Reactions of Co-ordinated Ligands. Part 44.[1] The Reactivity of the Carbyne Complex $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$ towards Protonic Acids, Diphenylphosphine, and the π-Acid Tetracyanoethylene; Formation and Crystal Structures of $[MoH(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$, $[Mo\{\sigma-OC(O)CF_3\}\{\eta^2-HOC(O)CF_3\}\{P(OMe)_3\}_2(\eta-C_5H_5)]$, and $[Mo(\equiv CCH_2Bu^t)\{\eta^2-C_2(CN)_4\}\{P(OMe)_3\}(\eta-C_5H_5)]$ †

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Reaction of $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$ with $HBF_4\cdot(MeCO)_2O$ affords the crystallographically identified hydrido–carbyne $[MoH(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$ [Mo–H, 1.74(3) Å]. In contrast, reaction with CF_3CO_2H or CF_3SO_3H leads to loss of the carbyne fragment and the formation of $[Mo\{\sigma-OC(O)CF_3\}\{\eta^2-HOC(O)CF_3\}\{P(OMe)_3\}_2(\eta-C_5H_5)]$ and $[Mo(\sigma-OSO_2CF_3)(\eta^2-HOSO_2CF_3)\{P(OMe)_3\}_2(\eta-C_5H_5)]$, the former being structurally identified by *X*-ray crystallography. The reaction of $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$ with Ph_2PH and tetracyanoethylene was also examined. The phosphine reaction also leads to loss of the CCH_2Bu^t group, with formation of $[Mo(PPh_2)(HPPh_2)\{P(OMe)_3\}(\eta-C_5H_5)]$ and $[Mo(PPh_2)\{P(OMe)_3\}_2(\eta-C_5H_5)]$. Both of these complexes are also formed on reaction of Ph_2PH with $[Mo(\eta^3-1-MeC_3H_4)\{P(OMe)_3\}_2(\eta-C_5H_5)]$. Tetracyanoethylene reacts at room temperature with the carbyne to displace one of the trimethyl phosphite ligands with formation of the *X*-ray crystallographically characterised alkene–carbyne complex $[Mo(\equiv CCH_2Bu^t)\{\eta^2-C_2(CN)_4\}\{P(OMe)_3\}(\eta-C_5H_5)]$. The carbon–carbon bond of the co-ordinated tetracyanoethylene is orthogonal to the Mo≡C vector.

In 1977 we reported[2] that protonation of the electron rich carbyne $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)]$ (**1**) leads to the formation of the cationic hydrido species $[MoH(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$. This was of particular interest because although carbyne complexes had been known[3] since 1973 there had been no previously published studies of their reactivity towards electrophilic reagents. This observation raised the interesting question as to whether protonation occurred directly on the molybdenum centre or on the carbyne carbon, followed by hydrogen transfer to the metal, *i.e.* an α-hydrogen elimination reaction. The problem of the identity of the initial site of electrophilic attack was further emphasised by subsequent reports that $[W(\equiv CH)(PMe_3)_4Cl]$ reacts with CF_3SO_3H to give $[W(=CH_2)(PMe_3)_4Cl][CF_3SO_3]$, whereas $[W(\equiv CH)(Me_2PCH_2CH_2PMe_2)_2Cl]$ forms $[WH(\equiv CH)(Me_2PCH_2CH_2PMe_2)_2Cl][CF_3SO_3]$.[4] In addition, it was shown[5] that $[Os(\equiv CPh)(CO)(PPh_3)_2Cl]$ reacts with HCl to give $[Os(=CHPh)(CO)(PPh_3)_2Cl_2]$, which parallels the finding[6,7] that treatment of $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ with aqueous HI affords the iodocarbene complex $[W(=CHC_6H_4Me-4)(I)(CO)_2(\eta-C_5H_5)]$. Thus protonation seemed to be able to occur at either carbon or the metal; moreover, there was the potential for the occurrence of more complex reactions, as shown by the observations that reaction of $HBF_4\cdot Et_2O$ or HCl–Et_2O with $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ gives, respectively, $[W_2(\mu-H)(\mu-RC_2R)(CO)_4(\eta-C_5H_5)_2]^{6,7}$ ($R = C_6H_4Me-4$) and $[WCl_2\{\eta^2-C(CH_2R)=O\}(CO)(\eta-C_5H_5)]^8$ ($R = C_6H_4Me-4$). In this paper we present a full account of our study[9] of the reactivity of $HBF_4\cdot(MeCO)_2O$, CF_3SO_3H, and CF_3CO_2H towards the carbyne (**1**), and also the extension of our investigations to include reactions between (**1**) and the weak proton acid Ph_2PH, and the π-acid tetracyanoethylene.

Results and Discussion

Addition of $HBF_4\cdot(MeCO)_2O$ to a solution of (**1**) in Et_2O cooled to −78 °C led to a rapid loss of colour and the formation (83% yield) of the white crystalline cationic complex $[MoH(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta-C_5H_5)][BF_4]$, (**2**). Elemental analysis and ^1H and $^{13}C-\{^1H\}$ n.m.r. spectroscopy (see Experimental section) suggested that (**2**) had the hydridocarbyne structure illustrated in Scheme 1. Since such species were unknown at the time a low-temperature (200 K) *X*-ray diffraction study was carried out on a single crystal of (**2**) as its BF_4 salt. This established the structure of the cation shown in Figure 1, selected bond lengths and angles being listed in Table 1. Thus, (**2**) is in fact a cationic hydridocarbyne, the hydride being located at 1.74(3) Å from the molybdenum in a position bisecting the two trimethyl phosphite ligands and *trans* to the carbyne ($\equiv CCH_2Bu^t$) group. The refined Mo–H distance compares with those found for other terminally bonded molybdenum–hydrides in well determined *X*-ray[10–13] and neutron diffraction[14] studies.

Comparison between the molecular parameters of (**2**) and the parent carbyne (**1**)[15] also supports the hydrido–carbyne formulation. The interligand angle between the trimethyl phosphite ligands in (**2**) is much greater, 121.9(1)°, than that of 93.5(1)° found in (**1**). This opening out is explained by the need to accommodate the hydride ligand. The Mo≡C triple bond length in (**2**) is identical [1.798(2) Å] to that found[15] in (**1**). The carbyne unit is linear, Mo–C(7)–C(8) = 170°, providing further evidence that the α-carbon C(7) is not involved in an unusual interaction with a hydrogen atom. The mean Mo–P distance of 2.390(1) Å in (**2**) is considerably longer than that observed

