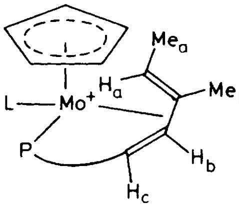


p.p.m. each of intensity 3 H. A coalescence temperature of −60 °C was observed.

Reaction of o-*Diphenylphosphinostyrene with Carbonyl*-(η-*cyclopentadienyl*)*bis*(3,3-*dimethylbut*-1-*yne*)*molybdenum*(II) *Tetrafluoroborate*.—Similarly, reaction of dpps (0.6 g, 2 mmol) and $[Mo(CO)(HC_2Bu^t)_2(\eta\text{-}C_5H_5)][BF_4]$ (3) (0.88 g, 2 mmol) in methylene chloride (40 cm^3) gave red *crystals* of (4) (1 g, 90%) (Found: C, 60.5; H, 5.3. $C_{31}H_{27}BF_4MoP$ requires C, 60.2; H, 5.2%). ^{1}H N.m.r. (CD_3NO_2): δ 10.18 [d, 1 H, HC≡C, *J*(HP) 25.5], 7.9—7.2 (m, 14 H, aromatic H), 5.67 [d, 5 H, C_5H_5, *J*(PH) 2], 4.48 (ddd, 1 H, H_c, *J*(H_cH_a) 14.3, *J*(H_cH_s) 11.0, *J*(H_cP) 3.0], 2.53 [dd, 1 H, H_s, *J*(H_sH_c) 11.0, *J*(H_sH_a) 3.2], 1.04 [dd, 1 H, H_a, *J*(H_aH_c) 14.3, *J*(H_aH_s) 3.2], and 1.52 p.p.m. (s, 9 H, Bu^tC≡C).

Reaction of (2) *with Acetonitrile*.—A solution of (2) (0.6 g, 1 mmol) in acetonitrile (50 cm^3) was heated under reflux for 24 h. Volatile material was removed *in vacuo*, and the residue dissolved in CH_2Cl_2 (20 cm^3), filtered through Kieselguhr, and diethyl ether added to give orange *crystals* of (5) (0.6 g, 90%) (Found: C, 59.3; H, 5.3; N, 1.9. $C_{31}H_{31}BF_4MoNP$ requires C, 59.0; H, 5.0; N, 2.2%). N.m.r.: ^{1}H (CD_3NO_2), δ 7.8—7.2 (m, 14 H, aromatic H), 5.57 [d, H_b (minor), *J*(HH) 8.8], 4.94 [d, C_5H_5 (major), *J*(HP) 0.7], 4.87 [d, C_5H_5 (minor), *J*(HP) 1.5], 4.80 [d, H_b (major), *J*(HH) 9.8], 4.15 [d, H_c (minor), *J*(HH) 9], 3.59 [d, H_c (major), *J*(HH) 9.8], 2.05 [d, MeCN (major), *J*(HP) 2], 1.86 [s, br, MeCN (minor)], 2.49 [s, Me_b (major)], 2.33 [s, Me_b (minor)], 1.80 [m, H_a (major)], 1.46 [m, H_a (minor)], 1.00 [d, Me_a (minor), *J*(HH) 6.3, *J*(HP) 0.7], 0.96 [dd, Me_a (major), *J*(HH) 6.4, *J*(HP) 1.0]; ^{13}C-{^{1}H} (CD_2Cl_2, −70 °C), δ 133—126 (m, aromatic C), 110.8 [C_β (minor)], 97.8 [C_β (major)], 92.6 [C_5H_5 (major)], 92.3 [C_5H_5 (minor)], 86.7 [d, C_δ (minor), *J*(CP) 4.6], 82.2 [d, C_δ (major), *J*(CP) 4.6], 78.0 [C_γ (major)], 73.4 [C_γ (minor)], 63.7 [C_α (major)], 2.04 [Me_b (major)], 20.1 [Me_b (minor)], 15.8 [Me_a (major or minor)], 4.2 [*Me*CN (major)], and 3.8 p.p.m. [*Me*CN (minor)]; ^{31}P-{^{1}H} (CH_2Cl_2), δ 90.6 [s, P (minor)], and 76.6 p.p.m. [s, P (major)].





