Syntheses involving Co-ordinatively Unsaturated Cyclopentadienyl-molybdenum and -tungsten Complexes. Molecular and Crystal Structure of $[\overline{\mathrm{Mo{\cdot}C(CF_3){:}C(CF_3){\cdot}C}}_5\mathrm{H_5(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)}]$

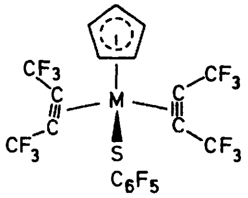
By **Jack L. Davidson, Michael Green, F. Gordon A. Stone,* and Alan J. Welch,** Department of Inorganic Chemistry, The University, Bristol BS8 1TS

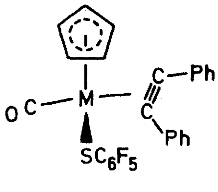
The 16-electron chloro-complexes $[\mathrm{MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}]$ (M = Mo or W) react with $\mathrm{TlSC_6F_5}$ to give compounds $[\mathrm{M(SC_6F_5)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}]$; the related species $[\mathrm{M(SC_6F_5)(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)}]$ were similarly obtained from $[\mathrm{MCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)}]$. Cyclopentadienylthallium reacts with the compounds $[\mathrm{MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}]$ to afford insertion products $[\overline{\mathrm{MC(CF_3)C(CF_3)C}}_5\mathrm{H_5(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)}]$, the molybdenum compound being characterised by a single-crystal *X*-ray diffraction study. It crystallises in the centrosymmetric monoclinic space-group $P2_1/n$, with lattice parameters $a = 12.904(6)$, $b = 9.641(3)$, $c = 15.302(6)$ Å, $\beta = 103.34(4)°$. The structure was elucidated *via* analysis of 2 148 independent diffracted data, and refined to *R* 0.39, *R'* 0.044.

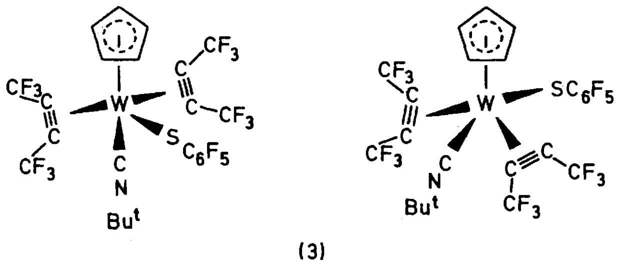
The molybdenum compound $[\mathrm{MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}]$ undergoes an unusual reaction with the tris-(pyrazolyl)borate anion to give a complex containing no boron but an η^3-allyl group, linking two pyrazole ligands and formed by condensation of the two hexafluorobut-2-yne ligands originally co-ordinated to the metal. Buta-1,3-diene reacts with $[\mathrm{MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}]$ to give $[\mathrm{MoCl_2(\eta^4\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)}]$ and with $[\mathrm{MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)}]$ to yield the same compound or $[\mathrm{MoCl(CO)(\eta^4\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)}]$, depending on the solvent. The tungsten compound $[\mathrm{WCl(CO)(\eta^4\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)}]$ was also prepared. Reactions of bicyclo[2.2.1]-heptadiene with the compounds $[\mathrm{MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}]$ were also studied.

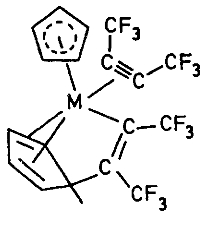
EARLIER we described the synthesis of several co-ordinatively unsaturated complexes of molybdenum and tungsten in which acetylene molecules are ligands. These included species such as $[\mathrm{M(SC_6F_5)(CO)(R'C_2R')(\eta^5\text{-}C_5H_5)}]$

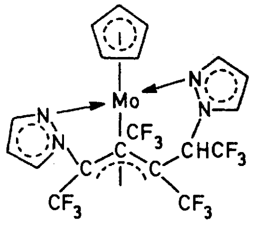
(M = Mo or W; R′ = CF_3, Me, or Ph) [1] and [MCl($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)].[2,3] These 16-electron complexes should react with a variety of reagents, thereby extending the organometallic chemistry of molybdenum and tungsten. In this paper we report such studies.

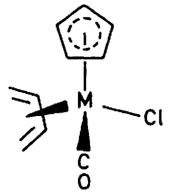

(1)
a; M = Mo
b; M = W

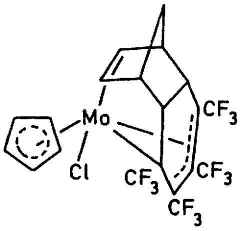

(2)
a; M = Mo
b; M = W


(3)


(4)
a; M = Mo
b; M = W


(5)


(8)
a; M = Mo
b; M = W


(9)

RESULTS AND DISCUSSION

The 16-electron chloro-complexes [MCl($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)] react readily at room temperature in tetrahydrofuran with the thallium reagent $TlSC_6F_5$ to give crystalline compounds [M(SC_6F_5)($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)] (1; M = Mo or W). The related species [M(SC_6F_5)(CO)(PhC_2Ph)(η^5-C_5H_5)] (2; M = Mo or W) were similarly prepared from the complexes [MCl(CO)(PhC_2Ph)(η^5-C_5H_5)]. Compound (2a) has previously been obtained by allowing diphenylacetylene to react with [Mo(SC_6F_5)(CO)$_3$(η^5-C_5H_5)].[1] The new compounds have been characterised as indicated in Tables 1 and 2. Like its molybdenum analogue (2a),[1] complex (2b) shows a single carbonyl stretching band (1 938s cm^{-1}) in the i.r. region.

The complexes (1) display i.r. bands due to the pentafluorophenyl group near 1 640 and 1 500 cm^{-1}; and two weak $\nu_{C\equiv C}$ stretching modes (1a, 1 793 and 1 765; 1b, 1 773 and 1 745 cm^{-1}). The latter are similar to those observed [2,3] in the spectra of the chloro-complexes [MCl($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)]. The ^{19}F n.m.r. spectrum of (1b) (Table 2) shows a single peak due to the CF_3 groups, both at room temperature and at −90 °C. This is in contrast with the behaviour of the chloro-analogue [WCl($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)], the spectrum of which shows two CF_3 group resonances at −80 °C.[3] It is apparent that there is a much lower barrier to rotation of the acetylene in (1b) than in the chloro-compound.

