Reactions of Sixteen-electron Bis(alkyne)-molybdenum and -tungsten Complexes with Phosphines and Isocyanides; Molecular and Crystal Structure of the Insertion Product $[MoCF_3(Bu^tNC)\{(CF_3)_4C_5NBu^t\}(\eta\text{-}C_5H_5)]$

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Diphenylacetylene reacts thermally, and but-2-yne on u.v. irradiation, with $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$ to give respectively, $[Mo(CF_3)(CO)(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ and $[Mo(CF_3)(CO)(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)]$. In contrast, the corresponding reaction (u.v.) of hexafluorobut-2-yne or dimethyl acetylenedicarboxylate affords $[Mo(CF_3)(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)]$ and $[Mo(CF_3)\{\eta^2\text{-}C_2(CO_2Me)_2\}_2(\eta\text{-}C_5H_5)]$. Treatment of $[Mo(CF_3)(CO)(\eta^2\text{-}MeC_2Me)(\eta\text{-}C_5H_5)]$ with $CF_3C_2CF_3$ gives $[Mo(CF_3)(\eta^2\text{-}MeC_2Me)(\eta^2\text{-}CF_3C_2CF_3)(\eta\text{-}C_5H_5)]$. The co-ordinatively unsaturated bis(acetylene)complexes, and also $[MCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)]$ (M = Mo or W), react with PMe_3 or PPh_3 to give the 18-electron species $[MX(\eta^2\text{-}RC_2R)_2L(\eta\text{-}C_5H_5)]$ (M = Mo or W; X = CF_3 or Cl; L = PMe_3 or PPh_3). These complexes exist in solution as equilibrating *cis* and *trans* isomers. An analogous reaction of $[Mo(CF_3)(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)]$ or $[WCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)]$ with Bu^tNC affords initially isostructural 1 : 1 adducts; however, excess of isocyanide gives cyclopentadienimine complexes. A single-crystal *X*-ray diffraction study has established the structure of $[Mo(CF_3)(Bu^tNC)\{(CF_3)_4C_5NBu^t\}(\eta\text{-}C_5H_5)]$. Crystals are monoclinic, space group $P2_1/a$ with a = 17.452(6), b = 35.410(18), and c = 9.182(4) Å, β = 95.91(3)°, Z = 8. The structure has been determined from the analysis of 7 900 data with $I \geqslant 1.0\sigma$ collected to 2θ 55.0° (Mo-K_α radiation) on a four-circle diffractometer, and refined by least squares to R 0.127. In contrast, excess of isocyanide reacts with $[MoCl(\eta^2\text{-}PhC_2Ph)_2(\eta\text{-}C_5H_5)]$ and with $[MCl(\eta^2\text{-}CF_3C_2CF_3)(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ (M = Mo or W) to give respectively, the cationic species $[M(CNBu^t)_3(\eta^2\text{-}RC_2R)(\eta\text{-}C_5H_5)]^+$ (M = Mo or W; R = Ph or CF_3) isolated as Cl^- or $[PF_6]^-$ salts. Oxygen reacts with $[MX(CO)(\eta^2\text{-}RC_2R)(\eta\text{-}C_5H_5)]$ (M = Mo or W; X = Cl or CF_3; R = Ph or CF_3) to give the oxo-complexes $[MoX(O)(\eta^2\text{-}RC_2R)(\eta\text{-}C_5H_5)]$.

PREVIOUS studies have shown[1] that the organothio-complexes $[M(SR)(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo or W; R = CF_3 or C_6F_5) react with acetylenes to give the formally 16-electron monocarbonyl species $[M(SR)(CO)(\eta^2\text{-}RC_2R)(\eta\text{-}C_5H_5)]$, whereas related reactions with the halogeno-complexes $[MX(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo or W; X = Cl, Br, or I) afforded the bis(acetylene) species $[MX(\eta^2\text{-}RC_2R)_2(\eta\text{-}C_5H_5)]$, together with cyclopentadienone and duroquinone complexes.[2] In order to extend the scope of these syntheses we have investigated reactions of acetylenes with the (trifluoroacetyl)molybdenum complex $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$. We also report reactions of trimethylphosphine, triphenylphosphine, and t-butyl isocyanide with co-ordinatively unsaturated bis(acetylene)-molybdenum and -tungsten complexes, in order to explore further the chemistry of these interesting 16-electron molecules. Some aspects of this chemistry have been mentioned previously.[3]

RESULTS AND DISCUSSION

In refluxing hexane, diphenylacetylene and $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$ afford purple air-sensitive complex (1) in high yield; i.r. spectroscopy showed that the reaction involves the intermediacy of $[Mo(CF_3)(CO)_3(\eta\text{-}C_5H_5)]$ formed *via* the well known decarbonylation

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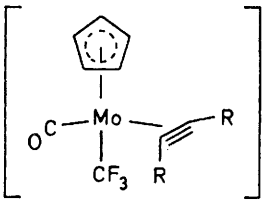
[1] P. S. Braterman, J. L. Davidson, and D. W. A. Sharp, *J.C.S. Dalton*, 1976, 241.

[2] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2531; J. L. Davidson, M. Green, D. W. A. Sharp, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 706; J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1976, 738.

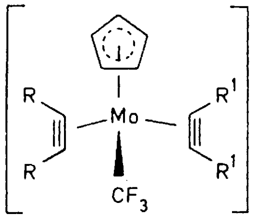
[3] J. L. Davidson, M. Green, J. A. K. Howard, S. A. Mann, J. Z. Nyathi, F. G. A. Stone, and P. Woodward, *J.C.S. Chem. Comm.*, 1975, 803.

reaction.[4] Examination of the i.r. and n.m.r. (^{1}H and ^{19}F) spectra showed that (1) is a 16-electron complex similar to [Mo(SC$_6$F$_5$)(CO)(η^2-CF$_3$C$_2$CF$_3$)(η-C$_5$H$_5$)], a species which has been structurally characterised[5] by *X*-ray crystallography, the metal being essentially octahedrally co-ordinated, with the η-C$_5$H$_5$ ring occupying a face and the C≡C axis of the η^2-co-ordinated acetylene lying parallel to the Mo–CO axis. The corresponding reaction of but-2-yne with [Mo(COCF$_3$)(CO)$_3$(η-C$_5$H$_5$)] did not proceed thermally; however, u.v. irradiation gave a good yield of the very air-sensitive complex (2). The ^{1}H n.m.r. spectrum of (2) showed a singlet at τ 4.54 assigned to the cyclopentadienyl protons, and a singlet at τ 7.82 which is assigned to the methyl protons of the but-2-yne ligand, suggesting dynamic behaviour. However, low-temperature n.m.r. measurements were frustrated by the high oxygen sensitivity of this complex.



R
(1) Ph
(2) Me

It is interesting that attempts to convert both (1) and (2) into bis(acetylene) complexes by further reaction with PhC$_2$Ph or MeC$_2$Me were unsuccessful, contrasting with the corresponding reactions of the halogeno-species[2] [MX(CO)$_3$(η-C$_5$H$_5$)] (X = Cl, Br, or I). However, u.v. irradiation of a hexane solution of [Mo(COCF$_3$)(CO)$_3$(η-C$_5$H$_5$)] with the electronegatively substituted acetylene CF$_3$C$_2$CF$_3$ afforded the bis(acetylene) complex (3). When this reaction was monitored by i.r. spectroscopy there was no evidence for the existence of a monocarbonyl species, *i.e.* [Mo(CF$_3$)(CO)(η^2-CF$_3$C$_2$CF$_3$)(η-C$_5$H$_5$)]. The i.r. spectrum of (3) showed bands at 1 775 and 1 760 cm^{-1}, which are assigned to ν(C≡C), similar bands (1 778 and 1 762 cm^{-1}) being observed[2] in the spectrum of the tungsten complex [WCl(η^2-CF$_3$C$_2$CF$_3$)$_2$(η-C$_5$H$_5$)] whose structure has been confirmed by a single-crystal *X*-ray diffraction study.[2] A related complex (4) was obtained when the acyl complex [Mo(COCF$_3$)(CO)$_3$(η-C$_5$H$_5$)] was treated with C$_2$(CO$_2$Me)$_2$ in refluxing diethyl ether. A medium–strong band in the i.r. spectrum at 1 760 cm^{-1} is assigned to ν(C≡C), whilst the strong band at 1 715 cm^{-1} is assigned to the methoxycarbonyl groups of the co-ordinated acetylene.



(3) R = R^1 = CF$_3$
(4) R = R^1 = CO$_2$Me
(5) R = Me, R^1 = CF$_3$

When the monocarbonyl complex (2) was treated with CF$_3$C$_2$CF$_3$ in hexane solution at room temperature the yellow crystalline complex (5) was formed in quantitative yield. A band at 1 780 cm^{-1} in the i.r. spectrum is assigned to the ν(C≡C) stretch of co-ordinated hexafluorobut-2-yne, the relatively low frequency implying significant π back donation.