Reaction of (5) *with* Bu^tCN.—An excess of Bu^tCN (5 cm^3) was added to a solution of (5) (0.6 g, 0.95 mmol) in CH_2Cl_2 (10 cm^3), and the resultant solution heated under reflux for 2 h. The volatile material was removed *in vacuo*, and the residue extracted into CH_2Cl_2, filtered through a Kieselguhr plug and diethyl ether added to give orange *crystals* of (6) (0.6 g, 94%) (Found: C, 60.2; H, 5.8; N, 2.1. $C_{34}H_{37}BF_4MoNP$ requires C, 60.6; H, 5.5; N, 2.1%). ^{1}H N.m.r. (CD_3NO_2): δ 7.6—6.9 (m, 14 H, aromatic H), 5.50 [d, H_b (minor), *J*(HH) 9.0], 4.80 [m, C_5H_5 (major)], 4.79 [m, C_5H_5 (minor)], 4.76 [d, H_b (major), *J*(HH) 9.0], 4.08 [d, H_c (minor), *J*(HH) 8.0], 3.48 [d, H_c (major), *J*(HH) 9.0], 2.50 [s, Me_b (major)], 2.32 [s, Me_b (minor)], 1.90 [m, H_a (major)], 1.20 [d, Me_a (major), *J*(HH) 6.0], and 0.97 p.p.m. [d, Me_a (minor), *J*(HH) 6.5].

Reaction of (5) *with Carbon Monoxide*.—An excess of CO was bubbled through a solution of (5) (0.6 g, 1 mmol) in CH_2Cl_2 (30 cm^3) for 30 min. There was no visible colour change, but the solution now exhibited a ν_{CO} band (2 002 cm^{-1}). The volume of the solvent was reduced *in vacuo* to 10 cm^3, and diethyl ether added giving yellow *crystals* of (7) (0.5 g, 85%) (Found: C, 55.0; H, 4.6. $C_{30}H_{28}BF_4MoOP$ requires C, 55.4; H, 4.4%); ν_{CO} (CH_2Cl_2) 2 002 s cm^{-1}. N.m.r.: ^{1}H (CD_3NO_2), δ 7.8—7.3 (m, 14 H, aromatic H), 5.98 [d, 1 H, H_b, *J*(HH) 8.5], 5.33 [d, 5 H, C_5H_5, *J*(HP) 1.0], 4.76 [d, 1 H, H_c, *J*(HH) 9.0], 2.36 (s, 3 H, Me_b), 1.78 (m, 1 H, H_a), 1.37 [d, 3 H, Me_a, *J*(HH) 7.0]; ^{13}C-{^{1}H} (CD_3NO_2), δ 221.7 [d, CO, *J*(CP) 10.3], 150.5, 150.2, 148.9, 141.1, 138.6, 136.5, 136.1, 134.5, 134.2, 134.0, 133.8, 133.3, 132.7, 132.6, 132.3, 131.1, 130.7, 130.1, 129.8, 119.9 (C_β), 94.5 (C_5H_5), 81.1 [d, C_δ, *J*(CP) 2.9], 77.8 (C_γ), 65.8 [d, C_α, *J*(CP) 4.4], 21.5 (Me_b), and 18.0 p.p.m. (Me_a).