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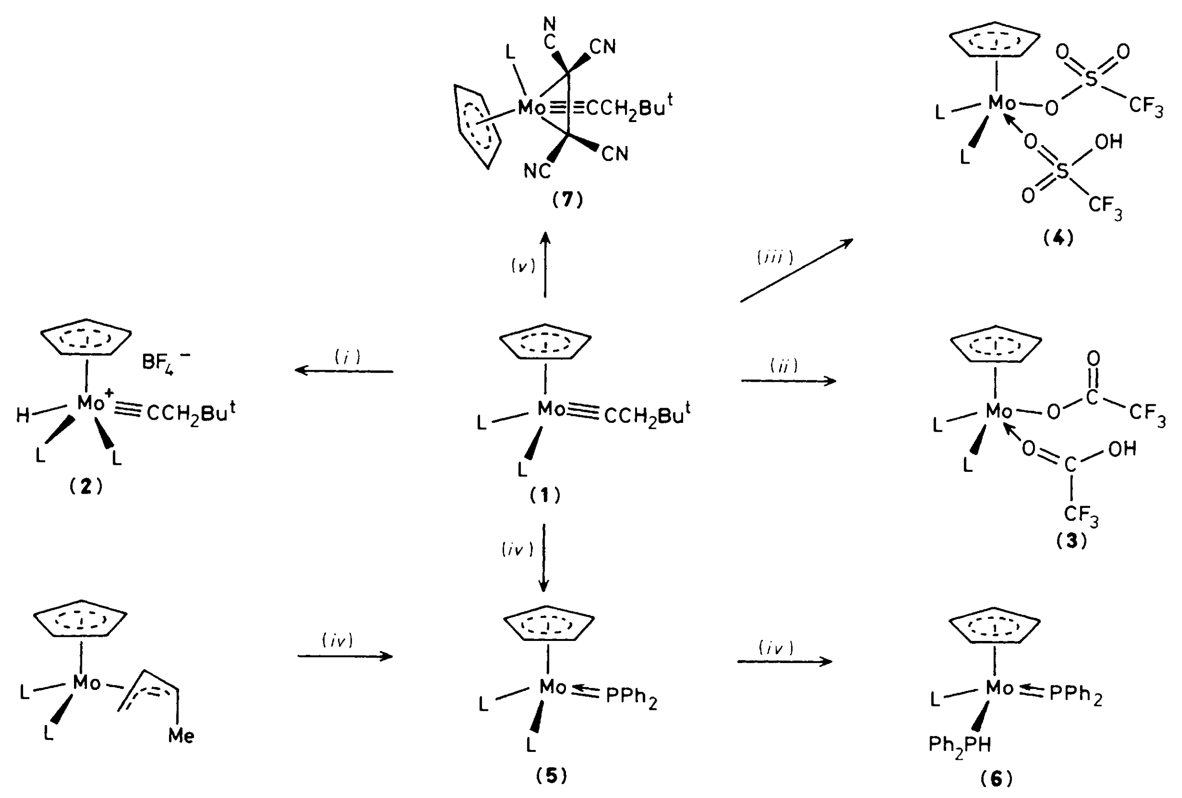
† (η-Cyclopentadienyl)hydrido(t-butylmethylmethylidyne)bis(trimethyl phosphite)molybdenum tetrafluoroborate, (η-cyclopentadienyl)(trifluoroacetato)(trifluoroacetic acid)bis(trimethyl phosphite)molybdenum, and (η-cyclopentadienyl)(t-butylmethylmethylidyne)(η^2-tetracyanoethylene)(trimethyl phosphite)molybdenum.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



Scheme 1. L = P(OMe)$_3$. (*i*) HBF$_4$·(MeCO)$_2$O; (*ii*) CF$_3$CO$_2$H; (*iii*) CF$_3$SO$_3$H; (*iv*) Ph$_2$PH; (*v*) (CN)$_2$C=C(CN)$_2$

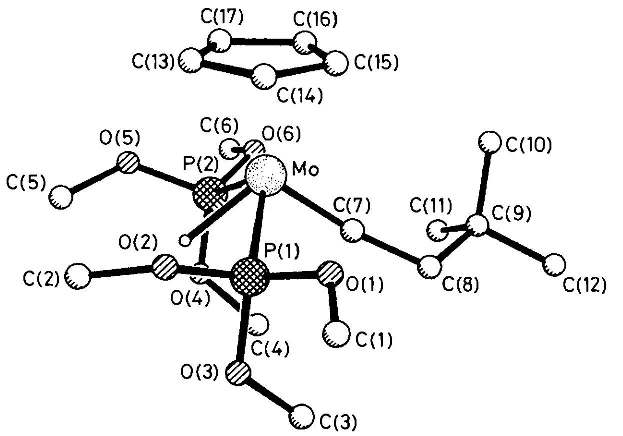


Figure 1. Structure of [MoH(≡CCH$_2$Bu^t){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)][BF$_4$], (2)

[2.329(1) Å] for the parent carbyne (**1**), presumably a consequence of the increased co-ordination number and higher oxidation state of molybdenum in (**2**).

Following these observations it was interesting to examine whether the choice of the proton source had an influence on the course of the reaction. Addition of trifluoroacetic acid to a stirred solution of (**1**) in diethyl ether at −78 °C resulted, on warming to room temperature, in a change in colour of the reaction mixture from yellow to orange-red. When the solvent was removed and the resultant red oil recrystallised (0 °C, Et$_2$O–pentane), orange crystals of [Mo{σ-OC(O)CF$_3$}{η^2-HOC(O)CF$_3$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)], (**3**), were formed. Examination of the ^{1}H n.m.r. spectrum of (**3**) showed signals corresponding to the presence of cyclopentadienyl and trimethyl phosphite ligands. However, there were no resonances attributable to the CH$_2$Bu^t group or any organic fragment derived from this, indicating that cleavage of this fragment had taken place. There was also a further ^{1}H signal, integrating for one proton, at 7.67 p.p.m., which appeared as a triplet, presumably due to coupling to two equivalent phosphorus nuclei, with *J*(HP) 78 Hz. A parallel study of the reaction of (**1**) with CF$_3$SO$_3$H gave (**4**), [Mo(σ-OSO$_2$CF$_3$)(η^2-HOSO$_2$CF$_3$){P(OMe)$_3$}$_2$(η-C$_5$H$_5$)], an analogous product to (**3**). Again the ^{1}H n.m.r. spectrum showed no resonances corresponding to a CH$_2$Bu^t fragment but did include an acidic proton triplet signal at 8.94 p.p.m. [*J*(HP) 76 Hz]. The ^{13}C-{^{1}H} n.m.r. spectrum showed, in addition to η-C$_5$H$_5$ and P(OMe)$_3$ signals, a quartet centred at 119.4 p.p.m. [*J*(CF) 319 Hz] attributable to the presence of a CF$_3$SO$_3$ group; this being confirmed by the ^{19}F n.m.r. spectrum which consisted of a singlet at −78 p.p.m.

In order to determine the nature of these compounds a single crystal *X*-ray study was carried out on (**3**); the resulting structure is illustrated in Figure 2(*a*) and (*b*), and selected bond lengths and angles are listed in Table 2. Although the data were collected at low temperature, the structure refined to a final *R* of only 0.075 due to disorder of a CF$_3$CO$_2$ moiety, and the structures in Figure 2(*a*) and (*b*) illustrate the molecular geometries of the major (62%) and minor (38%) conformers respectively. The molybdenum has a four-legged piano-stool geometry where the two P(OMe)$_3$ ligands are *cisoid*; P–Mo–P 89.0(1)°. The other two sites are occupied by two monodentate trifluoroacetate groups, one of which is disordered. The low accuracy of the structure and the problem of disorder meant that direct location of the acidic hydrogen, which had been observed by ^{1}H n.m.r., and was required for neutrality of the complex, was not possible. The geometry of the disordered CF$_3$CO$_2$ ligand suggested that the hydrogen is associated with