Thus, the reaction of [Mo(COCF$_3$)(CO)$_3$(η-C$_5$H$_5$)] with acetylenes bearing electronegative substituents yields products[2] analogous to [MoX(η^2-RC$_2$R)$_2$(η-C$_5$H$_5$)] (X = Cl, Br, or I) and [WCl(η^2-CF$_3$C$_2$CF$_3$)$_2$(η-C$_5$H$_5$)]. A single-crystal *X*-ray diffraction study of the latter complex has shown that the metal is in an approximately octahedral environment with the η-C$_5$H$_5$ ligand occupying three *facial* sites, the η^2-CF$_3$C$_2$CF$_3$ and Cl ligands occupying the remaining sites. It is suggested that complexes (3)—(5) are isostructural in the solid state. Examination of the ^{1}H and ^{19}F n.m.r. spectra shows that in solution a propeller rotation of the acetylene occurs about an axis through the metal and perpendicular to the C≡C bond of the acetylene, as has been established[2] for the related halogeno-complexes. The CF_3C≡C resonances in the ^{19}F n.m.r. spectrum of (3) show two quartets at −90 °C which collapse to a broad peak at −50 °C, above which temperature only one quartet is observed (58.2 p.p.m.). The ^{1}H spectrum of (4) consists of two singlets at $\leqslant -35$ °C coalescence occurring at −30 °C. The ^{1}H spectrum of (5) shows two methyl resonances at −80 °C, coalescence occurring at −60 °C to a single resonance. The ^{19}F spectrum of the same complex shows two CF_3C≡C resonances in the range 30 to −90 °C demonstrating that only the but-2-yne moiety rotates; evidently the barrier to rotation for the CF$_3$C$_2$CF$_3$ ligand is relatively high due to significant back bonding. In the case of (3) and (4) two good back-bonding acetylenes are competing for the electron density on the metal, and hence the extent of back bonding to an individual acetylene is less than in complex (5).

The formally co-ordinatively unsaturated complex (3) reacts with trimethylphosphine at room temperature to give pink crystals of the 1 : 1 adduct (6). The i.r. spectrum of this complex has bands at 1 795 and 1 775 cm^{-1} attributable to ν(C≡C), these being *ca.* 20 cm^{-1} higher than in the parent complex (3). This is consistent with the presence in (6) of η^2-bonded CF$_3$C$_2$CF$_3$ with reduced back bonding compared with the acetylenes in (3). The ^{1}H n.m.r. spectrum of (6) shows two singlets at τ 4.12 and 4.16 assigned to the η-C$_5$H$_5$ protons and two doublets [*J*(HP) 13.0 Hz] at τ 8.46 and 8.50, which are assigned to the methyl protons of co-ordinated PMe$_3$. The two sets of resonances clearly establish the presence

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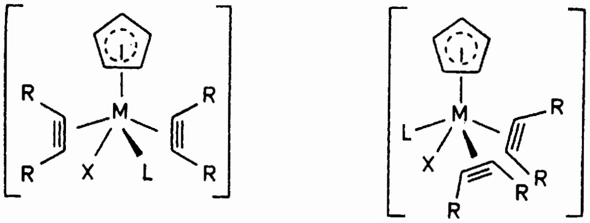
[4] R. B. King and M. B. Hursthouse, *J. Organometallic Chem.*, 1964, **2**, 15.

[5] J. A. K. Howard, R. F. D. Stansfield, and P. Woodward, *J.C.S. Dalton*, 1976, 246.

in solution of two isomers in the ratio 1 : 1 (independent of the temperature range 30 to −50 °C). The ^{19}F spectrum also shows peaks corresponding to two isomers, and it is suggested that these have structures (6a) and (6b).



(a) (b)

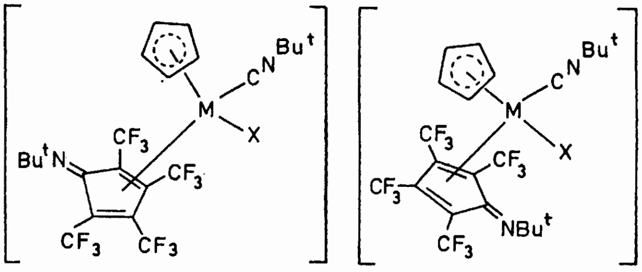
	M	R	L	X
(6)	Mo	CF_3	PMe_3	CF_3
(7)	Mo	CO_2Me	PPh_3	CF_3
(8)	Mo	CF_3	PPh_3	Cl
(9)	Mo	CF_3	PMe_3	Cl
(10)	W	CF_3	PMe_3	Cl
(11)	Mo	CF_3	Bu^tNC	CF_3
(12)	W	CF_3	Bu^tNC	Cl

Similar reactions occur on treatment of (4) with PPh_3, $[\mathrm{MoCl}(\eta^2\text{-}\mathrm{CF_3C_2CF_3})_2(\eta\text{-}\mathrm{C_5H_5})]$ with PPh_3 or PMe_3, and $[\mathrm{WCl}(\eta^2\text{-}\mathrm{CF_3C_2CF_3})_2(\eta\text{-}\mathrm{C_5H_5})]$ with PMe_3, giving respectively the 18-electron species (7), (8), (9), and (10), which were isolated as crystalline 1 : 1 adducts. The i.r. spectrum of (7) has a strong band at 1 675 cm^{-1} assignable to the ketonic carbonyls of the CO_2Me group. However, no band ascribable to ν(C≡C) could be identified, although it is possible that there is overlap with the carbonyl band. The ^{1}H spectrum showed a broad signal at τ 2.6 due to the phenyl protons of PPh_3, a singlet at τ 4.50 assigned to the $\eta\text{-}C_5H_5$ protons, and four singlets due to the methyl groups of the acetylenes. On cooling to −50 °C, two $\eta\text{-}C_5H_5$ resonances were observed in the ratio of 1 : 2 implying the presence in solution at low temperatures of two isomers, possibly (7a) and (7b). In agreement with this suggestion, it is interesting to note that intramolecular ligand rearrangement between *cis* and *trans* conformers of the general formula $[\mathrm{MoR(CO)_2L}(\eta\text{-}\mathrm{C_5H_5})]$ (R = alkyl, aryl, halide, or hydride; L = tertiary phosphine) has been observed,[6] the barrier to rearrangement depending on the size of the R group.

The ^{19}F spectrum of (8) showed four multiplets of equal intensity indicating the presence of only one isomer, either (8a) or (8b). The i.r. spectrum showed a single ν(C≡C) stretching mode at 1 808 cm^{-1}. In contrast, both (9) and (10) showed two ν(C≡C) bands in their i.r. spectra, suggesting that each isomer [(a) or (b)] has only one ν(C≡C) stretching mode, unlike the parent complexes where two are observed. Moreover, the ^{19}F n.m.r. spectra of (9) and (10) were more complex than that of (8). Thus (9) showed eight CF_3 multiplets, and (10) a spectrum with six resonances corresponding to eight CF_3 groups with the signals of two pairs overlapping. It is thus apparent that the isomers of (9) and (10) do not have a plane of symmetry even in the *trans* isomers (a), suggesting that steric crowding is sufficient to force the acetylenes to adopt asymmetric orientations with respect to each other. It is also clear that acetylene rotation does not occur in these 18-electron species, presumably for the same reason.

The related reactions of t-butyl isocyanide were more complex. Addition of a molar equivalent of Bu^tNC to a diethyl ether solution of (3) gave pale pink crystals of a 1 : 1 adduct (11). Examination of the i.r. and ^{1}H and ^{19}F n.m.r. spectra showed that the adduct was isostructural with the phosphine adducts, but that only one isomer [either (11a) or (11b)] was present in solution. A similar reaction between Bu^tNC and $[\mathrm{WCl}(\eta^2\text{-}\mathrm{CF_3C_2CF_3})_2(\eta\text{-}\mathrm{C_5H_5})]$ gave an analogous 1 : 1 adduct (12), which again existed in solution as one preferred isomer, the presence of four CF_3 environments in the ^{19}F spectrum at room temperature indicating the absence of acetylene rotation.

Treatment of either (11) or (12) with an excess of Bu^tNC led to another reaction and the formation, respectively, of the 1 : 2 adducts (13) and (14). The occurrence in the i.r. spectra of both complexes of bands attributable to ν(C=N) suggested that an isocyanide had become involved in a novel cyclisation reaction. In order to confirm this important point a single-crystal *X*-ray diffraction study of (13) was undertaken.



(a) (b)

	M	X
(13)	Mo	CF_3
(14)	W	Cl

Figure 1 displays the projection of a single molecule on to the plane defined by the co-ordinated cyclopentadienyl ring and demonstrates the atomic-numbering scheme adopted. There are two crystallographically independent molecules (A and B) in the asymmetric portion of the unit cell, the Figure representing type A. Molecule B can be constructed from Figure 1 by simply rotating the t-butyl group of the terminal isocyanide by *ca.* $\frac{\pi}{3}$ counter clockwise about the bond N(61)–C(62).

With one exception [C(30)–F(302)], corresponding bond lengths (Table 1, uncorrected for thermal effects) of the independent species A and B agree to within three times the greater single error. The same relation holds for the majority of interbond angles (Table 2 and Appendix B),

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[6] J. W. Faller, A. S. Anderson, and C. C. Chen, *J. Organometallic Chem.*, 1969, **17**, P7.

the only exceptions being some of the angles involving either fluorine atoms of the η^4-ligand or methyl carbons of the isocyanide functions. Both are atom types involved in relatively high thermal motion (Appendix C), and hence relatively inaccurate placements. Molecular parameters referred to in this discussion will therefore be the average of two.