Reactions of t-butyl isocyanide with the complexes [MX($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)] (M = Mo or W; X = CF_3 or Cl) give several types of compound some of which involve formation *in situ* of *N*-t-butyltetrakis(trifluoromethyl)cyclopentadienimine ligands.[4] The products of these

---

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

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

[3] J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J.C.S. Dalton*, 1976, 738.

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

TABLE 1

Physical and analytical [a] data for the complexes

	Compound	Colour	M.p. (θ/°C)	C	H	Molecular weight [b]
(1a)	$[Mo(SC_6F_5)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$	Dark blue	90—93	33.4 (33.3)	0.69 (0.73)	
(1b)	$[W(SC_6F_5)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ [c]	Orange	130	29.3 (29.5)	0.64 (0.65)	772 (772)
(2b)	$[W(SC_6F_5)(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ [d]	Dark red	190—192	47.6 (47.7)	2.3 (2.3)	654 (654)
(3)	$[W(SC_6F_5)(Bu^tNC)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ [e]	Pale orange	118—121 (decomp.)	33.6 (33.8)	1.8 (1.6)	
(4a)	$[MoC(CF_3)=C(CF_3)C_5H_5(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]$	Yellow	125—128	38.2 (39.3)	1.8 (1.8)	550 (550)
(4b)	$[WC(CF_3)=C(CF_3)C_5H_5(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]$	Pale yellow	144—146 (decomp.)			638 (638)
(5)	$[Mo\{C_4(CF_3)_4H(C_3H_3N_2)_2\}(\eta^5\text{-}C_5H_5)]$ [f]	Orange-red	178—179			620 (620)
(6)	$[MoCl(MeC_2Me)_2(\eta^5\text{-}C_5H_5)]\cdot C_5HF_6O_2Tl$ [g]	Yellow	97—98	29.9 (30.2)	2.6 (2.6)	
(7)	$[MoCl_2(1\text{—}4\text{-}\eta\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)]$ [h]	Brown	>308 (decomp.)	37.0 (37.9)	3.9 (3.9)	285 (285)
(8a)	$[MoCl(CO)(1\text{—}4\text{-}\eta\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)]$	Black	>150 (decomp.)	44.0 (43.1)	4.0 (3.8)	278 (278)
(8b)	$[WCl(CO)(1\text{—}4\text{-}\eta\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)]$	Black	>135 (decomp.)	31.6 (32.7)	3.3 (3.0)	366 (366)
(9)	$[MoCl\{C_{11}H_8(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$	Orange	192—193	41.3 (42.7)	2.7 (2.9)	612 (612)

[a] Calculated values in parentheses. [b] Mass spectrometry. [c] Found: S, 5.1. Reqd.: 4.1%. [d] Found: F, 15.6; S, 5.1. Reqd.: F, 14.5; S, 4.9%. [e] Found: N, 1.7. Reqd.: 1.6%. [f] Complex fully characterised by *X*-ray crystallography (ref. 4). [g] Found: Cl, 5.0; F, 16.2. Reqd.: Cl, 5.0; F, 15.9%. [h] Found: Cl, 24.4. Reqd.: 24.8%.

reactions depend markedly on the nature of the group X and, therefore, the reaction between (1b) and t-butyl isocyanide was investigated. Complex (3) formed in high yield, but even the use of a large excess of the isocyanide failed to bring about a cyclisation reaction. The ^{19}F and ^{1}H n.m.r. spectra of the 18-electron complex (3) suggested the presence of two isomers, one in low concentration, in contrast to $[WCl(Bu^tNC)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ which exists in one isomeric form only. Moreover, the latter reacts further with isocyanide to give the cyclopentadienimine complex $[WCl(Bu^tNC)\{Bu^tNC_5(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$,[4] thus implying that the SC_6F_5 derivative is less reactive.

TABLE 2

N.m.r. data for the complexes

	Complex	^{19}F [a]	^{1}H [b]
(1a)	$[Mo(SC_6F_5)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ [c]		4.10 (5 H, s)
(1b)	$[W(SC_6F_5)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$	57.0 (12 F, s), 132.5 (2 F, m), 158.6 (1 F, m), 165 (2 F, m)	4.00 (5 H, s)
(2b)	$[W(SC_6F_5)(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$	133.8 (2 F, m), 158.6 (1 F, m), 162.8 (2 F, m)	2.55 (10 H, m), 4.42 (5 H, s)
(3)	$[W(SC_6F_5)(Bu^tNC)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ [d]	52.4 (3 F, s), 56.1 (3 F, s), 56.2 (3 F, s), 56.6 (3 F, s), 129.4 (2 F, m), 154.5 (1 F, m), 164.8 (2 F, m)	4.10 (5 H, s), 8.23, 8.28 (9 H, s)
(4a)	$[MoC(CF_3)=C(CF_3)C_5H_5(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]$	50.1 (3 F, m), 54.4 (3 F, m), 55.2 (3 F, m), 60.7 (3 F, m)	3.71 (1 H, m), 4.30 (1 H, m), 4.69 (5 H, s), 5.33 (1 H, m), 6.08 (1 H, m), 6.23 (1 H, m)
(4b)	$[WC(CF_3)=C(CF_3)C_5H_5(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]$	49.9 (3 F, m), 55.6 (3 F, m), 56.2 (3 F, m), 60.7 (3 F, m)	3.25 (1 H, m), 3.76 (1 H, m), 4.40 (1 H, m), 4.65 (5 H, s), 6.69 (2 Hm ,)
(5)	$[Mo\{C_4(CF_3)_4H(C_3H_3N_2)_2\}(\eta\text{-}C_5H_5)]$ [e]	50.58 (3 F, q, J_{FF} 7.0), 51.62 (3 F, s), 54.16 (3 F, q), 68.63 (3 F, dq, J_{FF} 11.9, J_{FH} 7.5)	2.21 (1 H, s), 2.74 (1 H, d, J 2.2), 3.05 (1 H, d, J 2.2), 3.63 (1 H, t, J 2.6), 4.04 (1 H, t, J 2.4), 4.26 (1 H, q, J 6.8), 4.78 (5 H, s). 8.37 (1 H, s, br)
(8a)	$[MoCl(CO)(1\text{—}4\text{-}\eta\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)]$		3.22 (1 H, m), 4.70 (6 H, s), 6.85 (1 H, d, J_{HH} 6.8), 8.15 (2 H, m), 9.26 (1 H, d, J_{HH} 6.8)
(8b)	$[WCl(CO)(1\text{—}4\text{-}\eta\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)]$		3.30 (1 H, m), 4.75 (5 H, s), 5.03 (1 H, m), 6.87 (1 H, d, J_{HH} 7.8), 8.20 (2 H, m), 8.96 (1 H, d, J_{HH} 5.9)
(9)	$[MoCl\{C_{11}H_8(CF_3)_4\}(\eta^5\text{-}C_5H_5)]$	57.9 (3 F, q, J 13.4), 60.1 and 62.9 (9 F, m, br)	4.26 (5 H, s), 5.35 (1 H, d, br), 5.65 (1 H, m), 6.90 (1 H, d, J 9.0), 7.50 (1 H, m), 7.70 (1 H, m), 8.15 (2 H, m), 8.25 (1 H, m)