Reaction of (5) *with Trimethyl Phosphite*.—Complex (5) (0.6 g, 1 mmol) was dissolved in CH_2Cl_2 (10 cm^3) and $P(OMe)_3$ (0.15 cm^3, 1 mmol) added dropwise. The reaction mixture slowly turned yellow. After 1 h at room temperature diethyl ether was added giving a precipitate of yellow *crystals* of (8) (0.6 g, 58%) (Found: C, 53.6; H, 5.2. $C_{32}H_{37}BF_4MoO_2P_2$ requires C, 53.8; H, 5.2%). N.m.r.: ^{1}H ($CDCl_3$), δ 7.8—7.2 (m, 14 H, aromatic H), 5.32 [dd, 1 H, H_b, *J*(HH) 8.9, *J*(HP) 3.9], 4.85 [dd, 5 H, C_5H_5, *J*(HP) 3.9, *J*(HP′) 1.0], 4.32 [dd, 1 H, H_c, *J*(HH) 8.9, *J*(HP) 23.3], 3.33 [d, 9 H, $P(OMe)_3$, *J*(HP) 10.4], 2.17 (s, 3 H, Me_b), 1.20 (m, 1 H, H_a), 0.92 [d, 3 H, Me_a, *J*(HH) 6.2]; ^{13}C-{^{1}H} (CD_3NO_2), δ 153.8, 153.7 152.4, 152.2, 141.3, 141.1, 140.5, 140.2, 139.4, 139.3, 138.4, 138.3, 138.2, 136.2, 134.2, 133.8, 133.4, 132.9, 132.8, 132.7, 131.5, 131.4, 130.5, 130.1, 129.7, 128.9, 128.6, 115.9 (C_β), 92.6 (C_5H_5), 81.5 [dd, C_δ, *J*(CP) 22.5, *J*(CP′) 4.9], 77.1 (C_γ), 60.9 [d, C_α, *J*(CP) 4.9], 55.4 [d, $P(OMe)_3$, *J*(CP) 8.8], 21.7 (Me_b), and 17.2 p.p.m. (Me_a); ^{31}P-{^{1}H} ($CDCl_3$), δ 161.3 [d, $P(OMe)_3$, *J*(PP) 37.8], and 81.7 p.p.m. [d, PPh_2, *J*(PP) 37.8].

Synthesis of α-[^{2}H]-o-*Diphenylphosphinostyrene*.—(*a*) α-[^{2}H]-(o-*bromophenyl*)*ethanol*. A solution of *o*-bromoacetophenone (50 g, 0.257 mmol) in diethyl ether (50 cm^3) was added dropwise over 1 h with stirring to a cooled (−35 °C) suspension of $LiAlD_4$ (2.5 g, 0.664 mmol) in Et_2O (150 cm^3). When the addition was complete the reaction mixture was allowed to warm to room temperature, and stirring continued for 2 h. Aqueous 10% NH_4Cl solution (50 cm^3) was added, the ether layer separated, dried (Na_2SO_4), and the solvent removed *in vacuo* to give α-[^{2}H]-(*o*-bromophenyl)ethanol (49 g, 97%). ^{1}H N.m.r. ($CDCl_3$); δ 7.52—6.8 (m, 4 H, aromatic), 4.12 (s, 1 H, OH), and 1.4 p.p.m. (s, 3 H, Me).

(*b*) α-[^{2}H]-o-*Bromostyrene*. The above carbinol was dehydrated by dropwise addition to fused $KHSO_4$ at 230 °C, using picric acid as a polymerisation inhibitor. The reaction was carried out in three batches of 15 g (3 g $KHSO_4$). The combined product was distilled to give α-[^{2}H]-*o*-bromostyrene (26 g, 62%) (b.p. 64—65 °C, 3 mmHg). ^{1}H N.m.r. ($CDCl_3$): δ 7.6—6.88 (m, 4 H, aromatic), 5.34 (d, 1 H, =CH_2, *cis*), and 5.66 (s, =CH_2, *trans*).

(*c*) α-[^{2}H]-o-*Diphenylphosphinostyrene*. This was prepared by the procedure described by Bennett *et al.*[8] for the protio-compound (65% yield). ^{1}H N.m.r. ($CDCl_3$): δ 7.7—6.8 (m, 4 H, aromatic), 5.08 (d, 1 H, =CH_2, *cis*), and 5.5 (d, 1 H, =CH_2, *trans*).