Complex (**13**) thus crystallises as completely asymmetric, neutral, monomer molecules in one isomeric form only, and comprises an essentially seven-co-ordinate, formally Mo^{II}, metal atom bonded to: (*i*) a t-butyl isocyanide ligand, (*ii*) a trifluoromethyl group, (*iii*) an η-cyclopentadienyl ligand, and (*iv*) an η^4-bonded substituted cyclopentadienimine function. Details of the first two bonded ligands are unexceptional. The sequence of lengths Mo–C(61), C(61)–N(61), and N(61)–C(62) is 2.091, 1.158, and 1.47 Å respectively, with near-linear angles at N and C of 174.6 and 177.2°. The mean Mo–C(11) distance is 2.227 Å and, as expected, the three valence angles at C(11) containing this vector are significantly larger than the F–C(11)–F set. The cyclopentadienyl group is planar (Table 3) and, within experimental error, a regular pentagon, although the molybdenum atom, 2.015 Å above the ring, bonds unevenly to it, in projection being displaced *ca.* 0.12 Å from its centre in a direction towards C(2). Thus, although the mean Mo–C(1—5) distance (2.343 Å) compares favourably with similar average separations,[2,7,8] individual Mo–$C(C_5H_5)$ lengths in the present complex differ by almost 0.1 Å.

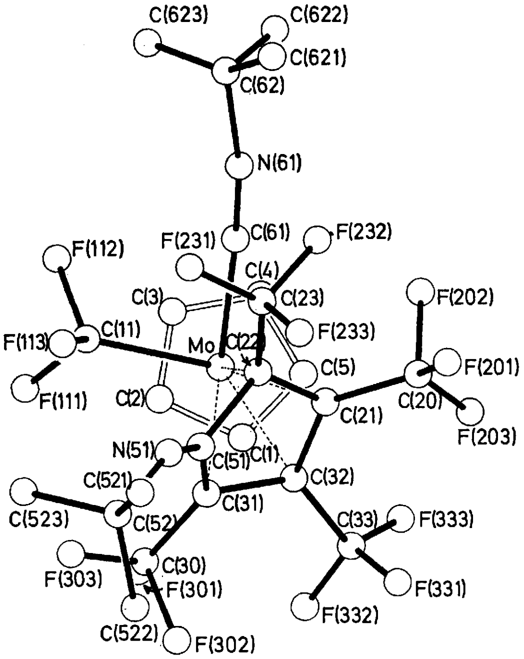

FIGURE 1 Perspective view of a single molecule of $[Mo(CF_3)(CNBu^t)\{(CF_3)_4C_5NBu^t\}(\eta\text{-}C_5H_5)]$ (**13**) with the cyclopentadienyl H atoms omitted for clarity

TABLE 1

Interatomic distances (Å) for complex (**13**) $[Mo(CF_3)(CNBu^t)\{(CF_3)_4C_5NBu^t\}(\eta\text{-}C_5H_5)]$

	Molecule	
	A	B
Mo–C(1)	2.323(12)	2.320(14)
Mo–C(2)	2.304(17)	2.301(19)
Mo–C(3)	2.330(16)	2.328(20)
Mo–C(4)	2.389(18)	2.397(19)
Mo–C(5)	2.357(17)	2.383(19)
Mo–C(11)	2.236(15)	2.217(16)
Mo–C(21)	2.181(14)	2.223(15)
Mo–C(22)	2.301(13)	2.299(14)
Mo–C(31)	2.332(14)	2.335(15)
Mo–C(32)	2.217(13)	2.220(15)
Mo–C(61)	2.100(14)	2.082(14)
C(1)–C(2)	1.42(2)	1.40(3)
C(2)–C(3)	1.41(2)	1.43(3)
C(3)–C(4)	1.39(3)	1.40(3)
C(4)–C(5)	1.41(2)	1.38(3)
C(5)–C(1)	1.37(3)	1.42(3)
C(11)–F(111)	1.38(2)	1.35(2)
C(11)–F(112)	1.37(2)	1.38(2)
C(11)–F(113)	1.33(2)	1.36(2)
C(20)–F(201)	1.30(3)	1.30(2)
C(20)–F(202)	1.33(2)	1.39(2)
C(20)–F(203)	1.33(2)	1.27(3)
C(20)–C(21)	1.49(2)	1.48(2)
C(21)–C(22)	1.456(18)	1.431(20)
C(22)–C(23)	1.49(2)	1.52(2)
C(23)–F(231)	1.32(2)	1.29(2)
C(23)–F(232)	1.37(2)	1.36(2)
C(23)–F(233)	1.33(2)	1.35(2)
C(30)–F(301)	1.35(2)	1.31(2)
C(30)–F(302)	1.32(2)	1.42(2)
C(30)–F(303)	1.33(2)	1.32(2)
C(30)–C(31)	1.47(2)	1.47(2)
C(31)–C(32)	1.484(20)	1.433(22)
C(32)–C(33)	1.50(2)	1.52(2)
C(33)–F(331)	1.34(2)	1.34(2)
C(33)–F(332)	1.37(2)	1.32(2)
C(33)–F(333)	1.27(2)	1.32(2)
C(21)–C(32)	1.454(19)	1.425(18)
C(51)–C(22)	1.51(2)	1.53(2)
C(51)–C(31)	1.53(2)	1.56(2)
C(51)–N(51)	1.226(19)	1.226(19)
N(51)–C(52)	1.47(2)	1.48(2)
C(52)–C(521)	1.54(4)	1.54(3)
C(52)–C(522)	1.53(4)	1.52(3)
C(52)–C(523)	1.54(5)	1.56(4)
C(61)–N(61)	1.159(19)	1.156(21)
N(61)–C(62)	1.46(2)	1.48(3)
C(62)–C(621)	1.55(4)	1.55(6)
C(62)–C(622)	1.49(4)	1.53(5)
C(62)–C(623)	1.53(4)	1.50(7)

TABLE 2

Important interbond angles (°) for complex (**13**)

	Molecule	
Atomic sequence	A	B
C(1)–Mo–C(2)	35.8(6)	35.3(8)
C(2)–Mo–C(3)	35.5(6)	35.9(7)
C(3)–Mo–C(4)	34.1(6)	34.4(7)
C(4)–Mo–C(5)	34.5(5)	33.6(7)
C(5)–Mo–C(1)	33.9(6)	35.0(7)
C(22)–Mo–C(21)	37.8(5)	36.8(5)
C(21)–Mo–C(32)	38.6(5)	37.4(5)
C(32)–Mo–C(31)	38.0(5)	36.6(6)
C(51)–N(51)–C(52)	135.7(13)	138.4(13)
C(11)–Mo–C(61)	83.6(6)	81.9(6)
Mo–C(61)–N(61)	176.1(13)	173.1(15)
C(61)–N(61)–C(62)	179.2(15)	175.2(20)

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[7] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1977, 287.

[8] J. L. Davidson, M. Green, J. Z. Nyathi, C. Scott, F. G. A. Stone, A. J. Welch, and P. Woodward, *J.C.S. Chem. Comm.*, 1976, 714.

TABLE 3

Equations of molecular planes for complex (13) and deviations (Å) from the planes in square brackets

Plane 1A: C(1A), C(2A), C(3A), C(4A), C(5A)
$-7.432x + 12.729y + 7.964z = 2.274$
[C(1A) +0.007, C(2A) +0.002, C(3A) −0.010, C(4A) +0.014, C(5A) −0.013, Mo(A) −2.014]
Plane 2A: C(22A), C(21A), C(32A), C(31A)
$15.417x - 13.026y - 3.433z = 3.043$
[C(22A) +0.010, C(21A) −0.016, C(32A) +0.016, C(31A) −0.010, Mo(A) −1.921, C(51A) +0.644, C(23A) +0.325, C(20A) +0.289, C(33A) +0.426, C(30A) −0.071]
Plane 1B: C(1B), C(2B), C(3B), C(4B), C(5B)
$9.125x + 9.101y - 7.889z = -1.350$
[C(1B) +0.002, C(2B) −0.003, C(3B) +0.002, C(4B) −0.001, C(5B) −0.001, Mo(B) +2.016]
Plane 2B: C(22B), C(21B), C(32B), C(31B)
$10.769x + 25.708y - 3.319z = 1.634$
[C(22B) +0.001, C(21B) −0.001, C(32B) +0.001, C(31B) −0.001, Mo(B) −1.942, C(51B) +0.617, C(23B) +0.239, C(20B) +0.265, C(33B) +0.388, C(30B) −0.094]
Dihedral angles (°): 1A—2A 41.4, 1B—2B 40.9
Angles of fold (°): across C(22A) · · · C(31A) 39.3, across C(22B) · · · C(31B) 36.1

At an angle of 40.7° to the η-C_5H_5 ring is a plane containing the metal-bonded carbon atoms of the η^4-cyclopentadienimine ligand, formally produced by cyclisation of two $CF_3C_2CF_3$ and one Bu^tNC molecules. The corresponding dihedral angle in the related complex $[Mo\cdot\{C(CF_3)\colon C(CF_3)\cdot C_5H_5\}(\eta^2\text{-}CF_3C_2CF_3)(\eta\text{-}C_5H_5)]$ [2,7] is 47.6°. In this latter molecule, Mo–C(η^4) separations fall into two distinct groups by virtue of a 'side-on' tipping of the diene, whilst the present structure represents an 'end-on' distortion such that the Mo–C(22,31) distance (mean 2.317 Å) is appreciably longer than Mo–C(21,32) (mean 2.209 Å). Similar division of the Mo–C(η^4) lengths into pairs has been previously noted [9] for $[Mn(CO)_3\{(CF_3)_4C_4SC_6F_5\}]$ and $[Co\{(CF_3)_4C_4PO(OH)\}(\eta\text{-}C_5H_5)]$.[8]

