Formation of Sixteen-electron Alkyne Complexes by Reaction of Halogeno(tricarbonyl)(η^5-cyclopentadienyl)-molybdenum and -tungsten Complexes with Alkynes; Crystal and Molecular Structure of [$WCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)$]

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Reaction of hexafluorobut-2-yne with [$MoCl(CO)_3(\eta^5-C_5H_5)$] affords the cyclopentadienone complex [$MoCl(CO)(C_8F_{12}CO)(\eta^5-C_5H_5)$]. If the displaced carbon monoxide is removed, then the product is [$MoCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)$] together with minor amounts of [{$MoCl(CF_3C_2CF_3)(\eta^5-C_5H_5)$}$_2$]. The reaction of $CF_3C_2CF_3$ with [$WCl(CO)_3(\eta^5-C_5H_5)$] affords only [$WCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)$] (II), which was structurally identified by *X*-ray crystallography as an octahedral 16-electron species, in which the acetylene acts as a 2-electron donor. Treatment of [$MoCl(CO)_3(\eta^5-C_5H_5)$] with $MeC{\vdots}CMe$ affords either [$MoCl(MeC_2Me)_2(\eta^5-C_5H_5)$] or [$MoCl(CO)\{C_4Me_4(CO)_2\}(\eta^5-C_5H_5)$] depending on the reaction conditions. The latter compound is formulated as a duroquinone complex. U.v. irradiation of [$WCl(CO)_3(\eta^5-C_5H_5)$] and $PhC{\vdots}CPh$ gives [$WCl(CO)(PhC_2Ph)(\eta^5-C_5H_5)$]. In refluxing hexane, [$MoCl(CO)_3(\eta^5-C_5H_5)$] reacts with PhC_2Ph to give [$MoCl(CO)(PhC_2Ph)(\eta^5-C_5H_5)$] and [$MoCl(PhC_2Ph)_2(\eta^5-C_5H_5)$]. The thermal reaction of MeC_2Ph with [$MoCl(CO)_3(\eta^5-C_5H_5)$] gives initially [$MoCl(CO)(PhC_2Me)(\eta^5-C_5H_5)$] which reacts further to yield [$MoCl(PhCMe)_2(\eta^5-C_5H_5)$]. Treatment (60 °C) of [$MoCl(CO)(PhC_2Ph)(\eta^5-C_5H_5)$] with MeC_2Me or $CF_3C_2CF_3$ affords [$MoCl(RC_2R)_2(\eta^5-C_5H_5)$] (R = Me or CF_3). At room temperature, [$MoCl(CF_3C_2CF_3)(PhC_2Ph)(\eta^5-C_5H_5)$] is formed. Similar reactions afforded the mixed acetylene complexes [$MoCl(CF_3C_2CF_3)(PhC_2Me)(\eta^5-C_5H_5)$], [$WCl(CF_3C_2CF_3)(PhC_2Ph)(\eta^5-C_5H_5)$], and [$WCl(CF_3C_2H)(PhC_2Ph)(\eta^5-C_5H_5)$]. Reaction of [$MoCl(CO)(PhC_2Ph)(\eta^5-C_5H_5)$] with $CF_3C{\vdots}CH$ gives [$MoCl(CF_3C_2H)_2(\eta^5-C_5H_5)$]. The temperature-dependent dynamic behaviour of these complexes is discussed in terms of a propeller-type rotation of the acetylene.

CONSIDERABLE interest continues in the reactions of acetylenes with transition-metal complexes. Acetylenes react with the organothio-complexes [$MSR(CO)_3(\eta^5-C_5H_5)$] (M = Mo or W; R = CF_3 or C_6F_5) to give the co-ordinatively unsaturated species [$MSR(CO)(R'C_2R')(\eta^5-C_5H_5)$] ($R' = CF_3$, Me, or Ph),[1] and an extension of this study to the reactions of [$MoX(CO)_3(\eta^5-C_5H_5)$] (X = Cl, Br, or I) with hexafluorobut-2-yne gave the 16-electron complexes [$MoX(CF_3C_2CF_3)_2(\eta^5-C_5H_5)$].[2,3] Clearly, reactions of such species are of interest, and in this paper, as a preliminary to such a study, we report a detailed investigation of the processes involved in the displacement of carbon monoxide from [$MCl(CO)_3(\eta^5-C_5H_5)$] (M = Mo or W), and the determination of the crystal and molecular structure of the 16-electron species [$WCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)$].