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

Mo–P(1)	2.378(1)	Mo–P(2)	2.401(1)
Mo–C(7)	1.798(2)	Mo–C(13)	2.431(3)
Mo–C(14)	2.375(2)	Mo–C(15)	2.353(2)
Mo–C(16)	2.355(2)	Mo–C(17)	2.400(2)
Mo–H	1.738(23)	P(1)–O(1)	1.579(1)
P(1)–O(2)	1.592(2)	P(1)–O(3)	1.591(2)
P(2)–O(4)	1.596(2)	P(2)–O(5)	1.592(1)
P(2)–O(6)	1.581(1)	F(1)–B	1.392(3)
F(2)–B	1.390(3)	F(3)–B	1.380(3)
F(4)–B	1.365(3)	O(1)–C(1)	1.455(3)
O(2)–C(2)	1.445(2)	O(3)–C(3)	1.438(4)
O(4)–C(4)	1.425(3)	O(5)–C(5)	1.443(3)
O(6)–C(6)	1.462(2)	C(7)–C(8)	1.485(3)
C(8)–C(9)	1.550(3)	C(8)–H(8a)	0.917(19)
C(8)–H(8b)	1.011(23)	C(9)–C(10)	1.525(3)
C(9)–C(11)	1.525(3)	C(9)–C(12)	1.536(3)
C(13)–C(14)	1.415(3)	C(13)–C(17)	1.404(3)
C(14)–C(15)	1.415(3)	C(15)–C(16)	1.413(3)
C(16)–C(17)	1.419(3)		
P(2)–Mo–C(13)	107.1(1)	C(7)–Mo–C(13)	154.5(1)
P(1)–Mo–C(14)	82.8(1)	P(2)–Mo–C(14)	140.3(1)
C(7)–Mo–C(14)	122.8(1)	C(13)–Mo–C(14)	34.2(1)
P(1)–Mo–C(15)	104.5(1)	P(2)–Mo–C(15)	133.3(1)
C(7)–Mo–C(15)	97.2(1)	C(13)–Mo–C(15)	57.4(1)
C(14)–Mo–C(15)	34.8(1)	P(1)–Mo–C(16)	138.4(1)
P(2)–Mo–C(16)	98.4(1)	C(7)–Mo–C(16)	104.0(1)
C(13)–Mo–C(16)	57.3(1)	C(14)–Mo–C(16)	57.7(1)
C(15)–Mo–C(16)	34.9(1)	P(1)–Mo–C(17)	131.6(1)
P(2)–Mo–C(17)	85.2(1)	C(7)–Mo–C(17)	136.7(1)
C(13)–Mo–C(17)	33.8(1)	C(14)–Mo–C(17)	56.8(1)
C(15)–Mo–C(17)	57.5(1)	C(16)–Mo–C(17)	34.7(1)
P(1)–Mo–H	63.9(7)	P(2)–Mo–H	61.2(7)
C(7)–Mo–H	106.0(8)	Mo–P(1)–O(1)	110.3(1)
Mo–P(1)–O(2)	116.2(1)	O(1)–P(1)–O(2)	101.5(1)
Mo–P(1)–O(3)	121.8(1)	O(1)–P(1)–O(3)	106.0(1)
O(2)–P(1)–O(3)	98.6(1)	Mo–P(2)–O(4)	120.5(1)
Mo–P(2)–O(5)	116.3(1)	O(4)–P(2)–O(5)	99.3(1)
Mo–P(2)–O(6)	111.2(1)	O(4)–P(2)–O(6)	106.2(1)
O(5)–P(2)–O(6)	101.1(1)	F(1)–B–F(2)	109.0(2)
F(1)–B–F(3)	109.3(2)	F(2)–B–F(3)	109.2(2)
F(1)–B–F(4)	110.8(2)	F(2)–B–F(4)	108.6(2)
F(3)–B–F(4)	109.8(2)	P(1)–O(1)–C(1)	121.5(1)
P(1)–O(2)–C(2)	120.9(1)	P(1)–O(3)–C(3)	122.7(1)
P(2)–O(4)–C(4)	124.2(1)	P(2)–O(5)–C(5)	121.7(1)
P(2)–O(6)–C(6)	120.9(1)	Mo–C(7)–C(8)	170.0(1)
C(7)–C(8)–C(9)	116.4(1)	C(7)–C(8)–H(8a)	103.9(15)
C(9)–C(8)–H(8a)	111.2(14)	C(7)–C(8)–H(8b)	110.5(14)
C(9)–C(8)–H(8b)	106.9(14)	H(8a)–C(8)–H(8b)	107.6(18)
C(8)–C(9)–C(10)	110.5(2)	C(8)–C(9)–C(11)	110.3(2)
C(8)–C(9)–C(12)	107.5(2)		

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

Mo–P(1)	2.403(3)	Mo–P(2)	2.413(3)
Mo–O(7)	2.157(8)	Mo–O(9′)	2.18(3)
Mo–O(9)	2.109(12)	Mo–C(11)	2.384(10)
Mo–C(12)	2.383(11)	Mo–C(13)	2.302(11)
Mo–C(14)	2.251(10)	Mo–C(15)	2.264(10)
P(1)–O(1)	1.562(9)	P(1)–O(2)	1.625(9)
P(1)–O(3)	1.571(9)	P(2)–O(4)	1.589(8)
P(2)–O(5)	1.596(7)	P(2)–O(6)	1.587(8)
F(1)–C(8)	1.30(3)		1.33(3)
		F(5′)–C(10)	1.30(3)
		F(5)–C(10)	1.25(2)
F(6)–C(10)	1.33(2)	O(1)–C(1)	1.46(2)
O(2)–C(2)	1.42(2)	O(3)–C(3)	1.41(3)
O(4)–C(4)	1.412(14)	O(5)–C(5)	1.439(13)
O(6)–C(6)	1.441(15)	O(7)–C(7)	1.280(15)
		O(9′)–C(9′)	1.18(4)
O(9)–C(9)	1.13(3)	O(10′)–C(9′)	1.27(5)
O(10)–C(9)	1.22(3)	C(7)–O(8)	1.17(2)
C(8)–F(2)	1.32(2)	C(8)–F(3)	1.27(3)
C(8)–C(7)	1.57(2)		
C(10)–F(6′)	1.41(3)	C(10)–F(4)	1.31(2)
C(10)–C(9′)	1.38(4)	C(10)–C(9)	1.55(3)
C(11)–C(12)	1.361(15)	C(11)–C(15)	1.397(14)
C(12)–C(13)	1.430(15)	C(13)–C(14)	1.416(15)
C(14)–C(15)	1.432(14)		
P(1)–Mo–P(2)	89.0(1)	P(1)–Mo–O(7)	139.8(2)
P(2)–Mo–O(7)	87.6(2)	P(1)–Mo–O(9′)	74.6(6)
P(2)–Mo–O(9′)	142.2(6)	O(7)–Mo–O(9′)	84.1(7)
P(1)–Mo–O(9)	84.3(3)	P(2)–Mo–O(9)	138.1(3)
O(7)–Mo–O(9)	72.2(4)		
Mo–P(1)–O(1)	113.4(3)	Mo–P(1)–O(2)	118.8(3)
O(1)–P(1)–O(2)	97.2(5)	Mo–P(1)–O(3)	118.1(4)
O(1)–P(1)–O(3)	109.8(5)	O(2)–P(1)–O(3)	96.7(5)
Mo–P(2)–O(4)	119.8(3)	Mo–P(2)–O(5)	112.4(3)
O(4)–P(2)–O(5)	100.9(4)	Mo–P(2)–O(6)	117.6(3)
O(4)–P(2)–O(6)	97.5(4)	O(5)–P(2)–O(6)	106.2(4)
P(1)–O(1)–C(1)	122.5(8)	P(1)–O(2)–C(2)	123.7(8)
P(1)–O(3)–C(3)	125.7(9)	P(2)–O(4)–C(4)	125.5(7)
P(2)–O(5)–C(5)	120.9(7)	P(2)–O(6)–C(6)	122.9(7)
Mo–O(7)–C(7)	126.6(8)	Mo–O(9)–C(9)	142.9(13)
Mo–O(9′)–C(9′)	144.0(3)		

its unco-ordinated oxygen (at least in the solid state).* The acetate moiety, which was unaffected by disorder, had C–O bond lengths of 1.280(15) Å and 1.17(2) Å for the co-ordinated and unco-ordinated oxygens respectively, these being due to C–O single and double bonds. In the two orientations of the disordered acetate the longer C–O bond is associated with the unco-ordinated oxygen [C(9)–O(9) 1.13(3), C(9)–O(10) 1.22(3), and C(9′)–O(9′) 1.18(4), C(9′)–O(10′) 1.27(5) Å].

In both of these reactions, the carbyne fragment is lost and it is interesting to note that the corresponding counter anion, *i.e.* CF_3CO_2 or CF_3SO_3, has the potential to bond onto the molybdenum centre. In order to explore further this idea the reaction of (**1**) with diphenylphosphine was also examined where, in principle, the molecule Ph_2PH could serve both as a source of a proton and of a diphenylphosphide ligand. The carbyne (**1**) reacted slowly (60 h) with Ph_2PH in toluene at 353 K to afford two complexes [(**5**) and (**6**), see Scheme 1], which were separated by column chromatography, and identified by elemental analysis and n.m.r. spectroscopy. Again the carbyne fragment has been lost and, as illustrated, both (**5**) and (**6**) (see Scheme 1) carry three electron-donor diphenylphosphide[16–18] ligands. The same complexes are also formed on reaction of Ph_2PH with the relatively electron rich η^3-allyl complex $[Mo(\eta^3\text{-}1\text{-}MeC_3H_4)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$,[19] presumably *via* loss of butene. It was also found that the yield of (**6**) could be improved at the expense of (**5**) by using an excess of Ph_2PH leading to an easier displacement of a trimethyl phosphite ligand from (**5**).