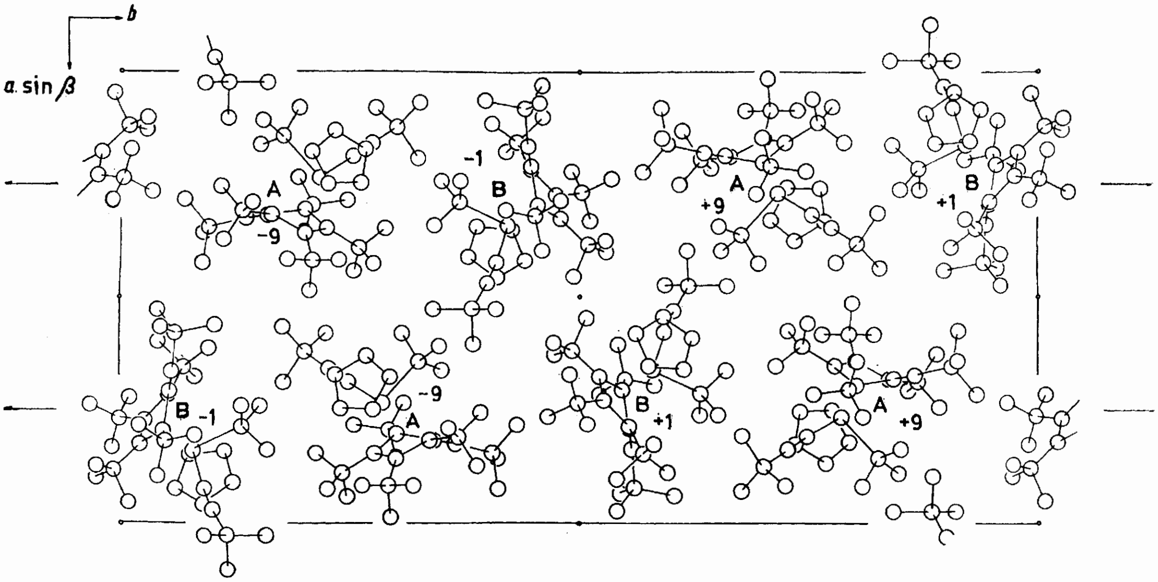
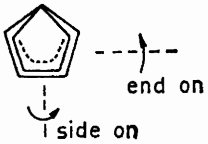


FIGURE 2 The contents of the unit cell, as seen along the c axis, looking towards the origin. Only sufficient symmetry elements to complete the array are shown



Rehybridisation at atoms C(22), C(21), C(32), and C(31) on co-ordination to the metal results in three of the pendant CF_3 groups [C(23), C(20), and C(33)] bending out of the C_4 plane and away from the molybdenum by an average of 12.1°. The one exception [$C(30)F_3$] is fractionally displaced *towards* the metal (Table 3). This apparent anomaly is quickly rationalised by examination of intraligand non-bonded contacts (Table 4), which demonstrate the close approaches of C(522) and C(523) to F(302) and F(303). The consequence of this crowding (caused by the in-plane bending, at N, of the bridging isocyanide, $\diagup\dot{N}\!=\!C\!\langle$) is shared by that function in as much as the N(51)–C(51)–C(31) angle (144.1°) is considerably wider than N(51)–C(51)–C(22) (120.7°).

TABLE 4

Intramolecular non-bonding contacts (Å) for complex (13)

	Molecule	
	A	B
C(522) * · · · F(302)	3.26(4)	3.12(2)
C(523) · · · F(303)	2.97(5)	3.22(3)
C(522) · · · F(303)		3.16(3)
C(621) · · · F(232)	3.18(3)	3.04(5)

* The van der Waals radius of a methyl group was estimated as 2.0 Å.

The crystal packing is reproduced, in *c*-axis projection, in Figure 2. The numbers given are the approximate

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[9] M. J. Barrow, J. L. Davidson, W. Harrison, D. W. A. Sharp, G. A. Sim, and F. B. Wilson, *J.C.S. Chem. Comm.*, 1973, 583.

values, in hundredths, of the metal z co-ordinate. Interestingly, both molecules, as defined in Table 5, have almost exactly similar orientations with respect to the c axis. The closest F $\cdots$ H and F $\cdots$ Me intermolecular contacts are: F(112B) at x, y, z, H(5A) at $\frac{1}{2} - x, y - \frac{1}{2}, -z$ (2.36 Å); and F(201B), C(523A) both at x, y, z [3.17(5) Å].

In solution, both (13) and (14) exist as a mixture of two isomers (a) and (b). For example, the i.r. spectrum of (13) has sharp bands at 2 180 and 2 170 cm^{-1} assignable to terminally bonded isocyanide. The ^{1}H n.m.r. spectrum shows singlets at τ 4.26 and 4.58 assignable to the η-C_5H_5 protons, and singlets at τ 8.30, 8.62, 8.34, and 8.58 to the *Bu*^{t}N protons. At room temperature the isomers are present in a ratio of 1 : 3, and at −60 °C, 1 : 6. The ^{19}F spectrum also showed resonances due to two isomers, the same temperature dependence being observed as in the ^{1}H spectrum.

The formation of (13) and (14) is formally analogous to the production of a cyclopentadienone complex $[\mathrm{MoCl(CO)\{(CF_3)_4C_4CO\}(\eta\text{-}C_5H_5)}]$ in the reaction of $[\mathrm{MoCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)}]$ with carbon monoxide.[2] However, in the isocyanide reaction there was no evidence for the formation of a di-imine analogue of the duroquinone [2] complex reported previously. It is clear that (11) and (12) are the precursors of (13) and (14), and a plausible reaction path is illustrated in the Scheme. This involves the initial conversion (reversible) of the co-ordinatively saturated bis(acetylene) complex into a molybdacyclopentadiene complex, a transformation which would require that the two η^2-bonded $CF_3C_2CF_3$ ligands have a relative *cis* disposition as in the (b) isomer. This would allow the co-ordination of a second molecule of isocyanide. However, a difficulty here is that the molybdenum would achieve a formally rather high co-ordination number of eight. Migration on to co-ordinated isocyanide, followed by reductive ($Mo^{IV} \longrightarrow Mo^{II}$) carbon–carbon bond formation, would then result in the formation of the cyclopentadienimine ring. The

TABLE 5

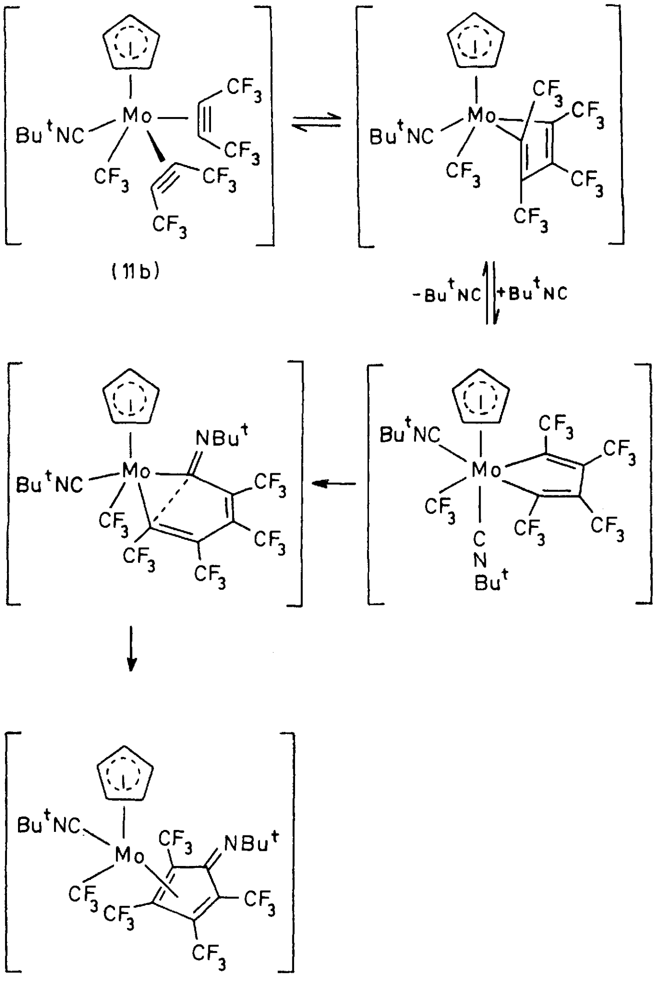
Final atomic positional parameters * (× 10^4) (Mo, × 10^5) for complex (13)