RESULTS AND DISCUSSION

Detailed study of the reaction of hexafluorobut-2-yne with tricarbonyl(chloro)cyclopentadienylmolybdenum in hexane solution revealed that if higher relative concentrations of the tricarbonyl complex were used in a sealed tube then the main product is a cyclopentadienone complex (I). This formulation was supported by the i.r. spectrum which showed a strong band at 1 700 cm^{-1} characteristic of an η^4-co-ordinated tetrakis(trifluoromethyl)cyclopentadienone, and by the appearance in the mass spectrum of peaks due to $[M]^+$, $[M - CO]^+$, and $[C_4(CF_3)_4CO]^+$.

The ^1H n.m.r. spectrum at room temperature showed two singlet peaks of equal intensity at τ 3.55 and 3.95 assignable to an $\eta^5-C_5H_5$ ligand. The spectrum changed when the sample was cooled (Figure 1) suggesting the presence in solution of two species. This was supported by the i.r. spectrum (Table 1) which showed two terminal and two ketonic carbonyl bands, and by the ^{19}F n.m.r. spectrum (Table 2) which consisted of a number of overlapping multiplets the shape and position of which were temperature dependent. These observations suggest the presence of interconverting isomers (Ia) and (Ib).

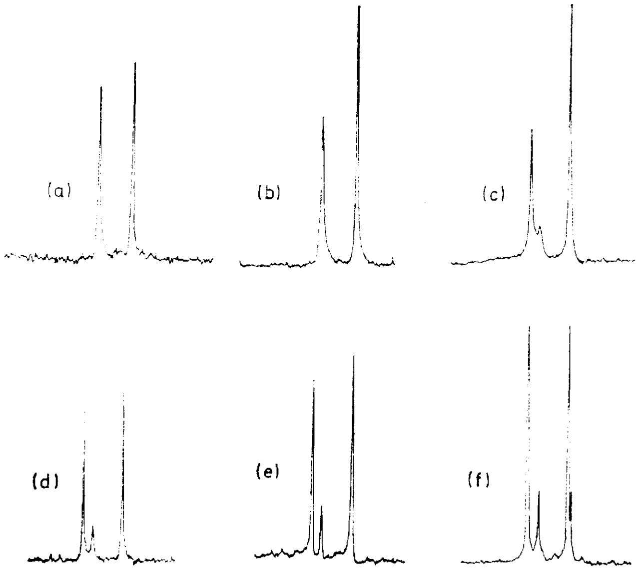
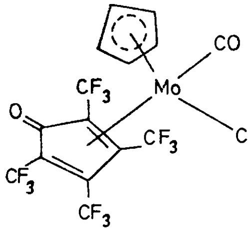
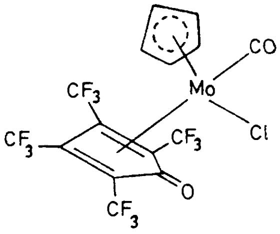


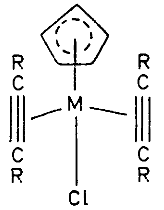
FIGURE 1 Variable-temperature ^1H n.m.r. spectra of [$MoCl(CO)(C_8F_{12}CO)(\eta^5-C_5H_5)$]; (a) 20, (b) 0, (c) −30, (d) −45, (e) −60, and (f) −80 °C



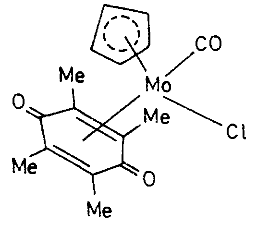
(Ia)



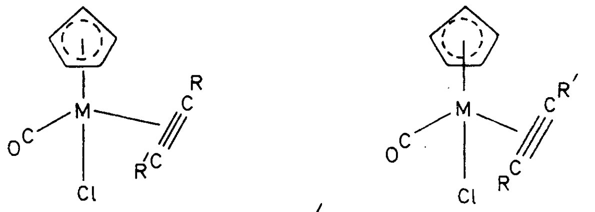
(Ib)



(II) M = W, R = CF_3
(X) M = Mo, R = Ph
(XI) M = W, R = Ph



(III)



(IV) M = W, R = R' = Ph
(V) M = Mo, R = Ph, R' = Me
(IX) M = W, R = Ph, R' = Me

If the quantity of the reactant [$MoCl(CO)_3(\eta^5-C_5H_5)$] is small relative to the size of the reaction vessel, or if the displaced carbon monoxide is removed at intervals from the reaction mixture, the main product of the reaction with $CF_3C_2CF_3$ is [$MoCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)$]. Small quantities of a red complex [$\{MoCl(CF_3C_2CF_3)(\eta^5-C_5H_5)\}_2$], previously obtained by u.v. irradiation of the bis-acetylene complex, are also obtained, but there was no evidence for the formation of (I).