Crystal Structure Determinations.—Crystals suitable for diffraction measurements were grown from dichloromethane–diethyl ether. A crystal of (2), as its CH_2Cl_2 solvate, of approximate dimensions 0.4 × 0.3 × 0.2 mm was mounted in a thin-walled glass capillary under N_2 for structure analysis.

Table 5. Atomic co-ordinates ($\times 10^4$) for (2)

Atom	x	y	z	Atom	x	y	z
Mo(1)	8 358(1)	7 818(1)	0	C(19)	8 905(4)	8 818(8)	1 147(5)
P(1)	9 129(1)	6 109(2)	487(1)	C(20)	8 550(4)	9 924(8)	736(6)
C(1)	8 996(3)	5 119(7)	1 555(5)	C(21)	8 469(3)	8 804(8)	−1 207(5)
C(2)	9 252(3)	5 566(8)	2 373(5)	C(22)	8 967(3)	8 150(7)	−1 021(5)
C(3)	9 150(3)	4 770(8)	3 171(5)	C(23)	8 180(5)	9 745(12)	−1 915(7)
C(4)	8 816(3)	3 548(8)	3 158(5)	C(24)	9 572(4)	7 995(9)	−1 460(6)
C(5)	8 555(4)	3 085(9)	2 359(6)	C(25)	7 308(3)	8 278(10)	−76(9)
C(6)	8 642(3)	3 876(8)	1 544(5)	C(26)	7 442(3)	6 986(10)	−540(7)
C(7)	9 338(3)	4 663(7)	−280(4)	C(27)	7 657(3)	5 998(9)	95(8)
C(8)	9 068(3)	4 526(8)	−1 144(5)	C(28)	7 646(4)	6 679(11)	949(7)
C(9)	9 197(4)	3 391(9)	−1 697(6)	C(29)	7 428(3)	8 048(10)	837(7)
C(10)	9 609(5)	2 354(8)	−1 413(7)	C(30)	11 621(5)	11 760(13)	−988(9)
C(11)	9 871(5)	2 449(8)	−580(7)	Cl(1)	11 173(2)	10 319(3)	−1 375(2)
C(12)	9 747(3)	3 593(7)	12(7)	Cl(2)	12 266(2)	11 836(6)	−1 596(4)
C(13)	9 770(3)	7 271(8)	749(4)	B	11 581(7)	13 471(18)	1 349(11)
C(14)	10 369(3)	6 945(9)	671(5)	F(1)	11 457(4)	14 267(9)	603(6)
C(15)	10 780(3)	8 082(11)	861(6)	F(2)	12 067(7)	12 740(20)	1 045(9)
C(16)	10 576(4)	9 434(10)	1 126(5)	F(3)	11 819(7)	14 093(14)	2 037(7)
C(17)	9 972(4)	9 694(9)	1 218(5)	F(4)	11 197(7)	12 582(14)	1 495(10)
C(18)	9 567(3)	8 619(7)	1 036(4)				

Table 6. Atomic co-ordinates ($\times 10^4$) for (5)