Atom	x	y	z
(*i*) Molecule A			
Mo	23 394(6)	21 529(3)	−9 314(10)
C(1)	2 483(10)	2 252(5)	1 581(12)
C(2)	1 767(10)	2 067(5)	1 203(17)
C(3)	1 300(8)	2 324(5)	341(17)
C(4)	1 715(10)	2 655(5)	229(16)
C(5)	2 452(9)	2 604(6)	966(15)
H(1)	2 933	2 143	2 195
H(2)	1 623	1 806	1 490
H(3)	765	2 277	−109
H(4)	1 524	2 890	−287
H(5)	2 881	2 792	1 030
C(51)	3 182(7)	1 587(4)	−2 475(14)
N(51)	3 253(7)	1 358(4)	−3 454(13)
C(52)	3 446(10)	954(5)	−3 529(17)
C(521)	3 573(21)	896(11)	−5 151(38)
C(522)	4 239(20)	891(10)	−2 699(37)
C(523)	2 832(27)	689(14)	−2 991(50)
C(11)	1 436(8)	1 757(5)	−1 922(16)
F(111)	1 094(8)	1 537(4)	−925(14)
F(112)	810(7)	1 935(4)	−2 633(13)
F(113)	1 632(6)	1 507(3)	−2 905(12)
F(201)	4 416(11)	2 530(6)	−2 916(20)
F(202)	3 454(9)	2 867(5)	−2 568(16)
F(203)	4 248(9)	2 745(4)	−825(16)
C(20)	3 894(9)	2 584(5)	−2 022(16)
C(21)	3 458(8)	2 233(4)	−1 760(13)
C(22)	3 032(8)	1 997(4)	−2 855(12)
C(23)	2 953(10)	2 083(5)	−4 454(17)
F(231)	2 340(7)	1 919(3)	−5 136(12)
F(232)	2 838(6)	2 457(3)	−4 780(11)
F(233)	3 566(6)	1 988(3)	−5 127(11)
F(301)	2 908(6)	1 429(3)	1 572(12)
F(302)	3 727(7)	1 118(4)	513(13)
F(303)	2 554(8)	1 084(4)	−241(14)
C(30)	3 101(11)	1 326(5)	239(19)
C(31)	3 166(7)	1 634(4)	−818(13)
C(32)	3 568(7)	1 996(4)	−462(14)
C(33)	4 176(10)	2 078(5)	766(17)
F(331)	4 866(7)	2 051(4)	251(13)
F(332)	4 167(7)	1 803(4)	1 821(13)
F(333)	4 150(8)	2 385(4)	1 481(14)
C(61)	1 870(8)	2 522(4)	−2 570(14)
N(61)	1 583(7)	2 734(4)	−3 418(13)
C(62)	1 228(11)	3 003(6)	−4 475(20)
C(621)	1 908(18)	3 231(9)	−5 016(33)
C(622)	685(16)	3 241(8)	−3 708(29)
C(623)	809(20)	2 766(10)	−5 694(37)
(*ii*) Molecule B			
Mo	16 257(7)	−7 836(3)	1 327(11)
C(1)	1 531(12)	−737(6)	2 629(15)
C(2)	1 599(11)	−1 120(6)	2 272(20)
C(3)	916(13)	−1 215(5)	1 365(20)
C(4)	444(11)	−895(6)	1 193(17)
C(5)	817(12)	−602(6)	1 963(16)
H(1)	1 920	−585	3 248
H(2)	2 038	−1 291	2 590
H(3)	794	−1 469	925
H(4)	−71	−881	617
H(5)	617	−339	2 036
C(51)	2 922(8)	−529(5)	−1 399(13)
N(51)	3 371(8)	−556(4)	−2 342(14)
C(52)	4 209(10)	−588(5)	−2 430(18)
C(521)	4 322(16)	−431(8)	−3 953(29)
C(522)	4 718(13)	−394(7)	−1 221(23)
C(523)	4 383(17)	−1 022(9)	−2 455(30)
C(11)	2 140(10)	−1 308(4)	−662(18)
F(111)	2 602(8)	−1 500(4)	348(15)
F(112)	1 617(8)	−1 582(4)	−1 161(14)
F(113)	2 600(8)	−1 293(4)	−1 775(14)
F(201)	1 290(9)	289(5)	−2 245(16)
F(202)	486(10)	−64(5)	−1 478(18)
F(203)	1 027(12)	297(6)	−7(22)
C(20)	1 203(11)	97(5)	−1 069(19)
C(21)	1 778(8)	−207(4)	−751(13)
C(22)	2 061(8)	−459(5)	−1 794(13)
C(23)	1 827(9)	−479(5)	−3 426(16)
F(231)	1 959(6)	−798(3)	−4 025(11)
F(232)	1 066(6)	−401(3)	−3 747(10)
F(233)	2 172(6)	−201(3)	−4 136(10)
F(301)	3 252(6)	−798(3)	2 602(11)
F(302)	4 021(7)	−396(3)	1 780(12)
F(303)	3 876(7)	−948(4)	808(14)
C(30)	3 466(10)	−678(5)	1 351(18)
C(31)	2 864(9)	−528(4)	282(13)
C(32)	2 290(10)	−253(4)	541(14)
C(33)	2 358(10)	30(5)	1 789(17)
F(331)	2 657(8)	353(4)	1 340(14)
F(332)	2 831(7)	−84(3)	2 914(12)
F(333)	1 713(8)	114(4)	2 360(14)
C(61)	789(9)	−903(5)	−1 576(16)
N(61)	317(9)	−1 005(5)	−2 458(16)
C(62)	−254(15)	−1 166(8)	−3 591(27)
C(621)	−259(29)	−905(15)	−4 950(54)
C(622)	−1 037(22)	−1 154(12)	−2 964(41)
C(623)	−253(37)	−1 586(20)	−3 410(67)

*As fractional co-ordinates of the unit-cell edges.

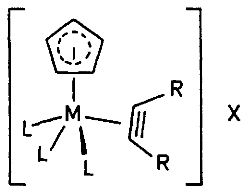
formation of (13) is important in that it provides an insight into the mode of formation of organic nitrogen compounds in the nickel-, palladium-, and cobalt-catalysed reactions of acetylenes with isocyanides.[10-13]

An attempt to extend these reactions was unsuccessful. Reaction of excess of Bu^{t}NC with [MoCl(η^2-PhC$_2$Ph)$_2$(η-C$_5$H$_5$)],[2] [MoCl(η^2-PhC$_2$Ph)(η^2-CF$_3$C$_2$CF$_3$)(η-C$_5$H$_5$)],[2] or [WCl(η^2-PhC$_2$Ph)(η^2-CF$_3$C$_2$CF$_3$)(η-C$_5$H$_5$)] [2] gave, respectively, the 18-electron cationic complexes (15) (isolated as its [PF$_6$]$^-$ salt), (16), and (17), where *clearly displacement* of acetylene competes with the cyclisation step. In these complexes the acetylene does not freely rotate as evidenced by the ^{19}F n.m.r. spectra of (16) and (17), which both show two C*F*$_3$C≡C environments at room temperature.

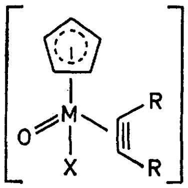


SCHEME

When (1), (2), or [MCl(CO)(η^2-PhC$_2$Ph)(η-C$_5$H$_5$)] (M = Mo or W) were allowed to oxidise slowly in air, either in solution or in the solid state, yellow-green crystals of the complexes (18), (19), (20), and (21) were formed, respectively. Elemental analyses and i.r. and n.m.r. spectroscopy suggest that these complexes have the illustrated structures. For example, the i.r. spectrum of (19) shows a sharp band at 945 cm^{-1} assignable to ν(MoO), and a weak band at 1 840 cm^{-1} due to a ν(C≡C) stretching mode. The relatively high acetylenic stretch is consistent with reduced back bonding from the metal, which is in a relatively high oxidation state. The ^{1}H n.m.r. spectrum at room temperature showed one η-C$_5$H$_5$ resonance and two C*H*$_3$C≡C resonances demonstrating a rigid structure. Thus (18) and the related complexes are isostructural with [Mo(SC$_6$F$_5$)O(η^2-CF$_3$C$_2$CF$_3$)(η-C$_5$H$_5$)], an *X*-ray crystallographic study[5] having shown that in the latter complex the metal is octahedrally co-ordinated with the axis of the acetylenic ligand parallel to the Mo–S bond.



	M	L	R	X
(15)	Mo	Bu^{t}NC	Ph	PF$_6$
(16)	Mo	Bu^{t}NC	CF$_3$	Cl
(17)	W	Bu^{t}NC	CF$_3$	Cl



	M	R	X
(18)	Mo	Ph	CF$_3$
(19)	Mo	Me	CF$_3$
(20)	Mo	Ph	Cl
(21)	W	Ph	Cl

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a Varian Associates HA 100 spectrometer operating at 100 MHz and are relative to SiMe$_4$ (τ 10.00) which was also the lock signal. Fluorine n.m.r. spectra were obtained either on the HA 100 spectrometer operating at 94.08 MHz, or on a JEOL PFT-100 FT n.m.r. spectrometer using a ^{2}H lock, and are relative to CCl$_3$F (0.00 p.p.m.). Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Molecular weights were obtained from molecular ions obtained from mass spectra on an A.E.I. MS 902 mass spectrometer operating at 70 eV.* All the syntheses were carried out under an

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* 1 eV ≈ 1.60 × 10^{-19} J.

[10] S. Otsuka and A. Nakamura, *Adv. Organometallic Chem.*, 1976, **14**, 245.

[11] R. S. Dickson, P. J. Fraser, and B. M. Gatehouse, *J.C.S. Dalton*, 1972, 2278.

[12] H. Yamazaki, K. Aoki, Y. Yamamoto, and Y. Wakatsuki, *J. Amer. Chem. Soc.*, 1975, **97**, 3546.