[a] Measured in $[^2H_6]$ acetone, chemical shifts in p.p.m. relative to CCl_3F (0.0 p.p.m.). Coupling constants in Hz. [b] Measured in $CDCl_3$ or $[^2H_6]$acetone: τ-scale. Coupling constants in Hz. [c] ^{19}F spectrum not measured due to sample decomposition. [d] ^{19}F peaks of low intensity, due to the presence of a second isomer, were observed at 52.2, 55.2, and 57.8 p.p.m. (attributable to $CF_3C_2CF_3$ ligands, fourth signal being obscured by high intensity peaks of predominant isomer). [e] ^{19}F spectrum measured at −80 °C. At ambient temperatures three signals were observed at 51.83 (3 F, s), 52.29 (6 F, m), and 67.6 (3 F, m) p.p.m. [f] Room-temperature spectrum (see text).

The complexes $[MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ react with thallium cyclopentadienide to give compounds (4). Spectroscopic studies (Table 2) indicated a structure for these products in which a hexafluorobut-2-yne molecule had inserted into the M–C bond of a probable intermediate species containing a $[Mo(\eta^1\text{-}C_5H_5)]$ group. Accordingly, a single crystal *X*-ray diffraction study was carried out on the molybdenum compound (4) to confirm this idea.

This study revealed the molecular structure depicted in Figure 1, in which the molecule (4a) is viewed normal to the η^5-cyclopentadienyl ring C(1—5). Figure 1 also gives the atomic numbering scheme adopted, which differs from that previously communicated.[2a] Internuclear distances (uncorrected for thermal effects) are listed in Table 3.

Of the ligands in the original $[MoCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$,[2a,3] the η^5-cyclopentadienyl ring and one hexafluorobut-2-yne moiety remain intact and, furthermore, maintain the same relative orientation.[1,5] The metal atom is located *ca.* 2.03 Å above the plane of the η^5-cyclopentadienyl ring with no individual Mo–C(1—5) separations differing significantly. The Mo–C(alkyne) distances [2.135(6) and 2.157(6) Å] are similarly consistent. Least-squares planes data show the four carbon atoms C(501—504) to be substantially co-planar, with Mo being <0.08 Å out of plane. The C(502)–C(503) bond length [1.278(9) Å] and C–C–C bond angles [139.8(6) and 137.8(6)°] are compatible with the description of the alkyne function as a two-electron donor.

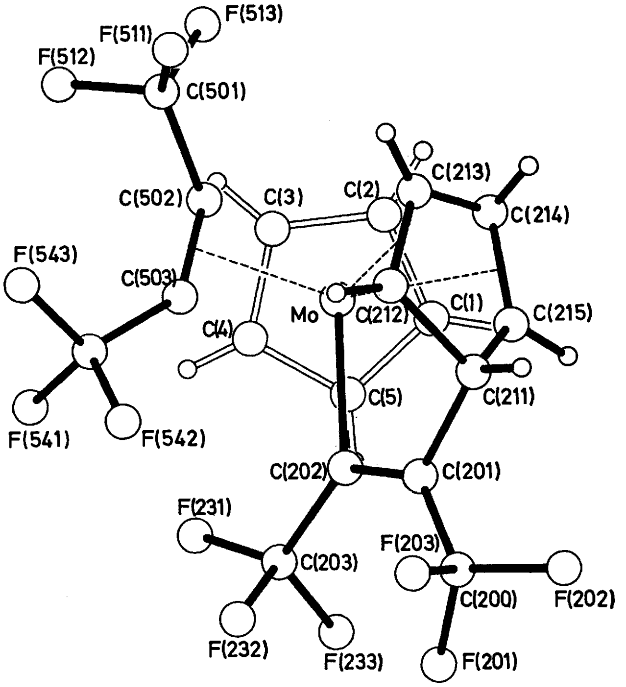


FIGURE 1 $[MoC(CF_3)=C(CF_3)C_5H_5(CF_3C_2CF_3)(\eta^5-C_5H_5)]$: single molecule viewed normal to the $(\eta^5-C_5H_5)$ ring. Hydrogen atoms take the same number as the carbon atom to which they are bonded. H(1) and H(5) are obscured by C(215) and C(202) respectively

The second $CF_3C_2CF_3$ group, C(200—203), occupies a σ,σ bridge between the metal atom and the $\eta^4-C_5H_5$ ring, and is thereby reduced to an η^1-alkene. This is clearly reflected in the C(201)–C(202), C(200)–C(201), and C(202)–C(203) distances, 1.329(9), 1.509(11), and 1.500(8) Å, respectively. A relatively high degree of thermal motion is exhibited by the fluorine atoms of all four CF_3 groups, especially so for $C(501)F_3$; the C–F distances recorded are consequently less than the true internuclear separation.