Atom	x	y	z	Atom	x	y	z
Mo(1)	3 327(1)	1 209(1)	1 022(1)	C(13)	1 523(3)	819(4)	1 960(1)
P(1)	2 089(1)	2 240(1)	1 570(1)	C(14)	803(3)	−459(4)	1 806(1)
F(1)	−2 423(2)	−2 037(3)	477(1)	C(15)	413(3)	−1 564(4)	2 091(1)
F(2)	−2 522(2)	590(3)	500(1)	C(16)	732(3)	−1 431(4)	2 530(1)
F(3)	−719(2)	−635(2)	711(1)	C(17)	1 441(3)	−180(4)	2 690(1)
F(4)	−2 337(2)	−789(3)	1 123(1)	C(18)	1 833(3)	941(4)	2 404(1)
B(1)	−2 004(4)	−727(5)	705(1)	C(19)	656(3)	3 364(4)	1 401(1)
N(1)	1 752(2)	1 740(3)	583(1)	C(20)	750(3)	4 958(4)	1 306(1)
C(1)	2 814(3)	4 801(4)	485(1)	C(21)	−281(3)	5 781(4)	1 138(1)
C(2)	3 546(3)	3 956(4)	848(1)	C(22)	−1 419(4)	5 063(5)	1 062(1)
C(3)	4 593(3)	3 073(4)	770(1)	C(23)	−1 519(4)	3 489(5)	1 150(1)
C(4)	5 109(3)	3 003(4)	329(1)	C(24)	−493(4)	2 649(5)	1 320(1)
C(5)	5 194(3)	2 269(4)	1 129(1)	C(25)	2 482(4)	−1 209(5)	917(1)
C(6)	4 698(3)	2 206(4)	1 543(1)	C(26)	3 211(4)	−950(5)	556(1)
C(7)	4 271(3)	3 530(4)	1 811(1)	C(27)	4 441(4)	−872(5)	713(1)
C(8)	5 160(3)	4 600(4)	2 014(1)	C(28)	4 509(4)	−1 066(5)	1 167(1)
C(9)	4 689(3)	5 745(4)	2 282(1)	C(29)	3 300(4)	−1 311(5)	1 295(1)
C(10)	3 448(3)	5 827(4)	2 362(1)	C(30)	879(4)	2 066(5)	372(1)
C(11)	1 764(3)	4 826(4)	2 226(1)	C(31)	−220(4)	2 538(5)	102(1)
C(12)	3 021(3)	3 622(4)	1 892(1)				

Diffraction intensities in the range $3 < 2\theta < 55°$ were measured for a unique octant of reciprocal space at room temperature (293 K) on a Nicolet *P*3*m* diffractometer by methods previously described.[19] Of a total of 2 692 measured intensities, 2 228 unique reflections with $I > 2.0\sigma(I)$ were used in the solution and refinement of the structure. The structure was solved by standard heavy-atom methods (Patterson and difference-Fourier) and refined by blocked-cascade full-matrix least squares to give final residual indices $R = 0.040$ and $R' = 0.041$.* A value of 0.000 45 for g gave a variance function $w(F_o - |F_c|)^2$ which showed little variation with magnitude of F_o, sin θ, or reflection indices. All non-hydrogen atoms were refined without positional constraints, all but B, C(1), C(2), C(3), C(4), C(5), and C(6) being assigned anisotropic thermal parameters. All hydrogen atoms [except H(19) and H(20A) which had no positional constraints] were ascribed idealised geometries with C–H fixed at 0.96 Å, and assigned fixed isotropic thermal parameters. A final difference electron-density synthesis showed no features of chemical significance.

The structure analysis of (5) followed a closely similar course differing only in the following respects. The crystal used was of dimensions 0.2 × 0.2 × 0.1 mm. A quadrant of reciprocal space in the range $3 < 2\theta < 50°$ was scanned, yielding 4 944 independent reflection intensities. These were corrected for absorption effects by a numerical method and 3 828 data with $I > 3.0\sigma(I)$ were used in structure solution and refinement. Final residual indices were $R = 0.029$, $R' = 0.030$, with $g = 0.000\,3$. All non-hydrogen atoms were ascribed anisotropic thermal parameters and of the hydrogen atoms only H(2), H(5), and H(6) were refined without positional constraints.

Crystal data for (2) (*CH_2Cl_2 solvate*). $C_{30}H_{30}BCl_2F_4MoP$, $M = 674.61$, Orthorhombic, space group $Pna2_1$, $a = 22.324(5)$, $b = 9.249(3)$, $c = 14.566(3)$ Å, $Z = 4$, $U = 3\,007(1)$ Å^3, $D_c = 1.49$ g cm^3, $F(000) = 1\,368$, Mo-K_α *X*-radiation, graphite monochromator, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 6.07 cm^{-1}.