[13] Y. Suzuki and T. Takizawa, *J.C.S. Chem. Comm.*, 1972, 837.

atmosphere of dry oxygen-free nitrogen. Starting materials were prepared by the published methods.[2,4]

Reactions of Tricarbonyl(η-cyclopentadienyl)(trifluoroacetyl)molybdenum.—(*a*) *With diphenylacetylene.* A solution of $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$ (0.30 g, 0.87 mmol) and diphenylacetylene (0.18 g, 1.0 mmol) was heated under reflux (24 h) in hexane (20 cm^3). The purple solution was filtered while hot, the volume of the solvent reduced (5 cm^3), and cooling afforded purple *crystals* of (1) (0.30 g, 80%), m.p. 108—110 °C (decomp.) (Found: C, 57.6; H, 3.5%; *M* 436. $C_{21}H_{15}F_3MoO$ requires C, 57.8; H, 3.4%; *M* 436), $\nu_{max.}$ in $CHCl_3$ at 1 962vs cm^{-1} (CO). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.70 (m, 10 H, C_6H_5) and 3.92 (s, 5 H, C_5H_5).

(*b*) *With but-2-yne.* A solution of $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$ (0.52 g, 1.52 mmol) was heated under reflux (24 h) in hexane (30 cm^3). The resulting solution of $[Mo(CF_3)(CO)_3(\eta\text{-}C_5H_5)]$ was placed in a Carius tube (fitted with a Westef stopcock), and but-2-yne (10 mmol) condensed (−196 °C) into the vessel. Irradiation (48 h, 250-W Hanovia u.v. lamp) of the tube and contents afforded a purple solution. Reduction of the volume of the solvent *in vacuo* gave air-sensitive purple *crystals* of (2) (0.24 g, 50%), m.p. 64—65 °C (decomp.) (Found: 42.8; H, 4.0%; *M* 312. $C_{11}H_{11}F_3MoO$ requires C, 42.3; H, 3.5%; *M* 312), $\nu_{max.}$ in hexane at 1 968vs cm^{-1} (CO). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.54 (s, 5 H, C_5H_5) and 7.82 (s, 6 H, *Me*C≡C). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed a single resonance at 9.70 p.p.m. (s, 3 F, CF_3).

(*c*) *With hexafluorobut-2-yne.* Irradiation (48 h) of a solution of $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$ (0.37 g, 1.1 mmol) and hexafluorobut-2-yne (2 mmol) in hexane (20 cm^3) afforded yellow crystals. Recrystallisation (−20 °C) from dichloromethane–hexane gave yellow *crystals* of (3) (0.30 g, 60%), m.p. 133—135 °C (decomp.) (Found: C, 30.3; H, 1.1. $C_{14}H_5F_{15}Mo$ requires C, 30.3; H, 0.9%), $\nu_{max.}$ in CH_2Cl_2 at 1 775m and 1 760m cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed a resonance at τ 4.00 (s, 5 H, C_5H_5). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at −6.61 (m, 3 F, CF_3Mo) and 58.2 p.p.m. [q, 12 F, CF_3C≡C, *J*(FF) 4.0 Hz; coalescence temperature −50 °C].

(*d*) *With dimethyl acetylenedicarboxylate.* A solution of $[Mo(COCF_3)(CO)_3(\eta\text{-}C_5H_5)]$ (0.20 g, 0.85 mmol) and dimethyl acetylenedicarboxylate (1 cm^3, 11.0 mmol) in diethyl ether (25 cm^3) was heated under reflux. After 5 d, the resulting yellow solution was filtered, the volume of the solvent reduced *in vacuo*, and cooling afforded yellow *crystals* of (4) (0.17 g, 40%), m.p. 123—125 °C (decomp.) (Found: C, 41.9; H, 3.2. $C_{18}H_{17}F_3MoO_8$ requires C, 42.2; H, 3.3%), $\nu_{max.}$ in $CHCl_3$ at 1 760m (C≡C) and 1 715s cm^{-1} (CO). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.10 (s, 5 H, C_5H_5) and 6.13 (s, 12 H, *Me*O_2CC≡C; coalescence temperature −30 °C).

Reactions of Oxygen.—(*a*) *With complex* (1). Exposure of a solution of (1) in hexane to air afforded yellow-green *crystals* of (18) (60%), m.p. 90—91 °C (decomp.) (Found: C, 56.6; H, 3.8%; *M* 424. $C_{20}H_{15}F_3MoO$ requires C, 56.6; H, 3.5%; *M* 424), $\nu_{max.}$ in CCl_4 at 950s cm^{-1} (MoO). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.50 (m, 10 H, C_6H_5) and 3.92 (s, 5 H, C_5H_5). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed a single resonance at 7.9 p.p.m. (s, 3 F, CF_3Mo).

(*b*) *With complex* (2). Similarly, oxidation of (2) gave yellow-green *crystals* of (19) (90%), m.p. 75—76 °C (Found: C, 40.4; H, 3.9. $C_{10}H_{11}F_3MoO$ requires C, 40.0; H, 3.7%), $\nu_{max.}$ in CCl_4 at 945s cm^{-1} (MoO). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at 3.92 (s, 5 H, C_5H_5), 7.00 (s, 3 H, *Me*C≡C), and 7.44 (s, 3 H, *Me*C≡C). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed a single resonance at 14.7 p.p.m. (s, 3 F, CF_3Mo).

(*c*) *With Carbonylchloro(η-cyclopentadienyl)(1—2-η-diphenylacetylene)molybdenum.* A solution of $[MoCl(CO)(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ (0.20 g, 0.05 mmol) in chloroform (30 cm^3) was stirred (22 h) at room temperature in air. The reaction mixture was filtered and the solvent removed *in vacuo*. Recrystallisation (−20 °C) of the residue from diethyl ether–hexane afforded yellow *crystals* of (20) (0.12 g, 57%), m.p. 152—154 °C (Found: C, 57.8; H, 3.9%; *M* 390. $C_{19}H_{15}ClMoO$ requires C, 58.3; H, 3.8%; *M* 390), $\nu_{max.}$ in Nujol at 947m and 936m cm^{-1} (Mo=O). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.45 (m, 10 H, C_6H_5) and 3.77 (s, 5 H, C_5H_5).

(*d*) *With carbonylchloro(η-cyclopentadienyl)(1—2-η-diphenylacetylene)tungsten.* A similar reaction of $[WCl(CO)(\eta^2\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)]$ but in the solid state gave *crystals* (from Et_2O) of (21) (55%), m.p. 154—155 °C (Found: C, 47.7; H, 3.3%; *M* 478. $C_{19}H_{15}ClOW$ requires C, 47.7; H, 3.2%; *M* 478), $\nu_{max.}$ in Nujol at 949m cm^{-1} (W=O). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.25 (m, 10 H, C_6H_5) and 3.33 (s, 5 H, C_5H_5).

Reaction of Complex (2) *with Hexafluorobut-2-yne.*—An excess of hexafluorobut-2-yne (1 mmol) was condensed into a tube containing a hexane (10 cm^3) solution of (2) (0.10 g, 0.32 mmol). After 1 h at room temperature the volume was reduced *in vacuo* giving yellow *crystals* of (5) (0.14 g, 90%), m.p. 120—121 °C (Found: C, 38.0; H, 2.5. $C_{14}H_{11}F_9Mo$ requires C, 37.7; H, 2.5%), $\nu_{max.}$ in CCl_4 at 1 780m cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.26 (s, 5 H, C_5H_5) and 7.00 (s, 6 H, *Me*C≡C; coalescence temperature −63 °C). The ^{19}F n.m.r. spectrum (in $CDCl_3$, −80 °C) showed resonances at 0.75 (m, 3 F, CF_3Mo), 55.6 (m, 3 F, CF_3C≡C), and 55.8 p.p.m. (m, 3 F, CF_3C≡C).

Reaction of Complex (3) *with Trimethylphosphine.*—Trimethylphosphine {from $[AgI(PMe_3)]$, 0.18 mmol} was condensed into a dichloromethane (10 cm^3) solution of (3) (0.10 g, 0.18 mmol). After 5 d at room temperature the mixture was filtered, hexane added, and cooled (−20 °C) to give pink round *crystals* of (6) (0.10 g, 90%), m.p. 164—166 °C (Found: C,. 33.0; H, 2.4%; *M* 630. $C_{17}H_{14}F_{15}MoP$ requires C, 32.4; H, 2.2%; *M* 630), $\nu_{max.}$ in CH_2Cl_2 at 1 795m and 1 775m cm^{-1} (C≡C). The ^1H n.m.r. spectrum (in $CDCl_3$, −50 °C) showed resonances corresponding to two isomers (1 : 1) at τ 4.12 (s, 5 H, C_5H_5), 4.16 (s, 5 H, C_5H_5), 8.46 [d, 9 H, *J*(HP) 13.0], and 8.50 [d, 9 H, *J*(HP) 13.0 Hz]. The ^{19}F n.m.r. spectrum (in $CDCl_3$ −50 °C) showed resonances at −4.8 (m, 3 F, CF_3Mo), 45.5 (m, 3 F, CF_3C≡C), 49.0 [q, 3 F, CF_3C≡C, *J*(FF) 6.0], 51.8 (m, 3 F, CF_3C≡C), 53.5 (s, 3 F, CF_3C≡C), 55.6 (s, 6 F, CF_3C≡C), 56.7 (s, 3 F, CF_3C≡C), and 61.9 p.p.m. [q, 3 F, CF_3C≡C, *J*(FF) 8.5 Hz].