Formal access to the metal atom of 18 valence electrons is completed by the η^4-bonded ring C(211—215). This is of envelope conformation with C(211) depressed *ca.* 0.45 Å out of the C(212—215) plane in a direction away from the metal atom. The sequence of lengths C(212)–C(213) 1.389(9), C(213)–C(214) 1.396(10), and C(214)–C(215) 1.421(10) Å alone make it impossible to formally regard C(212)–C(213) and C(214)–C(215) as co-ordinated double bonds, with C(213)–C(214) as a single bond between two sp^2-hybridised carbon atoms. On the other hand, Mo–C separations for the η^4-ligand clearly fall into two pairs of two, *viz.* Mo–C(212,213) mean 2.341 Å, and Mo–C(214,215) mean 2.298 Å. Regarded in conjunction with the C–C distances, these values do suggest at least some degree of π localisation.

TABLE 3

Internuclear distances (Å), with estimated standard deviations in parentheses, in $[MoC(CF_3)=C(CF_3)C_5H_5-(CF_3C_2CF_3)(\eta^5-C_5H_5)]$

Mo–C(1)	2.356(7)	C(200)–F(201)	1.323(7)
Mo–C(2)	2.353(8)	C(200)–F(202)	1.332(10)
Mo–C(3)	2.363(9)	C(200)–F(203)	1.301(10)
Mo–C(4)	2.347(7)	C(200)–C(201)	1.509(11)
Mo–C(5)	2.361(7)	C(201)–C(202)	1.329(9)
Mo–C(502)	2.135(6)	C(202)–C(203)	1.500(8)
Mo–C(503)	2.157(6)	C(203)–F(231)	1.335(9)
Mo–C(202)	2.251(6)	C(203)–F(232)	1.339(8)
Mo–C(212)	2.354(6)	C(203)–F(233)	1.343(7)
Mo–C(213)	2.328(6)		
Mo–C(214)	2.296(7)	C(211)–C(201)	1.500(8)
Mo–C(215)	2.299(7)	C(211)–C(212)	1.523(9)
		C(212)–C(213)	1.389(9)
		C(213)–C(214)	1.396(10)
C(1)–C(2)	1.418(12)	C(214)–C(215)	1.421(10)
C(2)–C(3)	1.388(12)	C(215)–C(211)	1.513(9)
C(3)–C(4)	1.402(12)		
C(4)–C(5)	1.402(12)	C(1)–H(1)	1.01(6)
C(5)–C(1)	1.395(11)	C(2)–H(2)	0.94(7)
		C(3)–H(3)	0.91(8)
C(501)–F(511)	1.267(10)	C(4)–H(4)	0.85(8)
C(501)–F(512)	1.297(12)	C(5)–H(5)	0.85(9)
C(501)–F(513)	1.275(11)		
C(501)–C(502)	1.468(10)	C(211)–H(211)	0.94(6)
C(502)–C(503)	1.278(9)	C(212)–H(212)	0.83(6)
C(503)–C(504)	1.473(9)	C(213)–H(213)	0.82(6)
C(504)–F(541)	1.327(8)	C(214)–H(214)	1.02(8)
C(504)–F(542)	1.321(11)	C(215)–H(215)	0.99(5)
C(504)–F(543)	1.327(8)		

The most important aspect of the crystal packing (Figure 2, viewed along the *b* axis looking towards the origin) is that in the solid state the molecules form infinite chains, two-dimensional in the *ab* plane and running parallel to *a*. With respect to the chosen origin, the asymmetric molecule is linked through its cyclopentadiene rings *via* van der Waals interactions across the symmetry centres at $0\frac{1}{2}0$ (η^5-C_5 ring) and $\frac{1}{2}\frac{1}{2}0$ (η^4-C_5 ring). These rings, necessarily parallel with their neighbours, are respectively *ca.* 3.77 and 4.49 Å from them (centroid to centroid).

Similarities in the chemistry of the cyclopentadienyl

---

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

group and the tris(pyrazolyl)borate ligand[6] suggested that the reaction of $[K\{BH(C_3H_3N_2)_3\}]$ with $[MoCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$ might be of interest. Complex (5) is produced in low yield, and its molecular structure was established by an *X*-ray crystallographic study.[4] This novel reaction therefore produced a metal complex containing an η^3-allyl group, formed by condensation of the two acetylene molecules originally co-ordinated to the metal. The proton attached to the $C(CF_3)$ group adjacent to the allyl moiety probably originated from either the solvent (tetrahydrofuran), or from degradation of the pyrazolylborate ligand.

The molecular geometry of (5) is essentially square pyramidal with the cyclopentadienyl ligand occupying the apical position. The stereochemistry is thus similar to other allylmolybdenum complexes,[7] *e.g.* $[Mo(CO)_2(\eta^3-C_3H_5)(\eta^5-C_5H_5)]$, with the pyrazole ligands formally replacing two carbonyl groups as two-electron donors in the basal position of the pyramid. As expected, the ^1H n.m.r. spectrum of (5) (Table 2) is complex, showing several different signals, each pyrazole proton being in a different environment. The signal at τ 8.37 can be assigned to the $CH(CF_3)$ group. In allyldicarbonylmolybdenum complexes isomerism has been observed due to the η^3-C_3 group being able to adopt two different conformations but in (5) this is prevented by the constraints imposed by the rest of the ligand. However, it was observed that the ^{19}F n.m.r. spectrum of (5) varied with temperature (Table 2), and it is possible that the complex undergoes a polytopal rearrangement.