In contrast, the corresponding reaction of hexafluorobut-2-yne with tricarbonyl(chloro)cyclopentadienyltungsten affords only the bis-acetylene complex (II). Variation of the reaction conditions provided no evidence for the formation of other species.

A detailed study of the reaction of [$MoCl(CO)_3(\eta^5-C_5H_5)$] with but-2-yne revealed that the products obtained are very dependent upon reaction conditions. In hexane (65 °C), [$MoCl(MeC_2Me)_2(\eta^5-C_5H_5)$] and duroquinone are formed; whereas, in benzene (30 °C) only trace amounts of these two compounds are obtained, the major product being a red complex (III). Reaction

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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, M. Green, D. W. A. Sharp, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1974, 706.

[3] J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2531.

of (III) with an excess of but-2-yne in benzene at 60 °C afforded [$MoCl(MeC_2Me)_2(\eta^5-C_5H_5)$] and duroquinone suggesting that (III) is a duroquinone complex. In agreement the i.r. spectrum (Table 1) shows a single terminal carbonyl band and a ketonic stretching mode at 1 606 cm^{-1}. The ^1H n.m.r. spectrum (Table 2) provided further support for this formulation showing five singlets with relative intensity 5 : 3 : 3 : 3 : 3. The low-field singlet (τ 4.76) is assigned to the $\eta^5-C_5H_5$ group and the remaining signals, centred near τ 8.0, are assigned to the inequivalent methyl groups of a 1,2,4,5-η bonded duroquinone. The spectrum of (III) is virtually temperature invariant in the range −60 to +20 °C; a rearrangement analogous to that involved in the interconversion of the related cyclopentadienone complexes (Ia) and (Ib) was not detected.

TABLE 1

Analytical [a] and i.r. data [b] for the acetylene complexes

	Compound	M.p. (θ_c/°C)	ν(CO)	ν(C=O)	ν(C≡C)	C	H	Cl
(I)	[$MoCl(CO)(C_8F_{12}CO)(\eta^5-C_5H_5)$]	>122	2 096m 2 068s	1 719s 1 700s		31.2 (31.4)	0.9 (0.8)	6.2 (5.6)
(II)	[$WCl(CF_3C_2CF_3)_2(\eta^5-C_5H_5)$]	147			1 778m 1 762m	25.9 (25.7)	0.8 (0.8)	
(III)	[$MoCl(CO)\{C_4Me_4(CO)_2\}(\eta^5-C_5H_5)$] [c]	>134	2 000vs	1 606s		49.9 (50.0)	4.7 (4.5)	9.9 (10.4)
(IV)	[$WCl(CO)(PhC_2Ph)(\eta^5-C_5H_5)$]					48.9 (48.2)	3.1 (3.1)	7.3 (7.7)
(V)	[$MoCl(CO)(PhC_2Me)(\eta^5-C_5H_5)$]	>120	1 944s			52.9 (52.0)	3.8 (3.9)	
(VI)	[$MoCl(PhC_2Me)_2(\eta^5-C_5H_5)$]	160—162				64.4 (64.0)	4.9 (4.8)	
(VII)	[$WCl(PhC_2Me)_2(\eta^5-C_5H_5)$]	>182				53.5 (53.5)	4.1 (4.0)	
(VIII)	[$WCl(CO)\{(PhC_2Me)_2CO\}(\eta^5-C_5H_5)$]	>213	1 962vs	1 611s		50.5 (50.6)	3.7 (3.5)	
(IX)	[$WCl(CO)(PhC_2Me)(\eta^5-C_5H_5)$]	142—147	1 921vs			40.3 (41.8)	3.0 (3.1)	
(X)	[$MoCl(PhC_2Ph)_2(\eta^5-C_5H_5)$]	145—150				71.6 (71.1)	4.5 (4.6)	
(XI)	[$WCl(PhC_2Ph)_2(\eta^5-C_5H_5)$]	162—164				61.8 (61.9)	3.9 (4.0)	
(XII)	[$\{WCl(PhC_2Ph)(\eta^5-C_5H_5)\}_2$]	>265						
(XIII)	[$MoCl(CF_3C_2CF_3)(PhC_2Me)(\eta^5-C_5H_5)$]	98—101			1 788w	45.5 (45.4)	2.7 (2.8)	
(XIV)	[$MoCl(CF_3C_2CF_3)(PhC_2Ph)(\eta^5-C_5H_5)$]	123—125			1 760w	51.5 (51.3)	2.8 (3.0)	21.3 (21.0)
(XV)	[$WCl(CF_3C_2CF_3)(PhC_2Ph)(\eta^5-C_5H_5)$]	125			1 760w	44.2 (44.6)	2.7 (2.7)	
(XVI)	[$MoCl(CF_3C_2H)_2(\eta^5-C_5H_5)$]	110—115			1 716w 1 700w	34.3 (34.3)	2.0 (1.8)	
(XVII)	[$WCl(CF_3C_2H)(PhC_2Ph)(\eta^5-C_5H_5)$]	200			1 682w	47.5 (47.6)	2.9 (2.8)	