Reaction of Complex (4) *with Triphenylphosphine.*—To complex (4) (0.10 g, 0.20 mmol) in dichloromethane (10 cm^3) was added triphenylphosphine (0.10 g, 0.4 mmol) when the yellow solution immediately became purple. Addition of hexane (5 cm^3) followed by cooling (−20 °C) afforded purple *crystals* of (7) (0.15 g, 98%), m.p. 145—146 °C (Found: C, 55.0; H, 4.5%; *M* 776. $C_{36}H_{32}F_3MoO_8P$ requires C, 55.7; H, 4.1%; *M* 776), $\nu_{max.}$ in CH_2Cl_2 at 1 675s cm^{-1} (CO). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.6 (m, 15 H, C_6H_5), 4.50 (s, 5 H,

C_5H_5), 6.24 (s, 3 H, MeO_2C), 6.50 (s, 3 H, MeO_2C), 6.70 (s, 3 H, MeO_2C), and 7.34 (s, 3 H, MeO_2C).

Reaction of Complex (3) *with t-Butyl Isocyanide*.—(*a*) *With equimolar amounts of reactants*. To complex (3) (0.21 g, 0.4 mmol) in diethyl ether (2 cm^3) was added Bu^tNC (0.032 g, 0.4 mmol) when the yellow colour changed to pink. Addition of hexane (2 cm^3) followed by cooling (−20 °C) gave pale pink *crystals* of (11) (0.23 g, 90%), m.p. 104—105 °C (sublimed) (Found: C, 36.2; H, 2.2; N, 2.3. $C_{19}H_{14}F_{15}MoN$ requires C, 35.8; H, 2.2; N, 2.2%), $\nu_{max.}$ in CCl_4 at 2 270s (NC) and 1 800s cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 3.89 (s, 5 H, C_5H_5) and 8.28 (s, 9 H, Bu^tN). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at 5.0 [q, 3 F, CF_3Mo, *J*(FF) 6.0], 54.7 (m, 6 F, $CF_3C{\equiv}C$), 56.7 (br, 3 F, $CF_3C{\equiv}C$), and 57.2 p.p.m. [q, 3 F, $CF_3C{\equiv}C$, *J*(FF) 3.6 Hz].

(*b*) *With an excess of* Bu^tNC. Addition (20 °C) of an excess of Bu^tNC (0.5 cm^3) to a solution of (3) (0.10 g, 0.18 mmol) in dichloromethane led to a change in colour from yellow to white. Hexane (1 cm^3) was added, the volume reduced *in vacuo* to 2 cm^3, and the reaction mixture cooled (−20 °C) giving off-white *crystals* of (13) (0.71 g, 98%), m.p. 131.5—132 °C (decomp.) (Found: C, 40.1; H, 3.3; F, 38.9; N, 4.0%; *M* 720. $C_{24}H_{23}F_{15}MoN_2$ requires C, 40.0; H, 3.2; F, 39.6; N, 3.9%; *M* 720), $\nu_{max.}$ in CCl_4 at 2 180s, 2 170s (NC), and 1 685s cm^{-1} (C=N). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances corresponding to the presence of two isomers at τ 4.26 (s, 5 H, C_5H_5), 4.58 (s, 5 H, C_5H_5), 8.30 (s), 8.34 (s), 8.58 (s), and 8.62 (s). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at −7.0 (m, 3 F, CF_3Mo), −2.0 (m, 3 F, CF_3Mo), 47.9 (m, 6 F, CF_3C), 50.9 (m, 6 F, CF_3C), 52.2 (m, 6 F, CF_3C), and 53.6 p.p.m. (m, 6 F, CF_3C).

Reactions of Chloro(η-*cyclopentadienyl*)*bis*(2—3-η-*hexafluorobut-2-yne*)*molybdenum*.—(*a*) *With triphenylphosphine*. A solution of [$MoCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)$] (0.20 g, 0.38 mmol) in dichloromethane (15 cm^3) was added to a solution of PPh_3 (0.10 g, 0.38 mmol) in dichloromethane (10 cm^3). After 1 h at room temperature the volume of solvent was reduced and hexane added. The solution was cooled (−20 °C) giving pale yellow *crystals* of (8) (0.25 g, 83%), m.p. 130—145 °C (decomp.) (Found: C, 47.2; H, 2.7. $C_{31}H_{20}ClF_{12}MoP$ requires C, 47.6; H, 2.6%), $\nu_{max.}$ in Nujol at 1 808m cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.50 (m, 15 H, C_6H_5) and 4.36 (s, 5 H, C_5H_5). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at 40.3 (m, 3 F, $CF_3C{\equiv}C$), 50.4 (m, 3 F, $CF_3C{\equiv}C$), 50.7 (m, 3 F, $CF_3C{\equiv}C$), and 51.5 p.p.m. (m, 3 F, $CF_3C{\equiv}C$).

(*b*) *With trimethylphosphine*. Trimethylphosphine (0.03 g, 0.39 mmol) was condensed (−196 °C) into a tube (Westef stopcock) containing a solution of [$MoCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)$] (0.13 g, 0.25 mmol) in benzene (15 cm^3). On warming to room temperature the orange solution became pale yellow. Volatile material was removed *in vacuo*, and the residue recrystallised (−20 °C) from dichloromethane–hexane to give pale yellow *crystals* of (9) (0.14 g, 94%), m.p. 175 °C (decomp.) (Found: C, 32.5; H, 2.5%; *M* 596. $C_{16}H_{14}ClF_{12}MoP$ requires C, 32.2; H, 2.4%; *M* 596), $\nu_{max.}$ in Nujol at 1 811w and 1 780w cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.00 (s, 5 H, C_5H_5), 8.15 [d, 9 H, CH_3P, *J*(HP) 13.6], and 8.31 [d, 9 H, CH_3P, *J*(HP) 13.2 Hz]. The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at 45.0 (m, 3 F, $CF_3C{\equiv}C$), 47.3 (m, 3 F, $CF_3C{\equiv}C$), 50.1 [q, 3 F, $CF_3C{\equiv}C$, *J*(FF) 4.0 Hz], 52.8 (m, 3 F, $CF_3C{\equiv}C$), 54.7 (m, 3 F, $CF_3C{\equiv}C$), 55.0 (m, 3 F, $CF_3C{\equiv}C$), 55.3 (m, 3 F, $CF_3C{\equiv}C$), and 55.9 p.p.m. (m, 3 F, $CF_3C{\equiv}C$).

Reaction of Chloro(η-*cyclopentadienyl*)*bis*(2—3-η-*hexafluorobut-2-yne*)*tungsten with Trimethylphosphine*.—Similarly, reaction of [$WCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)$] (0.15 g, 0.25 mmol) with PMe_3 (0.25 mmol) in benzene (15 cm^3) gave white *crystals* of (10) (0.12 g, 71%), m.p. 155 °C (decomp.) (Found: C, 28.3; H, 2.1%; *M* 684. $C_{16}H_{14}ClF_{12}PW$ requires C, 28.1; H, 2.1%; *M* 684), $\nu_{max.}$ in Nujol at 1 785w and 1 753w cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.00 (s, 5 H, C_5H_5), 4.02 (s, 5 H, C_5H_5), 8.20 [d, 9 H, CH_3P, *J*(HP) 13.6], and 8.36 [d, 9 H, CH_3P, *J*(HP) 13.0 Hz]. The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at 42.6 (m, 3 F, $CF_3C{\equiv}C$), 47.6 (m, 3 F, $CF_3C{\equiv}C$), 51.6 [q, 3 F, $CF_3C{\equiv}C$, *J*(FF) 4.4 Hz], 54.2 (m, 6 F, $CF_3C{\equiv}C$), 56.0 (m, 3 F, $CF_3C{\equiv}C$), and 57.0 p.p.m. (m, 6 F, $CF_3C{\equiv}C$).

Reactions of t-Butyl Isocyanide.—(*a*) *With chloro*(η-*cyclopentadienyl*)*bis*(1—2-η-*diphenylacetylene*)*molybdenum*. A solution of Bu^tNC (0.1 g, 12.0 mmol) in dichloromethane (5 cm^3) was added dropwise at room temperature with stirring to a solution of [$MoCl(\eta^2\text{-}PhC_2Ph)_2(\eta\text{-}C_5H_5)$] (0.1 g, 0.18 mmol) in dichloromethane (15 cm^3). After 0.5 h the solvent was removed, and the residue dissolved in acetone (20 cm^3). Addition of an aqueous solution of [NH_4][PF_6] afforded a precipitate, which was collected. Recrystallisation (−20 °C) from dichloromethane–hexane afforded yellow *crystals* of (15) (0.05 g, 45%), m.p. 181 °C (Found: C, 54.9; H, 5.4; N, 5.7. $C_{34}H_{42}F_6MoN_3P$ requires C, 55.6; H, 5.1; N, 5.7%), $\nu_{max.}$ in Nujol at 2 162m and 2 137m cm^{-1} (NC). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 2.62—2.88 (m, 10 H, C_6H_5), 4.65 (s, 5 H, C_5H_5), 8.61 (s, 9 H, Bu^tN), 8.63 (s, 9 H, Bu^tN), and 8.91 (s, 9 H, Bu^tN).