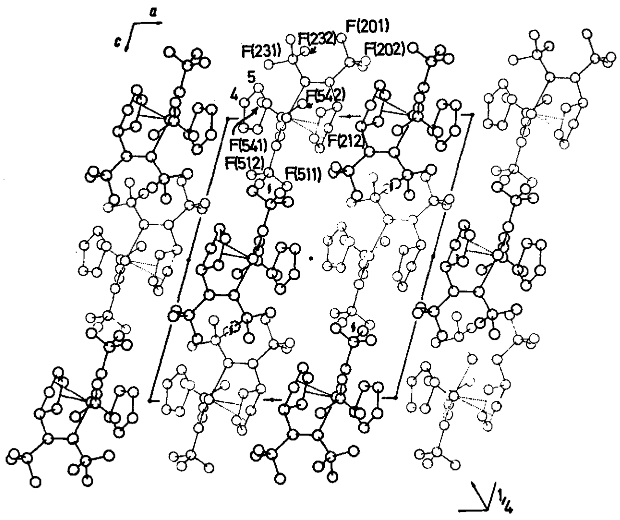


FIGURE 2 $[\overline{MoC(CF_3)=C(CF_3)C}_5H_5(CF_3C_2CF_3)(\eta^5-C_5H_5)]$: view of the crystal packing along the *b* axis, looking towards the origin

The compound $[MoCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$ also reacts with thallium 1,3-dimethylpropane-1,3-dionate and with thallium 1,3-bis(trifluoromethyl)propane-1,3-dionate to give complex mixtures, but the products of these reactions decomposed on work-up. The alkyne complex $[MoCl(CH_3C_2CH_3)_2(\eta^5-C_5H_5)]$ reacts with thallium 1,3-bis(trifluoromethyl)propane-1,3-dionate apparently without Mo–Cl bond cleavage to give an adduct (6) with a sharp melting point (Table 1) distinctly different from that of either component. The adduct dissociates in solution, since the measured ^1H n.m.r. spectrum was identical with that of $[MoCl(CH_3C_2CH_3)_2(\eta^5-C_5H_5)]$; coalescence of the methyl group resonances occurred at the same temperature as previously observed.[2] The mass spectrum showed peaks corresponding to thallium 1,3-bis(trifluoromethyl)propane-1,3-dionate and the bis(but-2-yne)molybdenum complex, and none at higher *m/e*. Reaction of $[WCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$ with the thallium compound gives a substance which may be similar to (6) but the bonding between the two components appears to be relatively weak, since repeated recrystallisation changed the composition until only $[WCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$ remained.

Reaction of $[MoCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$ with buta-1,3-diene in hexane at 60 °C affords a complex $[MoCl_2(\eta^4-C_4H_6)(\eta^5-C_5H_5)]$ (7). The same compound can be obtained by treating $[MoCl(CO)(PhC_2Ph)(\eta^5-C_5H_5)]$ with buta-1,3-diene in dichloromethane at 70 °C, but in tetrahydrofuran these same reactants gave $[MoCl(CO)(\eta^4-C_4H_6)(\eta^5-C_5H_5)]$ (8a). Our inability to observe a ^1H n.m.r. spectrum for (7) suggests that it is paramagnetic, as would be implied by its formulation; the mass spectrum indicates that it is not binuclear. Complex (8a) [ν_{CO} (max) 1 972s] has a ^1H n.m.r. spectrum with five signals of relative intensity 1 : 6 : 1 : 2 : 1. The resonances at τ 3.22, 6.85, 8.15, and 9.26 are characteristic of an η^4-C_4H_6 ligand;[8] the sixth signal due to this group coincides with the η^5-C_5H_5 resonance at τ 4.70.

Reaction of $[WCl(CO)(PhC_2Ph)(\eta^5-C_5H_5)]$ with buta-1,3-diene in tetrahydrofuran affords (8b), having spectroscopic properties very similar to (8a). The compound $[WCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$ does not react with buta-1,3-diene in hexane at 80 °C, again illustrating the lower reactivity of the tungsten alkyne complexes compared with their molybdenum analogues. This is well illustrated by studies on reactions of bicyclo[2.2.1]heptadiene (nbd) with the compounds $[MCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)]$. With M = W, only organic polymer and unreacted metal complex were recovered, whereas with M = Mo an orange crystalline product (9) was obtained. The mass spectrum showed a parent ion and non-metal-containing ions near *m/e* 400 suggesting the presence of a complex ligand in (9). The i.r. spectrum showed no bands above 1 500 cm^{-1} corresponding to co-ordinated $CF_3C_2CF_3$ or to an $Mo-C(CF_3)=C(CF_3)$ group. The ^1H n.m.r. spectrum exhibited a peak due to a C_5H_5 group at τ 4.26, and two proton signals near τ 5.5 probably due to a co-ordinated double bond. In the bicyclo[2.2.1]heptadiene complex $[\{RhCl(nbd)\}_2]$ the protons on the carbon–carbon double bond resonate at τ 6.12[9] whereas

---

[6] S. Trofimenko, *Accounts Chem. Res.*, 1971, **4**, 17.

[7] J. W. Faller and M. J. Incorvia, *Inorg. Chem.*, 1968, **7**, 840.

[8] M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Adv. Organometallic Chem.*, 1965, **3**, 1, and refs. cited therein.

[9] K. Vrieze, H. C. Volger, and A. P. Praat, *J. Organometallic Chem.*, 1968, **15**, 195.

in the complex formed by addition of hexafluorobut-2-yne with acetylacetonato(bicyclo[2.2.1]heptadiene)rhodium(I), which has a structure with an unco-ordinated CH=CH double bond, the resonances occur at τ 2.75 and 3.56.[10] On the basis of the above data we tentatively propose the structure shown for (9).

The ^{19}F n.m.r. spectrum of (9) varied with temperature becoming extremely complex at −90 °C, suggesting that many of the fluorine atoms become inequivalent, perhaps due to a freezing out of the rotation of the CF_3 groups. Normally these groups have a high thermal motion frequently revealed in *X*-ray crystallographic studies.

No products were obtained from reactions of cycloocta-1,5-diene, ethylene, or cyclohexa-1,3-diene with the alkyne complexes $[MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ and $[MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$.