The formation of complexes (**2**), (**3**), (**4**), and (**5**) can be explained if it is assumed that the carbyne (**1**) reacts with HX (X = BF_4, CF_3CO_2, CF_3SO_3, or PPh_2) by proton transfer to the carbyne carbon atom resulting in the formation of the cationic carbene complex (**A**) (Scheme 2) which is stabilised by an agostic Mo–μ-HC interaction. In the case of the formation of (**2**), the tetrafluoroborate anion does not co-ordinate onto the molybdenum centre of (**A**) so that complete hydrogen transfer to the metal can occur with formation of the hydridocarbyne. In

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* The value of the $J(HP)$ coupling constant and the appearance of only one ^{19}F signal in the spectrum of (**4**) suggests that, in solution, the hydrogen might be associated with the molybdenum.

contrast, in the presence of co-ordinating anions (CF$_3$CO$_2$, CF$_3$SO$_3$, or Ph$_2$P) the intermediate (**A**) can collapse to the carbene complexes (**B**) or (**C**), which can then either undergo a 1,2-hydrogen shift process to form labile η^2-alkene (CH$_2$=CH-Bu^t) complexes, forming (**3**), (**4**), or (**5**) *via* dissociative loss of the alkene, or undergo further protonation to form, successively, an alkyl ligand and alkane. Attempts to detect which organic product was formed were unsuccessful. The alternative pathway to these molecules, involving initial attack by a proton on the metal followed by transfer to the carbyne carbon can be excluded by the observation that neither CF$_3$CO$_2^-$, CF$_3$SO$_3^-$, or Ph$_2$P$^-$ react with the cation (**2**) to form (**3**), (**4**), or (**5**) respectively.

Recent theoretical work[20] suggests that these findings are best interpreted in terms of kinetic, charge-controlled attack by a proton on the carbyne carbon. The calculations[20] on [Mn(CR)(CO)$_2$(η-C$_5$H$_5$)]$^+$, isoelectronic with (**1**), show that the highest occupied molecular orbital (h.o.m.o.) is largely located on the metal, there being a build-up of negative charge on the carbyne carbon. Extended Hückel m.o. calculations[21] confirm this picture for the model complex [Mo(CCH$_2$Bu^t){P(OH)$_3$}$_2$(η-C$_5$H$_5$)], with net charges on Mo and carbyne carbon of +0.93 and −0.34 e (e = 1.6 × 10^{-19} C) respectively.

Finally, the range of electrophilic reagents was extended to include tetracyanoethylene (tcne), a π acid with a potential for undergoing one-electron transfer reactions. Treatment of (**1**) with (NC)$_2$C=C(CN)$_2$ in methylene chloride as solvent resulted in a rapid colour change from yellow to green. Column chromatography followed by crystallisation afforded a pink crystalline complex (**7**) (Scheme 1). Elemental analysis and n.m.r. spectroscopy showed that tetracyanoethylene had displaced one trimethyl phosphite ligand from (**1**), the ^{13}C-{^{1}H} spectrum of (**7**) showing a doublet centred at 338.9 p.p.m. consistent with the presence of a carbyne moiety co-ordinated

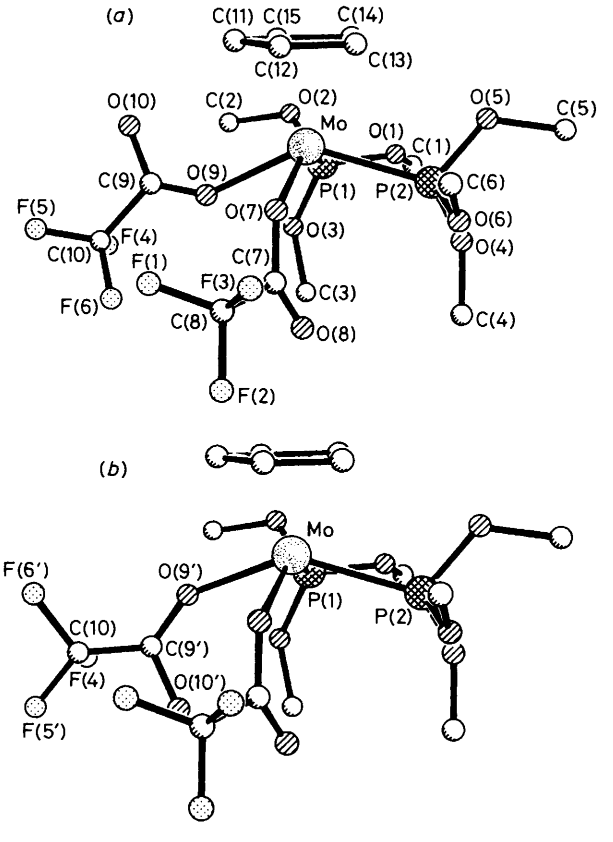
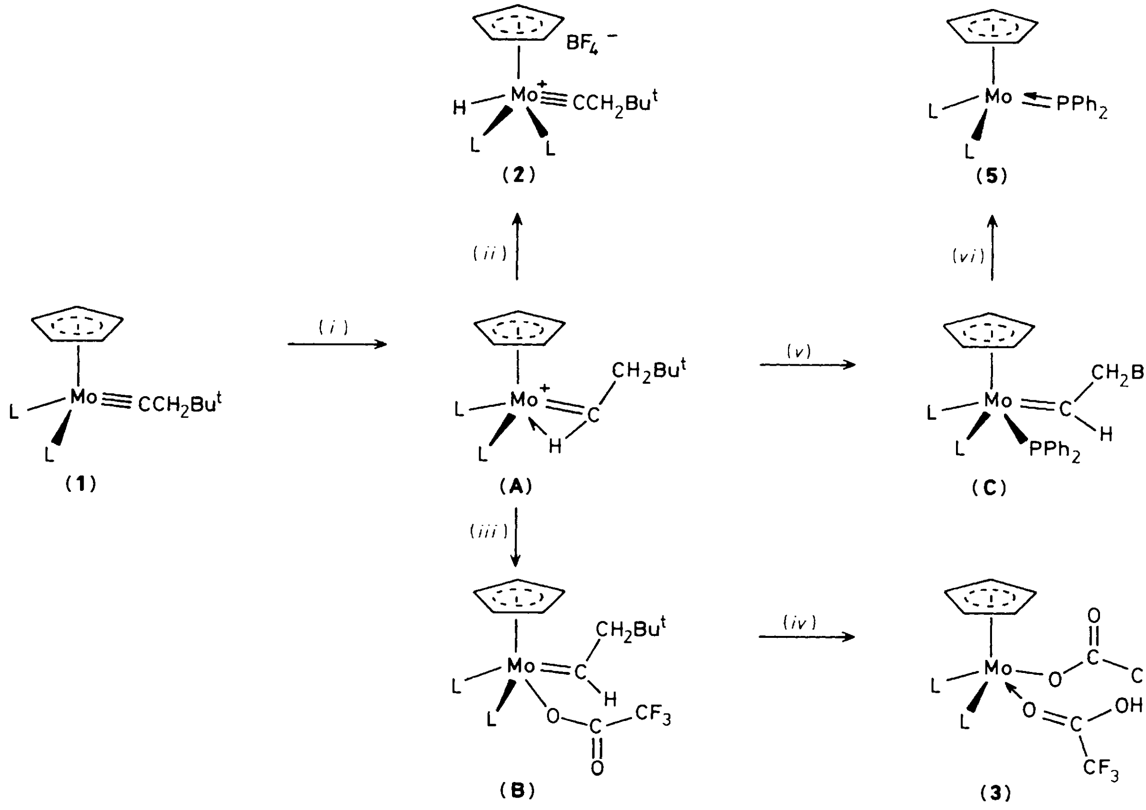