[a] Calculated values given in parentheses. [b] In cm^{-1}. [c] Found: O, 12.3; reqd. O, 11.9%.

TABLE 2

^1H and ^{19}F N.m.r. data for acetylene complexes †

Complex	$\eta^5-C_5H_5$	$C_6H_5C≡C$	MeC≡C	HC≡C	$CF_3C≡C$	Solvents
(I)	3.55s 3.95s				50.5m, 51.6m 54.4m, 55.3m	$(CD_3)_2CO$
(II) [a]	3.87s				58.3m	$CDCl_3$
(III)	4.76s		7.9, 8.0 8.1, 8.15			$CDCl_3$
(IV)	4.29s	2.50m				$CDCl_3$
(V)	4.40s	2.30m	6.55s			CD_2Cl_2
(VI) [b]	4.35s	2.50m	7.05s			$CDCl_3$
(VII) [c]	4.20s	2.50m	6.95br, s			$CDCl_3$
(VIII)	4.70s	2.80m	7.95, 8.50			CD_2Cl_2
(IX)	4.17s	2.20m	6.46s			$(CD_3)_2CO$
(X)	4.06s	2.60m				$(CD_3)_2CO$
(XI)	3.95s	2.60m				$(CD_3)_2CO$
(XIII) [d]	4.15s	2.32m	6.80s		55.0s	$CDCl_3$
(XIV) [e]	4.02s	2.40m			54.7s	$CDCl_3$
(XV) [f]	3.90s	2.50m			56.4s (60°)	$CDCl_3$
(XVI) [g]	4.26s			−0.1	56.3s	$CDCl_3$
(XVII)	4.00s	2.46m		−0.24	55.8s	$(CD_3)_2CO$

† Chemical shifts relative to Me_4Si (τ 10.00) and $CFCl_3$ (0.00 p.p.m.); coupling constants in Hz.

[a] ^{19}F Coalescence temperature −22 °C, ^{19}F resonances (−80 °C) 56.56, 58.63. [b] ^1H Coalescence temperature −20 to −45 °C. [c] ^1H Coalescence temperature −10 to −15 °C. [d] ^1H Coalescence temperature −70°, ^{19}F coalescence temperature +30 °C. ^{19}F Resonances (0 °C) 54.61, 54.13, ^{19}F resonances (−90 °C) 54.07, 54.52 (isomer I) and 54.32, 55.06 (isomer II). [e] ^{19}F coalescence temperature +8°, ^{19}F resonances (−30 °C) 54.21q, 54.40q (J_{FF} 4.4 Hz). [f] ^{19}F Coalescence temperature +40 °C, ^{19}F resonances (−20 °C) 55.74, 54.43. [g] ^{19}F Coalescence temperature −30 °C, ^{19}F resonances (−85 °C) 55.25, 57.78, ^1H resonances −1.79, −1.68 with coalescence temperature −30 °C.

Attempts to isolate pure products from the reaction of [$WCl(CO)_3(\eta^5-C_5H_5)$] with but-2-yne were unsuccessful, although a variety of conditions were examined.