EXPERIMENTAL

Hydrogen-1 and ^{19}F n.m.r. spectra were recorded on a Varian Associates HA100 spectrometer at 100 and 94.1 MHz, respectively. I.r. spectra were measured with a Perkin-Elmer 457 spectrophotometer. All operations were conducted in an atmosphere of dry oxygen-free nitrogen. Analytical data are given in Table 1, and i.r. and n.m.r. data in Table 2.

The compounds $[MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ and $[MCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W), used as reactants, were prepared as described previously.[2,3]

Reaction of $TlSC_6F_5$ *with the Compounds* $[MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (M = Mo or W).—Pentafluorophenylthiothallium (0.18 g, 0.45 mmol) was added to $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (0.25 g, 0.48 mmol) in tetrahydrofuran (25 cm^3) and the mixture stirred (1 h). The orange solution became dark red, and thallium(I) chloride precipitated. Solvent was removed *in vacuo*, and the residue extracted (20 cm^3 of dichloromethane) and filtered. The filtrate was reduced in volume, hexane was added, and on cooling dark blue *crystals* of air-sensitive $[Mo(SC_6F_5)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (1a) (0.18 g, 54%) were isolated. In this reaction ill-defined products were sometimes obtained, particularly if $TlSC_6F_5$ was used in excess.

The tungsten compound $[W(SC_6F_5)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (1b) (0.3 g, 78%) was similarly prepared from $TlSC_6F_5$ (0.20 g, 0.5 mmol) and $[WCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (0.3 g, 0.49 mmol).

Preparation of $[W(SC_6F_5)(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$.—The complex $[WCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (0.25 g, 0.51 mmol) in tetrahydrofuran (30 cm^3) was treated (1 h) with $TlSC_6F_5$ (0.22 g, 0.55 mmol) affording dark red *crystals* of $[W(SC_6F_5)(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (2b) (0.3 g, 93%), from dichloromethane–hexane.

Complex (2a)[1] was similarly prepared from $[MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ and identified by comparison with an authentic sample.

Preparation of $[W(SC_6F_5)(Bu^tNC)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$.—t-Butyl isocyanide (34 mg, 0.4 mmol) in diethyl ether (10 cm^3) was added to complex (1b) (0.3 g, 0.39 mmol) in diethyl ether (20 cm^3) giving an almost colourless solution. Addition of hexane and cooling gave pale orange *crystals* of $[W(SC_6F_5)(Bu^tNC)(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]$ (3) (0.25 g, 77%). ν_{NC}(max): 2 200m cm^{-1}; $\nu_{C\equiv C}$(max): 1 803w cm^{-1}; ν_{CF}(max): 1 275m, 1 235vs, 1 171m, 1 145m, 1 120m,br, and 1 092m cm^{-1}.

Mixing the reactants using a 2 : 1 or greater excess of Bu^tNC and heating the mixture at 50 °C for several hours did not result in further reaction.

Reactions of Thallium Cyclopentadienide.—The complex $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (0.3 g, 0.58 mmol) was treated with TlC_5H_5 (0.162 g, 0.6 mmol) in tetrahydrofuran (30 cm^3) and stirred (4 h). Volatile material was removed, dichloromethane (15 cm^3) was added, and the mixture filtered to give yellow *crystals* of $[\overline{MoC(CF_3)\text{=}C(CF_3)C_5H_5}(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)]$ (4a) (54 mg, 17%), recrystallised at −20 °C from dichloromethane–hexane; $\nu_{C\equiv C}$(max): 1 811w cm^{-1}; ν_{CF}(max): 1 279vs, 1 239m, 1 165s, and 1 130s,br cm^{-1}.

Complex (4b) (22 mg, 7%) was similarly prepared from $[WCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (0.3 g, 0.49 mmol) and TlC_5H_5 (0.135 g, 0.5 mmol).

Reaction of Potassium Tris(pyrazolyl)borate with $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$.—The complex $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (0.2 g, 0.38 mmol) and $[K\{BH(C_3H_3N_2)_3\}]$ (0.1 g, 0.4 mmol) were stirred (4 h) in tetrahydrofuran (30 cm^3). Solvent was removed *in vacuo* and dichloromethane (15 cm^3) added. After filtration, hexane was added to the filtrate which was cooled to −20 °C giving orange-red *crystals* of (5) (9.5 mg, 4%).

Reaction of $[MoCl(CH_3C_2CH_3)_2(\eta^5\text{-}C_5H_5)]$ *with Thallium* 1,3-*Bis(trifluoromethyl)propane*-1,3-*dionate.*—The acetylene complex (0.2 g, 0.66 mmol) and the thallium salt (0.29 g, 0.7 mmol) were stirred (2 h) in tetrahydrofuran (30 cm^3). Volatile material was removed and dichloromethane (15 cm^3) added. Filtration, followed by concentration of the filtrate, addition of hexane, and cooling (−20 °C), gave yellow *crystals* of (6) (0.25 g, 52%); ν_{CO}(max): 1 662s, and 1 650s cm^{-1}; ν_{CF}(max): 1 263vs, 1 200s, and 1 155s cm^{-1}.

Reactions with Buta-1,3-*diene.*—(i) A glass tube fitted with a Westef stopcock was charged with $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (0.2 g, 0.38 mmol), buta-1,3-diene (1 g, 18.5 mmol) and hexane (20 cm^3). The reaction vessel was heated at 60 °C for 15 h, when dark brown material formed. Brown *crystals* of (7) (35 mg, 32%) were recovered from dichloromethane–hexane. Use of diethyl ether as solvent gave a similar result. (ii) Complex (7) (27 mg, 19%) was similarly prepared from $[MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (0.2 g, 0.5 mmol) and buta-1,3-diene (1 g, 18.5 mmol) in dichloromethane (20 cm^3) at 70 °C for 20 h. (iii) Reaction of $[MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (0.3 g, 0.75 mmol) with buta-1,3-diene (1 g, 18.5 mmol) in tetrahydrofuran (25 cm^3) at 65 °C for 30 h gave a dark brown product. The tube was opened and volatiles removed *in vacuo*, and the residue extracted with dichloromethane and filtered. The filtrate was reduced in volume, hexane added, and on cooling to −20 °C black crystals of $[MoCl(CO)(1\text{—}4\text{-}\eta\text{-}C_4H_6)(\eta^5\text{-}C_5H_5)]$ (8a) (50 mg, 25%) were obtained. ν_{CO}(max): 1 972s cm^{-1}.