(*b*) *With chloro*(η-*cyclopentadienyl*)(1—2-η-*diphenylacetylene*)(2—3-η-*hexafluorobut-2-yne*)*molybdenum*. A solution of Bu^tNC (0.10 g, 12.0 mmol) in diethyl ether (10 cm^3) was added slowly to a solution of [$MoCl(\eta^2\text{-}PhC_2Ph)(\eta^2\text{-}CF_3C_2CF_3)(\eta\text{-}C_5H_5)$] (0.06 g, 0.1 mmol) in Et_2O (15 cm^3). The reaction mixture rapidly changed colour through red to yellow. Cooling (−20 °C) afforded yellow *crystals* of (16) (0.05 g, 79%), m.p. 105—108 °C (Found: C, 46.9; H, 5.4; F, 17.9; N, 6.6. $C_{24}H_{32}ClF_6MoN_3$ requires C, 47.4; H, 5.3; F, 18.7; N, 6.9%), $\nu_{max.}$ in Nujol at 2 195m, 2 173s (NC), and 1 804w cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.25 (s, 5 H, C_5H_5), 8.33 (s, 9 H, Bu^tN), and 8.62 (s, 18 H, Bu^tN). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at 55.0 [q, 3 F, $CF_3C{\equiv}C$, *J*(FF) 3.7] and 56.1 p.p.m. [q, 3 F, $CF_3C{\equiv}C$, *J*(FF) 3.7 Hz].

(*c*) *With chloro*(η-*cyclopentadienyl*)(1—2-η-*diphenylacetylene*)(2—3-η-*hexafluorobut-2-yne*)*tungsten*. Similarly, reaction of [$WCl(\eta^2\text{-}PhC_2Ph)(\eta^2\text{-}CF_3C_2CF_3)(\eta\text{-}C_5H_5)$] (0.045 g, 0.72 mmol) gave yellow *crystals* of (17) (0.03 g, 61%), m.p. 118—119 °C (Found: C, 41.1; H, 4.6; N, 6.0. $C_{24}H_{32}ClF_6N_3W$ requires C, 41.4; H, 4.8; N, 5.6%), $\nu_{max.}$ in Nujol at 2 193m, 2 165s (NC), and 1 773w cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 4.21 (s, 5 H, C_5H_5), 8.23 (s, 9 H, Bu^tN), and 8.52 (s, 18 H, Bu^tN). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at 54.7 [q, 3 F, $CF_3C{\equiv}C$, *J*(FF) 3.7] and 56.4 p.p.m. [q, 3 F, $CF_3C{\equiv}C$, *J*(FF) 3.7 Hz].

(*d*) *With chloro*(η-*cyclopentadienyl*)*bis*(2—3-η-*hexafluorobut-2-yne*)*tungsten*. Addition of Bu^tNC (0.034 g, 0.4 mmol) in diethyl ether (10 cm^3) to a solution of [$WCl(\eta^2\text{-}CF_3C_2CF_3)_2(\eta\text{-}C_5H_5)$] (0.25 g, 0.4 mmol) in diethyl ether (10 cm^3) resulted in a colour change from yellow to colourless. The volume of the solvent was reduced *in vacuo*, hexane added, and the solution cooled (−20 °C) affording pale yellow *crystals* of (12) (0.13 g, 44%), m.p. 85 °C (Found: C, 31.7; H, 2.1; N, 2.0. $C_{21}H_{14}ClF_{18}NW$ requires C, 31.3; H, 2.0; N, 2.0%), $\nu_{max.}$ in Nujol at 2 260m (NC) and 1 788m cm^{-1} (C≡C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances at τ 3.8 (s, 5 H, C_5H_5) and 8.35 (s, 9 H, Bu^tN). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at 54.2 (m, 3 F, $CF_3C{\equiv}C$), 55.5 (m, 3 F, $CF_3C{\equiv}C$), 55.9 (m, 3 F, $CF_3C{\equiv}C$), and 56.6 p.p.m. (m, 3 F, $CF_3C{\equiv}C$).

Reaction with an excess of Bu^tNC afforded, from diethyl ether–hexane, yellow *crystals* of (14) (36%), m.p. 90 °C (decomp.) (Found: C, 35.7; H, 3.0; N, 3.5%; *M* 774. $C_{23}H_{23}ClF_{12}N_2W$ requires C, 35.7; H, 3.0, N, 3.6%; *M* 774), $\nu_{max.}$ in Nujol at 2 000m (NC) and 1 690m cm^{-1} (N=C). The ^1H n.m.r. spectrum in $CDCl_3$ showed resonances corresponding to two isomers at τ 4.08 (s, 5 H, C_5H_5), 4.38 (s, 5 H, C_5H_5), 8.37 (s, Bu^tN), 8.41 (s, Bu^tN), 8.48 (s, Bu^tN), and 8.71 (s, Bu^tN). The ^{19}F n.m.r. spectrum in $CDCl_3$ showed resonances at 48.5 (m, CF_3C), 48.9 (m, CF_3C), 49.5 (m, CF_3C), 51.2 (m, CF_3C), 51.7 (m, CF_3C), and 55.0 p.p.m. (m, CF_3C).

Crystal-structure Determination of Complex (13).—Crystals, as prepared above, were recrystallised from dichloromethane–hexane. A single crystal, *ca.* 0.45 × 0.45 × 0.25 mm with faces 100, $\bar{1}\bar{1}0$, $\bar{1}10$, $1\bar{1}0$, 001, and $00\bar{1}$ developed, was mounted on a quartz fibre with epoxy-resin adhesive. Oscillation, and zero- and first-layer equi-inclination Weissenberg photographs about *a* yielded the space group and cell dimensions.

The specimen was then transferred to a computer-controlled Syntex $P2_1$ four-circle diffractometer. Setting and data collection followed the established procedure [14] with the following pertinent details. In the centring program, 15 reflections, $14 < 2\theta < 27°$ (Mo-K_α *X*-radiation), were taken from a 25-min rotation photograph recorded with generator settings of *ca.* 50 kV and 20 mA. For data collection: $0 \leqslant h \leqslant 25$, $0 \leqslant k \leqslant 50$, and $\bar{1}\bar{5} \leqslant l \leqslant 15$ (with equivalent $0kl$ and $0k\bar{l}$ reflections subsequently merged); $2.9 \leqslant 2\theta \leqslant 55.0°$ (graphite-monochromated Mo-K_α radiation, $\lambda_{\alpha 1} = 0.709\ 26$, $\lambda_{\alpha 2} = 0.713\ 54$ Å); θ—2θ scan in 96 steps at rates in the range 0.033 67—0.488 33° s^{-1} dependent on an initial 2-s peak count with 200 and 2 000 counts as the threshold; four reflections were monitored once every batch of 40 (subsequent analysis [15] of their net intensities as individual functions of time implied satisfactory crystal and machine stability throughout data collection); *T ca.* 295 °C; and of 10 362 independent data, 7 900 had $I \geqslant 1.0\sigma$ and were retained to solve and refine the structure.

Crystal data. $C_{24}H_{23}F_{15}MoN_2$, $M = 720.38$, Monoclinic, $a = 17.452(6)$, $b = 35.410(18)$, $c = 9.182(4)$ Å, $\beta = 95.51(3)°$, $U = 5\ 648(4)$ Å^3, $D_m = 1.70$ (flotation), $Z = 8$, $D_c = 1.694$ g cm^{-3}, $F(000) = 2\ 864$; Mo-K_α *X*-radiation, $\bar{\lambda} = 0.710\ 69$ Å, μ(Mo-$K_{\bar{\alpha}}$) = 5.9 cm^{-1}. Space group $P2_1/a$.

Observed data were corrected for Lorentz and polarisation but not for *X*-ray absorption effects, and the structure was solved *via* a three-dimensional Patterson synthesis (Mo atoms), full-matrix (later block-diagonal) least-squares refinement, and electron-density difference syntheses (F, N, and C atoms). Cyclopentadienyl H atoms were introduced into calculated positions with *r*(C–H) 1.00 Å and U_H 0.076 Å^2, but were not refined. No attempt was made to locate methyl H atoms. Weights were applied according to $w = (xy)^{-1}$ with $x = 0.3/\sin\theta$ if $\sin\theta < 0.3$, $x = 1$ if $\sin\theta \geqslant 0.3$, $y = F_o/50.0$ if $F_o > 50.0$, and $y = 1$ if $F_o \leqslant 50.0$.

In the final stages of refinement, atoms Mo, C(1)—(5), C(11), C(21), C(22), C(32) and C(51) were allowed anisotropic thermal motion. Refinement continued until the average shift : error of refined parameters was <0.003. Residuals of *R* 0.127 and *R'* 0.159 were obtained at a data : variable ratio of *ca.* 17.1 : 1. An ultimate difference Fourier (0.37 Å resolution) maximised at *ca.* 0.20, 0.44, 0.71 (*ca.* 1.6 eÅ^{-3}).

Atomic-scattering factors for neutral atoms were taken from ref. 16 for Mo and F, ref. 17 for N and C, and ref. 18 for H with appropriate correction for anomalous dispersion.[19] Table 5 lists the atomic positional parameters; structure factors (Appendix A), some bond angles (Appendix B), and the thermal parameters (Appendix C) are listed in Supplementary Publication No. SUP 22122 (39 pp.).*

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1976, Index issue.

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