Ultraviolet irradiation of [$WCl(CO)_3(\eta^5-C_5H_5)$] and diphenylacetylene in hexane gave the air-sensitive green complex (IV) analogous to the previously described molybdenum species.[3] These compounds, which are 16-electron complexes, are comparable structurally and spectroscopically with the organothio-complexes. An *X*-ray single-crystal structure determination of [$Mo(SC_6F_5)(CO)(CF_3C_2CF_3)(\eta^5-C_5H_5)$] has shown that the metal is essentially octahedrally co-ordinated, the $\eta^5-C_5H_5$ ring occupying a face and the C≡C axis of the co-ordinated $CF_3C_2CF_3$ being parallel to the Mo–CO axis.[4]

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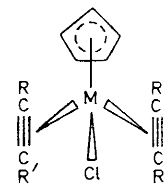
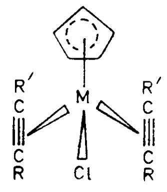
[4] J. A. K. Howard, R. F. D. Stansfield, and P. Woodward, *J.C.S. Dalton*, 1976, 246.

It has been shown [2,3] that in a sealed tube in hexane solution, diphenylacetylene reacts (90 °C) with [$\mathrm{MoCl(CO)_3(\eta^5\text{-}C_5H_5)}$] to give, *via* [$\mathrm{MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)}$], the cyclobutadiene complex [$\mathrm{MoCl(CO)(C_4Ph_4)(\eta^5\text{-}C_5H_5)}$]. However, in refluxing hexane in an open system these reactants give a mixture of [$\mathrm{MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)}$] and (X). The analogous tungsten system does not react with $\mathrm{PhC_2Ph}$ in refluxing hexane but in refluxing light petroleum (80—100 °C) the complex (XI) is formed in high yield, together with trace amounts of [{$\mathrm{WCl(PhC_2Ph)(\eta^5\text{-}C_5H_5)}$}$_2$] (XII) (Table 1). The latter complex is probably structurally analogous to [{$\mathrm{MoCl(CF_3C_2CF_3)(\eta^5\text{-}C_5H_5)}$}$_2$] [3] containing a bridging acetylene and a metal–metal double bond. Although it is reasonable to suggest that (XII) is formed by thermal decomposition of (IV) or (XI), heating these complexes in light petroleum under reflux did not afford the dimer.

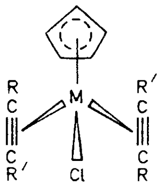
The thermal reaction (80 °C) of methylphenylacetylene with [$\mathrm{MoCl(CO)_3(\eta^5\text{-}C_5H_5)}$] in hexane in a sealed tube affords high yields of the bis-acetylene complex (VI). This reaction gives (V) initially, but the latter reacted readily with more acetylene. However, although u.v. irradiation of a hexane solution of the tungsten compound [$\mathrm{WCl(CO)_3(\eta^5\text{-}C_5H_5)}$] and $\mathrm{PhC_2Me}$ gave (IX) [$\mathrm{WCl(CO)(MeC_2Ph)(\eta^5\text{-}C_5H_5)}$] in good yield, in contrast, there was no evidence for formation of (IX) as an intermediate in the thermal reaction of $\mathrm{PhC_2Me}$ with [$\mathrm{WCl(CO)_3(\eta^5\text{-}C_5H_5)}$]. This reaction gave high yields of (VII) together with a minor product (VIII), thought to be a cyclopentadienone complex. This is suggested by the mass spectrum which showed a parent ion and peaks due to [$\mathrm{(PhC_2Me)_2CO}$]$^+$ and [$\mathrm{(PhC_2Me)_2C}$]$^+$, and a single terminal carbonyl band and an equally intense ketonic mode at 1 611 cm^{-1} in the i.r. spectrum. Although structurally analogous to (I), the spectroscopic data for (VIII) suggest the presence of only one isomer in solution. The ^{1}H n.m.r. spectrum showed a singlet at τ 4.7 due to an η^5-$\mathrm{C_5H_5}$ system, aromatic resonances centred at τ 2.8, and two equally intense singlets at τ 7.95 and 8.50 due to inequivalent methyl groups. Low temperature (−90 °C) ^{1}H n.m.r. studies did not reveal evidence for a second isomer, and therefore the dynamic process observed with (I) does not occur; this is possibly attributable to a steric effect of a phenyl substituent. Unfortunately the ^{1}H n.m.r. evidence does not show whether the acetylenes in (VIII) have joined head-to-head or head-to-tail.