Figure 2. Structure of [Mo{σ-OC(O)CF$_3$}{η^2-HOC(O)CF$_3$}{P(OMe)$_3$}$_2$(η-C$_5$H$_5$)] (**3**): (*a*) major conformer; (*b*) minor conformer



Scheme 2. L = P(OMe)$_3$. (*i*) H$^+$; (*ii*) BF$_4^-$; (*iii*) CF$_3$CO$_2^-$; (*iv*) + CF$_3$CO$_2$H, −Bu^{t}CH=CH$_2$; (*v*) PPh$_2^-$; (*vi*) −Bu^{t}CH=CH$_2$

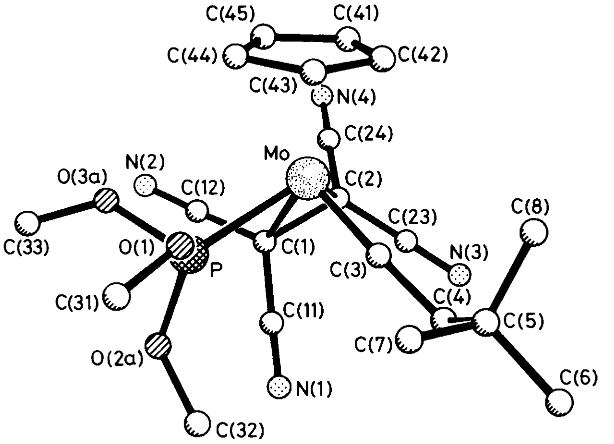


Figure 3. Structure of $[Mo(\equiv CCH_2Bu^t)\{\eta^2\text{-}C_2(CN)_4\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (**7**)

onto a $MoP(OMe)_3$ fragment. In order structurally to identify this molecule an *X*-ray diffraction study was carried out which established the molecular geometry shown in Figure 3, with selected bond lengths and angles listed in Table 3.

As expected one of the trimethyl phosphite ligands of (**1**) has been replaced by an η^2-bonded tetracyanoethylene molecule, the alkene double bond being orthogonal to the molybdenum–carbyne bond, thus maximising π bonding to the molybdenum by both the tetracyanoethylene and the carbyne ligand. The molybdenum to carbyne contact carbon distance Mo–C(3) 1.774(5) Å is slightly shorter than found[15] in (**1**) [1.796(2) Å] with a Mo–C(3)–C(4) angle of 177.1(5)° [176.7(2)° in (**1**)]. The lone phosphite ligand showed disorder in two of the three methoxy groups. Thus the resulting bond lengths and angles within the phosphite ligand are less reliable. The Mo–P bond of 2.427(2) Å is long, reflecting the exceptional π-acceptor capability of the tetracyanoethylene ligand. This property is also reflected by the long C(1)–C(2) bond of 1.512(7) Å, which together with the short Mo–C(1) and Mo–C(2) contacts of 2.243(5) Å and 2.210(5) Å indicates a strong π-interaction. The planarity of the $(NC)_2C{=}C(CN)_2$ ligand is lost on co-ordination, the four cyano substituents all being bent away from the molybdenum. The angle between the normals to the planes of C(11)–C(1)–C(12) and C(23)–C(2)–C(24), representing the two halves of the ligand is 74.1°. The crystal chosen for study contains only the enantiomer of (**7**) shown in Figure 3.

Thus, these structural studies established that the molecule (**7**) is an alkene–carbyne complex, the only previous examples of this type of complex being the partially characterised $[W(\equiv CH)(\eta^2\text{-}C_2H_4)(PMe_3)_3][CF_3SO_3]$,[22] the anionic complexes $[NEt_4][W(\equiv CR)Cl_2(\eta^2\text{-alkene})(py)(CO)]$[23] (alkene = maleic anhydride, fumaronitrile; R = Me or Ph; py = pyridine) and the *X*-ray crystallographically identified molecule $[W(\equiv CPh)Cl\{OC(O)CH{=}CHCO\}(py)_2(CO)]$[23] where the alkene also lies orthogonal to the W≡CPh vector, as in (**7**). The observation of only three resonances attributable to the tcne ligand in (**7**) in its room temperature ^{13}C n.m.r. spectrum is consistent with rapid rotation about the Mo–alkene bond on the n.m.r. time-scale, leading to one contact carbon and two cyano carbon environments.

Previously we have shown[24] that the phosphite ligands present in the carbyne complex (**1**) do not dissociate even at 373 K, and therefore, the obvious mechanism for the formation of (**7**) by capture of a co-ordinatively unsaturated $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ species by tetracyanoethylene can be excluded. However, a possible insight into the mode of formation of (**7**) came from preliminary cyclic voltammetry studies in methylene chloride which showed that (**1**) undergoes a facile, reversible one-electron oxidation process (E_p −0.11 V). Clearly, tetracyanoethylene could oxidise (**1**) to form a radical cation which might then readily undergo dissociative loss of trimethyl phosphite before reacting with tcne radical anion.

Table 3. Selected bond lengths (Å) and angles (°) for (**7**)

Mo–P	2.427(2)	Mo–C(1)	2.243(5)
Mo–C(2)	2.210(5)	Mo–C(3)	1.774(5)
Mo–C(41)	2.395(6)	Mo–C(42)	2.346(7)
Mo–C(43)	2.341(6)	Mo–C(44)	2.409(7)
Mo–C(45)	2.438(7)	P–O(1)	1.543(4)
P–O(2a)	1.593(6)	P–O(2b)	1.632(9)
P–O(3a)	1.644(7)	P–O(3b)	1.605(10)
O(1)–C(31)	1.408(11)		
		O(2a)–C(32)	1.402(10)
O(2b)–C(32)	1.323(12)	O(3b)–C(33)	1.398(13)
O(3a)–C(33)	1.315(11)	N(2)–C(12)	1.150(10)
N(1)–C(11)	1.147(8)	N(4)–C(24)	1.132(9)
N(3)–C(23)	1.142(8)	C(1)–C(11)	1.432(8)
C(1)–C(2)	1.512(7)	C(2)–C(23)	1.437(8)
C(1)–C(12)	1.419(8)	C(3)–C(4)	1.466(9)
C(2)–C(24)	1.441(8)	C(5)–C(6)	1.553(11)
C(4)–C(5)	1.522(9)	C(5)–C(8)	1.496(11)
C(5)–C(7)	1.532(11)	C(41)–C(45)	1.376(11)
C(41)–C(42)	1.358(11)	C(43)–C(44)	1.425(10)
C(42)–C(43)	1.399(10)		
C(44)–C(45)	1.408(11)		
P–Mo–C(1)	81.4(1)	P–Mo–C(2)	120.9(1)
C(1)–Mo–C(2)	39.7(2)	P–Mo–C(3)	88.7(2)
C(1)–Mo–C(3)	97.5(2)	C(2)–Mo–C(3)	93.3(2)
Mo–P–O(1)	111.5(2)	Mo–P–O(2a)	127.5(2)
O(1)–P–O(2a)	110.0(3)	Mo–P–O(2b)	98.5(4)
O(1)–P–O(2b)	93.0(5)		
Mo–P–O(3a)	103.8(3)		
O(2a)–P–O(3a)	98.4(3)	O(1)–P–O(3a)	101.0(3)
Mo–P–O(3b)	125.4(4)	O(1)–P–O(3b)	115.3(5)
		O(2b)–P–O(3b)	105.5(6)
		P–O(1)–C(31)	126.4(5)
Mo–C(1)–C(2)	69.0(3)	Mo–C(1)–C(11)	120.0(4)
C(2)–C(1)–C(11)	114.9(5)	Mo–C(1)–C(12)	114.1(4)
C(2)–C(1)–C(12)	116.6(5)	C(11)–C(1)–C(12)	114.7(5)
Mo–C(2)–C(1)	71.3(3)	Mo–C(2)–C(23)	115.4(4)
C(1)–C(2)–C(23)	117.4(5)	Mo–C(2)–C(24)	119.1(4)
C(1)–C(2)–C(24)	114.6(5)	C(23)–C(2)–C(24)	113.0(5)
Mo–C(3)–C(4)	177.1(5)	C(3)–C(4)–C(5)	118.3(5)
C(4)–C(5)–C(6)	108.1(6)	C(4)–C(5)–C(7)	110.5(6)
C(4)–C(5)–C(8)	110.7(6)	N(1)–C(11)–C(1)	177.3(7)
N(2)–C(12)–C(1)	178.0(8)	N(3)–C(23)–C(2)	179.0(6)
N(4)–C(24)–C(2)	178.8(7)		