Similarly complex (8b) (34 mg, 18%) was obtained (48 h, 70 °C) from $[WCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ (0.25 g, 0.51 mmol) and buta-1,3-diene (1 g, 18.5 mmol). The i.r. of (8b) showed ν_{CO}(max) 1 946s cm^{-1}.

Reaction of Bicyclo[2.2.1]*heptadiene with* $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$.—The compound $[MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (0.1 g, 0.19 mmol), bicyclo[2.2.1]heptadiene (1 g, 11 mmol), and hexane (30 cm^3) were heated at 65 °C for 8 h in a tube fitted with a Westef stopcock. White polymeric material was produced, and the solution became deep orange. Volatiles were removed *in vacuo*, and the residue extracted with diethyl ether (20 cm^3) and filtered. The filtrate was reduced

---

[10] D. M. Barlex, A. C. Jarvis, R. D. W. Kemmitt, and B. Y. Kimura, *J.C.S. Dalton*, 1972, 2549.

TABLE 4

Final positional (fractional co-ordinate, × 10^4; Mo × 10^5) and anisotropic temperature * (Å^2, × 10^3; Mo × 10^4) factors for the non-hydrogen atoms in compound (4a)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	24 093(4)	26 602(4)	10(3)	373(4)	307(4)	266(4)	−15(2)	84(2)	−18(2)
C(1)	1 454(6)	4 764(8)	−509(5)	70(5)	45(4)	55(4)	13(3)	14(3)	3(3)
C(2)	1 375(6)	4 486(8)	380(5)	80(5)	50(4)	56(5)	22(4)	21(4)	−11(4)
C(3)	781(6)	3 251(9)	332(6)	52(4)	76(5)	71(5)	20(4)	33(4)	9(4)
C(4)	520(5)	2 729(9)	−561(5)	38(4)	62(5)	73(5)	5(3)	5(3)	−5(4)
C(5)	925(6)	3 684(8)	−1 084(5)	59(5)	70(5)	44(4)	20(3)	4(3)	4(4)
C(501)	2 298(7)	854(8)	1 935(5)	92(5)	66(5)	45(4)	10(4)	42(4)	14(3)
C(502)	2 296(5)	1 120(6)	990(4)	45(3)	43(3)	38(3)	0(2)	18(2)	6(3)
C(503)	2 254(5)	440(6)	259(4)	49(4)	33(3)	42(4)	−4(2)	19(3)	3(2)
C(504)	2 184(6)	−1 042(7)	−47(5)	85(5)	38(3)	54(4)	−13(3)	30(4)	−2(3)
F(511)	3 195(6)	411(13)	2 436(4)	134(5)	399(14)	55(3)	100(7)	45(3)	87(5)
F(512)	1 614(7)	−107(8)	2 015(4)	247(9)	171(6)	87(4)	−98(6)	99(5)	−4(4)
F(513)	2 042(7)	1 912(7)	2 348(4)	294(9)	105(4)	81(4)	22(5)	116(5)	−5(3)
F(541)	1 210(4)	−1 339(5)	−591(4)	117(4)	72(3)	107(4)	−42(3)	19(3)	−24(3)
F(542)	2 872(5)	−1 343(5)	−516(4)	158(5)	53(3)	123(4)	3(3)	91(4)	−18(3)
F(543)	2 350(5)	−1 966(4)	631(3)	199(6)	39(2)	82(3)	−9(3)	49(3)	10(2)
C(200)	4 380(6)	1 920(8)	−1 956(5)	76(5)	64(4)	48(4)	9(3)	32(3)	9(3)
C(201)	3 763(5)	2 191(6)	−1 269(4)	56(4)	38(3)	34(3)	−1(3)	19(2)	3(2)
C(202)	2 746(5)	1 916(5)	−1 289(4)	50(4)	27(3)	32(3)	−3(2)	9(2)	0(2)
C(203)	1 965(6)	1 224(7)	−2 089(4)	67(4)	49(4)	36(3)	−10(3)	9(3)	−11(3)
F(201)	3 767(4)	1 814(6)	−2 807(3)	116(4)	136(4)	49(2)	1(3)	43(2)	−4(3)
F(202)	5 025(5)	3 006(6)	−1 988(4)	121(4)	125(4)	107(4)	−39(3)	82(3)	−10(3)
F(203)	4 958(5)	774(7)	−1 785(4)	174(6)	129(5)	117(4)	98(4)	99(4)	50(4)
F(231)	1 056(3)	793(5)	−1 919(3)	72(3)	93(3)	59(2)	−37(2)	11(2)	−21(2)
F(232)	2 359(4)	73(4)	−2 393(3)	110(3)	61(3)	61(3)	−9(2)	19(2)	−29(2)
F(233)	1 640(4)	2 095(5)	−2 807(2)	95(3)	84(3)	39(2)	−10(2)	−7(2)	7(2)
C(211)	4 381(4)	2 863(7)	−388(4)	41(3)	51(4)	41(3)	−11(3)	13(4)	−2(3)
C(212)	4 236(4)	1 977(7)	401(4)	35(3)	58(4)	39(3)	−5(3)	2(2)	7(3)
C(213)	4 080(5)	2 842(7)	1 086(4)	53(4)	70(5)	28(3)	−18(3)	3(2)	−6(3)
C(214)	3 766(6)	4 181(8)	723(4)	61(4)	57(4)	48(4)	−26(3)	13(3)	−23(3)
C(215)	3 744(5)	4 119(7)	−210(4)	61(4)	40(3)	43(4)	−18(3)	13(3)	1(3)

* Defined as $\exp\{-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)\}$.

in volume, hexane (5 cm^3) added, and on cooling to −20 °C orange *microcrystals* of (9) (25 mg, 21%) were obtained. I.r. $\nu_{max.}$ 1 330m, 1 320w, 1 305w, 1 280s, 1 253m, 1 237s, 1 230s, 1 215m, 1 205m, 1 180s, 1 171s, 1 160s, 1 147s, and 1 120m cm^{-1}.