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* $R = \Sigma|F_o - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}|F_o - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$; $w = [\sigma^2(F_o^2)/4F_o^2 + gF_o^2]^{-1}$, with $\sigma(F_o^2)$ from counting statistics and g values as in text.

Crystal data for (5). $C_{31}H_{31}BF_4MoNP$, $M = 630.71$, Monoclinic, space group, $P2_1/c$, $a = 10.836(2)$, $b = 8.551(2)$, $c = 30.896(6)$ Å, $\beta = 94.80(2)°$, $Z = 4$, $U = 2\,853(1)$ Å^3, $D_c = 1.46$ g cm^{-3}, $F(000) = 1\,288$, Mo-K_α *X*-radiation, graphite monochromator, μ(Mo-K_α) = 5.5 cm^{-1}.

Listings of the final atomic positional co-ordinates are given in Tables 5 and 6 for (2) and (5), respectively. All calculations were carried out with programs of the SHELXTL package using the Nicolet R3m/E structure determination facility.

Acknowledgements

We thank Dr. S. G. Barnes for a preliminary experiment and the S.E.R.C. for support and for a studentship (to S. R. A.).

References

1 Part 28, S. R. Allen, M. Green, N. C. Norman, K. E. Paddick, and A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1983, 1625.
2 Y. Wakatsuki, K. Aoki, and H. Yamazaki, *J. Am. Chem. Soc.*, 1979, **101**, 1123.
3 P. Caddy, M. Green, E. O'Brien, L. E. Smart, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1980, 962.
4 L. D. Brown, K. Itoh, H. Susuki, K. Hirai, and J. A. Ibers, *J. Am. Chem. Soc.*, 1978, **100**, 8232.
5 S. J. McHain, R. R. Schrock, P. R. Sharp, M. R. Churchill, and W. J. Youngs, *J. Am. Chem. Soc.*, 1979, **101**, 263.
6 M. Bottrill and M. Green, *J. Chem. Soc., Dalton Trans.*, 1977, 2365.
7 S. R. Allen, P. K. Baker, S. E. Barnes, M. Green, L. Trollope, L. M. Muir, and K. W. Muir, *J. Chem. Soc., Dalton Trans.*, 1981, 873.
8 M. A. Bennett, R. S. Nyholm, and J. D. Saxby, *J. Organomet. Chem.*, 1967, **10**, 301; L. V. Interrante and G. V. Nelson, *Inorg. Chem.*, 1968, **7**, 2059.
9 K. A. Mead, H. Morgan, and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1983, 271.
10 H. Luth, M. R. Truter, and A. Robson, *J. Chem. Soc. A*, 1969, 28.
11 J. N. Murrell, S. F. A. Kettle, and J. M. Tedder, 'Valence Theory,' 2nd edn., J. Wiley, London, 1970.
12 B. E. R. Schilling, R. Hoffmann, and D. L. Lichtenberger, *J. Am. Chem. Soc.*, 1979, **101**, 585.
13 B. E. R. Schilling, R. Hoffmann, and J. W. Faller, *J. Am. Chem. Soc.*, 1979, **101**, 592.
14 A. Stockis and R. Hoffmann, *J. Am. Chem. Soc.*, 1980, **102**, 2952.
15 J. W. Faller and A. M. Rosan, *J. Am. Chem. Soc.*, 1977, **99**, 4858.
16 M. Brookhart, J. R. Tucker, and G. R. Husk, *J. Am. Chem. Soc.*, 1983, **105**, 258.
17 A. Cutler, R. W. Fish, W. P. Giering, and M. Rosenblum, *J. Am. Chem. Soc.*, 1972, **94**, 4354.
18 R. Hoffmann and R. B. Woodward, 'The Conservation of Orbital Symmetry,' Verlag Chemie GmbH, Weinheim, 1970.
19 A. Modinos and P. Woodward, *J. Chem. Soc., Dalton Trans.*, 1974, 2065.

Received 18*th May* 1983; *Paper* 3/800