Experimental

The ^1H and $^{13}C\text{-}\{^1H\}$ n.m.r. spectra were recorded on JEOL FX 90 Q or FX 200 spectrometers as appropriate. Data given are for room temperature measurements, and coupling constants are in Hz. Chemical shifts are positive to high frequency of the reference; $SiMe_4$ for ^{13}C and ^1H, and H_3PO_4 (85%, external) for ^{31}P. All reactions were carried out in Schlenk tubes under an atmosphere of dry oxygen-free nitrogen, using freshly distilled solvents.

Reaction of $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, (**1**)[15].—(*a*) *With tetrafluoroboric acid.* The carbyne complex (**1**) (0.29 g, 0.59 mmol) was dissolved in diethyl ether (15 cm^3), cooled to −78 °C, and to this HBF_4–acetic anhydride (1:3 mixture) was added dropwise with stirring until the yellow colour had disappeared and a white precipitate formed. The solvent was decanted off, and the solid washed with diethyl ether. The resulting air- and moisture-sensitive solid was recrystallised from CH_2Cl_2 (5 cm^3) and diethyl ether (30 cm^3) to afford white *crystals* of $[MoH(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$ (**2**) (0.28 g, 83%) (Found: C, 35.0; H, 6.0. $C_{17}H_{35}BF_4MoO_6P_2$ requires C, 35.2; H, 6.0%). N.m.r.: $^1H(CDCl_3)$, δ 5.75 (s, 5 H, C_5H_5), 3.77 [apparent triplet (at), 18 H, POMe, $|J(HP) + J(HP')|$ 12.1], 2.39 [dt, 2 H, CH_2, $^4J(HH)$ 1.5, $^4J(HP)$ 3.6], 1.03 (s, 9 H, CMe_3), −2.60 [tt, 1 H, MoH, $^2J(HP)$ 66.7, $^4J(HH)$ 1.5]; ^{13}C $(CDCl_3)$, δ 346.4 [dtt, Mo≡C, $^2J(CP)$ 33.2, $^2J(CH)$ 5.9, $^2J(CH)$ 6.4], 96.4 [m, C_5H_5, $^1J(CH)$ 175, $^2J(CH)$ 6.7], 64.5 [dt, CH_2Bu^t, $^1J(CH)$ 125, $^3J(CH)$ 4.3], 53.7 [dq, POMe, $^1J(CH)$ 134, $^2J(CP)$ 6], 33.8 (CMe_3), 29.4 p.p.m. [q, CMe_3, $^1J(CH)$ 115].

(*b*) *With trifluoroacetic acid.* A solution of CF_3CO_2H (5 cm^3 of a 10% solution in Et_2O) was added dropwise with stirring to a solution of $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (0.30 g, 0.6 mmol) in Et_2O (10 cm^3). The colour of the solution immediately changed from yellow to deep orange. Volatile material was removed *in vacuo*, and the resultant red-orange oil was washed with pentane, and then dissolved in diethyl ether (10 cm^3). Reduction of the volume of the solvent afforded an orange precipitate which was recrystallised by layer diffusion of pentane (20 cm^3) into a methylene chloride (5 cm^3) solution, giving rod-shaped *crystals* of $[Mo\{\sigma\text{-}OC(O)CF_3\}\{\eta^2\text{-}HOC(O)CF_3\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**3**) (0.12 g, 40%) (Found: C, 28.2; H, 3.9. $C_{15}H_{24}F_6MoO_{10}P_2$ requires C, 28.3; H, 3.8%). N.m.r.: ^1H $(C_6D_5CD_3)$, δ 7.67 [t, 1 H, CF_3CO_2H, $J(HP)$ 77.8], 5.30 [t, 5 H, C_5H_5, $^3J(HP)$ 3.0], 3.39 [at, 18 H, POMe, $|J(HP) + J(HP')|$ 10.8]; $^{13}C\text{-}\{^1H\}(C_6D_5CD_3)$, δ 98.6 ($C_5H_5$), 53.5 p.p.m. (POMe); $^{31}P\text{-}\{^1H\}(C_6D_5CD_3)$, δ 168.4 p.p.m.

(*c*) *With trifluoromethanesulphonic acid.* An excess of CF_3SO_3H (0.35 cm^3) was added with stirring to a solution of (**1**) (0.26 g, 0.52 mmol) in Et_2O (5 cm^3) at room temperature. The resultant orange precipitate was washed with Et_2O (4 × 5 cm^3) and recrystallised (0 °C) from Et_2O–CH_2Cl_2 (1 : 1) to give orange *crystals* of $[Mo(\sigma\text{-}OSO_2CF_3)(\eta^2\text{-}HOSO_2CF_3)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**4**) (0.18 g, 48%). N.m.r.: ^1H (CD_2Cl_2), δ 8.94 [t, 1 H, CF_3SO_3H, $J(HP)$ 76], 5.32 (s, 5 H, C_5H_5), 3.82 [at, 18 H, POMe, $|J(HP) + J(HP')|$ 16.0]; $^{13}C\text{-}\{^1H\}(CD_2Cl_2)$, δ 119.4 [q, CF_3SO_3, $J(CF)$ 319], 99.6 (C_5H_5), 54.1 p.p.m. (POMe); $^{31}P\text{-}\{^1H\}(CD_2Cl_2)$, δ 160.4 p.p.m. (POMe); $^{19}F(CD_2Cl_2)$, δ −78.06 (CF_3SO_3).

(*d*) *With diphenylphosphine.* The carbyne complex, (**1**) (0.45 g, 0.9 mmol), was dissolved in toluene (30 cm^3) contained in a tube fitted with a Young's tap. Diphenylphosphine (0.17 cm^3, 0.9 mmol) was added and the tube sealed. After heating at 353 K for 60 h the solvent was removed *in vacuo*. The residue was taken up

Table 4. Structure analyses

Crystal data			
Complex	(**2**)	(**3**)	(**7**)
Formula	$C_{17}H_{35}BF_4MoO_6P_2$	$C_{15}H_{24}F_6MoO_{10}P_2$	$C_{20}H_{25}MoN_4O_3P$
M	580.0	636.2	496.1
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group (no.)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_12_12_1$ (no. 19)
a/Å	9.440(2)	8.524(3)	9.221(2)
b/Å	15.012(5)	13.938(7)	14.587(3)
c/Å	18.135(6)	19.591(6)	17.175(4)
α/°	90.0	90.0	90.0
β/°	103.97(2)	90.13(3)	90.0
γ/°	90.0	90.0	90.0
U/Å^3	2 494(1)	2 327.5(15)	2 310
T/K	200	250	295
Z	4	4	4
D_c/g cm^{-3}	1.55	1.82	1.43
$F(000)$	1 192	1 280	1 016
μ(Mo-K_α)/cm^{-1}	7.0	7.8	6.5
Data collection and reduction			
Crystal dimensions (mm)	0.6 × 0.55 × 0.50	0.25 × 0.16 × 0.14	0.6 × 0.5 × 0.35
$2\theta_{max.}$/°	50	50	65
Scan method	θ–2θ	θ–2θ	Wyckoff ω
Total data	5 944	4 084	2 881
Unique data	4 836	3 271	2 666
'Observed' data (n.o.)	4 609	2 483	2 510
Transmission coefficients (min., max.)	0.67, 0.77	0.88, 0.91	
Refinement			
Disordered atoms	None	C(9), O(9), O(10), F(5), F(6)	O(2), O(3)
Anisotropic atoms	All non-H	All non-H, except low (<0.5) occupancy	All non-H, except disordered
g*	0.0001	0.000 25	0.0002
Variables (n.v.)	319	306	282
R	0.022	0.075	0.036
R'	0.024	0.070	0.038
S	1.78	2.14	1.73
Final difference map features (e Å^{-3})	0.5, −0.5	+1.8, −1.1	0.8, −0.8

* $w = [\sigma_c^2(F_0) + gF_0^2]^{-1}$; $R = \Sigma\Delta|/\Sigma|F_0|$; $R' = \Sigma w^{\frac{1}{2}}|\Delta|/\Sigma w^{\frac{1}{2}}|F_0|$; $S = [\Sigma w\Delta^2/(\text{n.o.} - \text{n.v.})]^{\frac{1}{2}}$; $\sigma_c^2(F_0)$ = variance in F_0 due to counting statistics.