X-Ray Diffraction Study.—An irregularly shaped single crystal, *ca.* 0.2 mm was selected for analysis. Preliminary oscillation and equi-inclination Weissenberg photographs about b revealed $2/m$ Laue symmetry and systematic absences ($0k0$; $k = 2n + 1$ and $h0l$; $h + l = 2n + 1$) consistent with the centrosymmetric monoclinic spacegroup $P2_1/n$ if $a \approx 12.9$, $b \approx 9.5$, and $c \approx 15.3$ Å, $\beta \approx 105°$.

The specimen was then transferred to an automated Syntex $P2_1$ four-circle diffractometer on which accurate unit cell parameters, their associated standard deviations, and one unique set of diffracted intensities were recorded in a manner already documented.[11] Details applicable to the present experiment included: 15 reflections, $15 < 2\theta < 23°$, were taken from a 20-min rotation photograph, automatically centred in 2θ, ω, and χ, and used to generate the real-space vectors by which an accurately defined cell was obtained; graphite-monochromated Mo-K_α radiation ($\bar{\gamma}$ = 0.710 69 Å) and a θ—2θ scan procedure in 96 steps were used; for data collection $0 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 9$, $\bar{1}5 \leqslant l \leqslant 15$ (with equivalent $0kl$ and $0kl$ reflections afterwards merged), $2.9 \leqslant 2\theta \leqslant 50.0°$ and $T \approx 24$ °C; peaks were initially scanned at rates between 0.033 7 and 0.488 3 ° s^{-1}, the precise rate dependent on an initial 2-s peak count in which 250 and 2 500 were the respective minimum and maximum counts. Immediately before reflection $76\bar{4}$ these were lowered to 150 and 1 500 to slightly increase the rate of data collection; 3 check reflections, 204, 404, and 040, were each monitored once every batch of 20, but subsequent analysis [12] of their net counts as individual functions of time revealed no significant variation over *ca.* 110 h *X*-ray exposure. Of 2 180 independent reflections measured, 32 (excluding systematic absences) fell below the significance threshold, $I \geqslant 2.5\sigma(I)$; the remaining 2 148 were used to solve and refine the structure; no correction for *X*-ray absorption was made.

TABLE 5

Final positional (fractional co-ordinate, × 10^3) and isotropic * temperature (Å^2, × 10^3) factors of the hydrogen atoms in (4a)

Atom	x	y	z	U_j
H(1)	183(4)	563(7)	−66(4)	37(15)
H(2)	163(5)	510(8)	88(5)	59(20)
H(3)	61(6)	273(8)	77(5)	63(21)
H(4)	19(6)	197(9)	−77(5)	73(25)
H(5)	90(6)	356(8)	−164(5)	64(23)
H(211)	512(5)	301(7)	−30(4)	54(18)
H(212)	434(5)	111(6)	45(4)	50(17)
H(213)	413(4)	259(6)	161(4)	46(16)
H(214)	355(6)	508(8)	99(5)	75(22)
H(215)	359(4)	497(6)	−60(4)	31(13)

* Defined as $\exp\{-8\pi^2U_j(\sin^2\theta/\lambda^2)\}$.

Crystal Data.—$C_{18}H_{10}F_{12}Mo$, $M = 550.2$, Monoclinic, space group $P2_1/n$, $a = 12.904(6)$, $b = 9.641(3)$, $c = 15.302(6)$ Å, $\beta = 103.34(4)°$, $U = 1\,792.7(13)$ Å^3 $D_m = 2.03$ g cm^{-3} (flotation), $Z = 4$, $D_c = 2.038$ g cm^{-3}, $F(000) = 928$. Mo-K_α radiation, $\lambda_{\alpha1} = 0.709\,26$, $\lambda_{\alpha2} = 0.713\,54$ Å, μ(Mo-$K_{\bar{\alpha}}$) = 8.6 cm^{-1}.

Data were corrected for Lorentz and polarisation effects, and the structure solved *via* conventional Patterson (Mo) and difference-Fourier (C, F, and H atoms) techniques. F_o

---

[11] A. G. Modinos and P. Woodward, *J.C.S. Dalton*, 1974, 2065.

[12] A. G. Modinos, 'DRSYN,' a Fortran program for data analysis.

values were weighted such that $w^{-1} = x.y$ with $x = 0.23/\sin\theta$ if $\sin\theta < 0.23$, $x = 1$ if $\sin\theta \geqslant 0.23$, and $y = F_o/60$ if $F_o > 60$, $y = 1$ if $F_o \leqslant 60$.

With the variable parameters divided between three blocks, least-squares refinement of all atoms (Mo, C, F anisotropic; H isotropic) continued until the average shift-to-error ratio was <0.013. Final residuals R 0.039, R' 0.044 were obtained. Including the F scale and overall temperature factors, the data-to-variable ratio was 6.7 : 1.

Atomic scattering factors for neutral atoms were taken from ref. 13 for molybdenum and fluorine, ref. 14 for carbon, and ref. 15 for hydrogen, with the first three sets corrected [16] for both components of anomalous dispersion. Tables 4 and 5 list the derived atomic positional and thermal parameters. Important bond angles, details of molecular planes, and a comparison of observed and calculated structure factor amplitudes have all been deposited as Supplementary Publication No. SUP 21863 (11 pp., 1 microfiche).*

Structure solution and refinement employed the '*X*-Ray '72' system,[17] implemented on the University of London CDC 7600 computer.

We thank the I.C.I. for a Fellowship (J. L. D.) and the U.S.A.F. Office of Scientific Research for support.

[6/410 *Received*, 1*st March*, 1976]

---

[13] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[14] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[15] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[16] ' International Tables for *X*-Ray Crystallography,' vol. IV, Kynoch Press, Birmingham, 1974.

[17] Technical Report TR 192 of the Computer Science Centre, University of Maryland, June 1972.