Table 5. Fractional atomic co-ordinates (× 10^4) for (**2**)

Atom	*x*	*y*	*z*
Mo	2 122(1)	2 138(1)	131(1)
P(1)	3 625(1)	3 371(1)	637(1)
P(2)	−234(1)	2 330(1)	−723(1)
F(1)	10 566(1)	5 016(1)	2 639(1)
F(2)	8 886(2)	4 556(1)	1 595(1)
F(3)	9 235(2)	3 775(1)	2 688(1)
F(4)	8 142(2)	5 114(1)	2 582(1)
B	9 204(2)	4 619(2)	2 382(1)
O(1)	4 697(2)	3 111(1)	1 419(1)
O(2)	4 738(2)	3 698(1)	159(1)
O(3)	2 951(2)	4 312(1)	770(1)
O(4)	−1 190(2)	3 194(1)	−669(1)
O(5)	−268(2)	2 363(1)	−1 605(1)
O(6)	−1 253(1)	1 501(1)	−695(1)
C(1)	5 819(3)	3 722(2)	1 818(1)
C(2)	4 219(3)	4 098(2)	−581(1)
C(3)	2 049(3)	4 438(2)	1 297(2)
C(4)	−1 574(3)	3 478(2)	7(1)
C(5)	298(3)	3 115(2)	−1 938(1)
C(6)	−2 698(2)	1 436(2)	−1 215(1)
C(7)	1 369(2)	2 251(1)	948(1)
C(8)	967(2)	2 249(1)	1 691(1)
C(9)	15(2)	1 460(1)	1 840(1)
C(10)	724(2)	574(1)	1 725(1)
C(11)	−1 511(2)	1 520(2)	1 315(1)
C(12)	−97(3)	1 526(2)	2 669(1)
C(13)	3 708(2)	1 481(2)	−596(1)
C(14)	4 406(2)	1 443(1)	187(1)
C(15)	3 585(2)	882(1)	554(1)
C(16)	2 353(2)	588(1)	−2(1)
C(17)	2 439(2)	960(1)	−709(1)

Table 6. Fractional atomic co-ordinates (× 10^4) for (**3**)

Atom	*x*	*y*	*z*
Mo	0.259 81(11)	0.210 48(7)	0.091 04(5)
P(1)	0.413 2(4)	0.107 0(3)	0.163 11(14)
P(2)	0.494 1(4)	0.247 3(2)	0.027 31(14)
F(1)	0.011 8(12)	0.501 4(6)	0.136 0(7)
F(2)	0.213 0(15)	0.593 0(6)	0.138 2(7)
F(3)	0.120(2)	0.545 8(8)	0.047 3(7)
F(5′)[a]	0.014(3)	0.350 4(13)	0.332 3(9)
F(6′)[a]	−0.110(3)	0.249 8(14)	0.272 3(10)
F(4)	0.106(2)	0.220 9(9)	0.338 0(5)
F(5)[b]	−0.092 3(15)	0.283 6(11)	0.317 8(7)
F(6)[b]	0.096(2)	0.367 2(11)	0.287 8(9)
O(1)	0.560 2(11)	0.064 1(7)	0.126 7(5)
O(2)	0.337 6(11)	0.005 9(6)	0.188 2(4)
O(3)	0.460 3(13)	0.144 7(7)	0.235 9(5)
O(4)	0.658 1(3)	0.254 3(5)	0.065 6(4)
O(5)	0.532 1(3)	0.168 0(5)	−0.029 1(4)
O(6)	0.501 3(9)	0.347 8(5)	−0.010 6(4)
O(7)	0.196 7(10)	0.359 8(6)	0.081 7(5)
O(8)	0.382 2(14)	0.437 8(7)	0.141 0(6)
O(9′)[a]	0.157(3)	0.223(2)	0.192 1(12)
O(9)[b]	0.152 6(15)	0.252 8(9)	0.183 2(6)
O(10′)[a]	0.263(4)	0.330(3)	0.253 7(15)
O(10)[b]	−0.036(3)	0.167(2)	0.212 3(8)
C(1)	0.674(2)	0.004 3(12)	0.162 3(8)
C(2)	0.255(3)	−0.005 4(11)	0.250 2(7)
C(3)	0.540(3)	0.231 1(15)	0.249 8(8)
C(4)	0.721 0(15)	0.338 2(9)	0.095 4(7)
C(5)	0.670 4(13)	0.175 1(9)	−0.070 8(6)
C(6)	0.384 9(15)	0.378 1(10)	−0.059 5(8)
C(7)	0.261(2)	0.430 6(9)	0.112 5(7)
C(8)	0.147(3)	0.518 7(10)	0.107 9(10)
C(9′)[a]	0.153(4)	0.271(3)	0.242(2)
C(9)[b]	0.057(2)	0.232 4(14)	0.220 6(10)
C(10)	0.041 9(15)	0.277 9(10)	0.292 6(6)
C(11)	0.008 9(12)	0.144 1(8)	0.064 9(6)
C(12)	0.050 3(12)	0.199 6(8)	0.010 7(6)
C(13)	0.192 3(13)	0.162 2(8)	−0.017 5(6)
C(14)	0.237 0(13)	0.081 4(8)	0.021 8(5)
C(15)	0.122 6(12)	0.073 2(8)	0.074 9(5)

[a] Occupancy 0.32(1). [b] Occupancy 0.68(1).

in a mixture of diethyl ether and hexane (1:4) and chromatographed on an alumina-packed column. Elution with Et_2O–hexane (2:1) gave a trace of the pale green complex $[Mo(PPh_2)(HPPh_2)\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (**6**) (see below for characterisation) followed by the major product, a turquoise material. Collection and recrystallisation (195 K) from Et_2O–hexane afforded turquoise *crystals* of $[Mo(PPh_2)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ (**5**) (0.32 g, 59%) (Found: C, 46.4; H, 5.7. $C_{23}H_{33}MoO_6P_3$ requires C, 46.6; H, 5.6%). N.m.r.: ^1H-(CD_2Cl_2), δ 7.59 (m, 5 H, C_6H_5), 7.26 (m, 5 H, C_6H_5), 5.10 (s, 5 H, C_5H_5), 3.29 [at, 18 H, POMe, $|J(HP) + J(HP')|$ 11.2]; ^{13}C-$\{^1H\}[(CD_3)_2CO]$, δ 153.9 [d, PPh_2, $J(CP)$ 6.6], 131.4 [d, PPh_2, $J(CP)$ 7.7], 128.2 [d, PPh_2, $J(CP) < 0.5$], 128.0 [d, PPh_2, $J(CP)$ 8.8], 90.1 (C_5H_5), 51.3 (POMe); ^{31}P-$\{^1H\}(CD_2Cl_2)$, δ 216.7 [cm, POMe, $|^2J(PP')|$ 58.0], 224.4 p.p.m. [cm, PPh_2].

(*e*) *With tetracyanoethylene.* To a solution of the carbyne complex, (**1**) (0.50 g, 1 mmol), in CH_2Cl_2 (15 cm^3) was added (room temperature) solid tetracyanoethylene (0.15 g, 1.1 mmol). An instantaneous reaction occurred, the colour of the reaction mixture turning deep green. Column chromatography on alumina with elution by CH_2Cl_2 gave first a green band followed by a pink band. Attempts to recrystallise the green material afforded only the pink complex. Recrystallisation (273 K) of the pink species from CH_2Cl_2–hexane (2:1) afforded very pale pink *crystals* of $[Mo(\equiv CCH_2Bu^t)\{\eta^2\text{-}C_2(CN)_4\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$ (**7**) (0.22 g, 45%) (Found: C, 48.5; H, 5.3; N, 10.8. $C_{20}H_{25}MoN_4O_3P$ requires C, 48.3; H, 5.0; N, 11.3%). ν(CN)(CH_2Cl_2) 2 222 cm^{-1}. N.m.r.: $^1H(CDCl_3)$, δ 5.77 (s, 5 H, C_5H_5), 3.99 [d, 9 H, POMe, $J(HP)$ 11.4], 2.40 [d, 1 H, CCH_2Bu^t, $J(HP)$ 4.8], 2.34 [d, 1 H, CCH_2Bu^t, $J(HP)$ 6.6], 1.04 (s, 9 H, Bu^t); ^{13}C-$\{^1H\}(CDCl_3)$, δ 338.9 [d, Mo≡C, $J(CP)$ 31.8], 118.3, 116.8, 116.3 [$C_2(CN)_4$], 101.9 (C_5H_5), 63.3 (CH_2Bu^t), 55.2 [d, POMe, $J(CP)$ 7.3], 34.2 (CMe_3), 29.7 (CMe_3); ^{31}P-$\{^1H\}(CDCl_3)$, δ 157.1 p.p.m.

Reaction of Diphenylphosphine with $[Mo(\eta^3\text{-}1\text{-}Me\text{-}C_3H_4)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$.—The η^3-allyl complex (0.5 g, 1.0 mmol) was dissolved in toluene (20 cm^3) contained in a tube fitted with a Young's tap. Diphenylphosphine (0.19 cm^3, 1.0 mmol) was added and the tube and contents heated at 300 K for 48 h. Column chromatography and elution with Et_2O–hexane (2:1) gave a minor amount of (**6**) followed by a green band which was collected and recrystallised from Et_2O–hexane to give *crystals* of (**5**) (0.42 g, 60%). When the reaction was repeated using an excess of diphenylphosphine (3.0 mmol) the only product was (**6**), which was isolated as a green crystalline material (0.49 g, 70%) (Found: C, 58.5; H, 5.0. $C_{32}H_{35}MoO_3P_3$ requires C, 58.5; H, 5.3%). N.m.r.: ^1H $[(CD_3)_2CO]$, δ 8.32 [dd, 1 H, $HPPh_2$, $^1J(HP)$ 359.3, $^3J(HP)$ 10.4], 7.24 (m, 20 H, Ph), 5.08 (s, 5 H, C_5H_5), 3.22 [d, 9 H, POMe, $^3J(HP)$ 9.8]; ^{31}P-$\{^1H\}[(CD_3)_2CO]$, δ 215.0 [cm, PPh_2, $^2J(PP)$ 59.8, 48.8, 70.8], 212.5 [cm, POMe], 66.1 p.p.m. (m, $HPPh_2$).

Structure Analyses of $[MoH(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, (**2**), $[Mo\{\sigma\text{-}OC(O)CF_3\}\{\eta^2\text{-}HOC(O)CF_3\}\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$, (**3**), *and* $[Mo(\equiv CCH_2Bu^t)\{\eta^2\text{-}C_2(CN)_4\}\{P(OMe)_3\}(\eta\text{-}C_5H_5)]$, (**7**).—Details of the structure analyses

Table 7. Fractional atomic co-ordinates (× 10^4) for (**7**)

Atom	*x*	*y*	*z*
Mo	−22(1)	−31(1)	457(1)
P	807(2)	1 201(1)	1 296(1)
O(1)	2 451(4)	1 368(3)	1 204(3)
O(2a)[a]	325(7)	1 405(4)	2 170(3)
O(2b)[b]	1 018(14)	612(7)	2 096(5)
O(3a)[a]	144(9)	2 129(4)	886(4)
O(3b)[b]	−129(14)	2 084(5)	1 539(7)
N(1)	−2 256(7)	−163(5)	2 579(3)
N(2)	−3 449(8)	1 659(5)	673(5)
N(3)	−2 355(7)	−2 204(4)	1 244(4)
N(4)	−4 072(7)	−445(6)	−521(3)
C(1)	−2 088(5)	213(4)	1 116(3)
C(2)	−2 220(5)	−615(4)	590(3)
C(3)	765(5)	−827(4)	1 114(3)
C(4)	1 402(7)	−1 521(5)	1 628(4)
C(5)	3 021(7)	−1 710(4)	1 563(4)
C(6)	3 417(11)	−2 468(6)	2 161(6)
C(7)	3 893(8)	−843(6)	1 748(6)
C(8)	3 403(9)	−2 026(5)	761(5)
C(11)	−2 158(6)	18(5)	1 932(3)
C(12)	−2 850(7)	1 013(4)	882(4)
C(23)	−2 284(6)	−1 500(4)	956(3)
C(24)	−3 248(7)	−514(4)	−36(4)
C(31)	3 314(11)	1 950(6)	1 666(6)
C(32)	844(11)	917(6)	2 816(5)
C(33)	−127(12)	2 944(6)	1 180(6)
C(41)	−261(10)	−334(5)	−907(4)
C(42)	1 090(8)	−589(5)	−677(4)
C(43)	1 856(7)	191(5)	−441(3)
C(44)	914(9)	954(4)	−550(4)
C(45)	−402(8)	602(6)	−841(4)

[a] Occupancy 0.69(1). [b] Occupancy 0.31(1).

are given in Table 4. All diffraction measurements were made on Nicolet P3m diffractometers using graphite monochromated Mo-K_α *X*-radiation on single crystals mounted under N_2 in thin-walled glass capillaries. Data were collected for unique portions of reciprocal space, and corrected for Lorentz and polarisation effects, and, for (**2**) and (**3**), for *X*-ray absorption, by an empirical method based on 396 azimuthal scan data for (**2**) and on the basis of the indexed crystal faces for (**3**) {indices [distance from origin, mm]: (0, 1, 2) [0.07], (0, −1, −2) [0.07], (0, 1, −1) [0.08], (0, −1, 1) [0.08], (1, 0, 0) [0.125], (−1, 0, 0) [0.125]}. The structures were solved by conventional heavy-atom methods (Patterson and Fourier) and refined by full-matrix blocked-cascade least squares to the final residual indices given in Table 4, weights were modified by *g* to give minimal variation of *S* with $|F_0|$. Final difference electron density maps showed no features of magnitude greater than those quoted in Table 4. The handedness of the crystal of (**7**) chosen was confirmed by refinement, $\eta = 1.2$ (2).[25]

One trifluoroacetate group in (**3**) is disordered between two sites in the ratio 0.68(1):0.32(1), with atoms C(10) and F(4) refined in single sites common to both orientations. In (**7**) two methoxy groups showed a disorder in which each oxygen atom occupies one of two sites, with their associated carbon atoms in single positions, in the ratio 0.69(1):0.31(1). The P–O and O–C bond lengths of these groups were forced to be close to refined common values [1.615(5) and 1.368(7) Å]. Tables 5, 6, and 7 report the positional parameters of the non-hydrogen atoms in (**2**), (**3**), and (**7**) respectively. Hydrogen atoms were included in refinements in idealised positions and assigned fixed isotropic vibrational parameters, with the exception of hydride and methylene hydrogens in (**2**) which had no such constraints. All calculations were made with programs of the SHELX-TL system as implemented on a Nicolet R3m/E structure determination facility.[25] Complex neutral-atom scattering factors were taken from ref. 26. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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