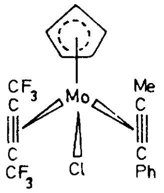
(VIa) M=Mo, R=Ph, R′=Me
(VIIa) M=W, R=Ph, R′=Me
(XVIa) M=Mo, R=$\mathrm{CF_3}$, R′=H



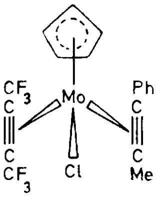
(VIb)
(VIIb)
(XVIb)



(VIc)
(VIIc)
(XVIc)



(XIIIa)



(XIIIb)

Since the complex [$\mathrm{MoCl(MeC_2Me)_2(\eta^5\text{-}C_5H_5)}$] forms *via* a duroquinone complex, it was reasonable to consider whether the cyclopentadienone complex (VIII) is a precursor of (VII). However, when the reaction is carried out at 130 °C increased yields of (VIII) relative to (VII) are obtained, implying that the former compound is not an intermediate.

It was also observed that treatment of the complex (I) with an excess of hexafluorobut-2-yne did not give the bis-acetylene complex [$\mathrm{MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}$]. However, the reverse reaction, *i.e.* formation of (I) from [$\mathrm{MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}$], could be demonstrated. Removal of carbon monoxide from the reaction vessel in the reaction of [$\mathrm{MoCl(CO)_3(\eta^5\text{-}C_5H_5)}$] with $\mathrm{CF_3C_2CF_3}$ results in the formation of only the bis-acetylene complex. It is suggested that an 18-electron species [$\mathrm{MoCl(CO)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}$] is the immediate precursor of (I). This is supported by the observation that triphenylphosphine reacts with [$\mathrm{MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}$] to give [$\mathrm{MoCl(PPh_3)(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}$].[2] It is interesting that attempts to obtain similar 18-electron species with the tungsten analogue have so far failed, thus providing an explanation for the absence of a tungsten compound similar to (I).

Earlier attempts [3] to prepare 16-electron complexes containing two different acetylenes had failed. The reaction of [$\mathrm{MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)}$] with but-2-yne or hexafluorobut-2-yne at 60 °C gave respectively [$\mathrm{MoCl(RC_2R)_2(\eta^5\text{-}C_5H_5)}$] (R = Me or $\mathrm{CF_3}$). However, if the reaction with $\mathrm{CF_3C_2CF_3}$ is carried out at room temperature (20 h) the mixed complex (XIV) (Table 1) is formed. Similar reactions afforded the complexes (XIII), (XV), and (XVII). The reaction of [$\mathrm{MoCl(CO)(PhC_2Ph)(\eta^5\text{-}C_5H_5)}$] with trifluoropropyne gave after only ½ h the complex (XVI), implying that $\mathrm{CF_3C_2H}$ is significantly more reactive than $\mathrm{CF_3C_2CF_3}$ in these reactions. Spectroscopic evidence was obtained for the intermediate [$\mathrm{MoCl(CF_3C_2H)(PhC_2Ph)(\eta^5\text{-}C_5H_5)}$] in this reaction when carried out at −20 °C. The direct reaction of [$\mathrm{MCl(CO)_3(\eta^5\text{-}C_5H_5)}$] with trifluoropropyne produced considerable amounts of decomposition products; however, trace amounts of the 16-electron bis-acetylene species were detected.

As expected, (XIV) reacted with hexafluorobut-2-yne above 40 °C to give [$\mathrm{MoCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)}$]. The tungsten system is less reactive as noted previously, and (XV) did not react with hexafluorobut-2-yne.

Molecular Structure and Dynamic Behaviour of the 16-Electron Complexes.—In order to provide a firm basis for a discussion of the temperature dependent dynamic behaviour of the 16-electron complexes, a single-crystal *X*-ray diffraction study of (II) was undertaken.

The molecular structure is illustrated in Figure 2 (Table 3 lists atomic parameters), which shows the projection of a single monomer molecule onto the plane of the cyclopentadienyl ligand. It is interesting to note that the species actually crystallises as a weakly linked dimer bridged by van der Waals interactions between related cyclopentadienyl groups across the centre of symmetry at 0, ½, ½.

TABLE 3

Positional (fractional co-ordinates, × 10^3; Cl × 10^4; W × 10^5) and isotropic thermal parameters *

Atom	*x*	*y*	*z*	U_j/Å^2 × 10^3
W	12 242(6)	29 299(5)	27 802(3)	†
Cl	4 640(5)	4 184(5)	3 352(4)	†
C(1)	48(4)	514(2)	296(2)	†
C(2)	176(3)	521(2)	395(2)	†
C(3)	93(3)	395(3)	440(1)	†
C(4)	−88(3)	306(2)	368(2)	†
C(5)	−118(3)	384(3)	286(2)	†
C(10)	−176(3)	−86(3)	268(2)	93(5)
C(11)	−6(2)	57(2)	285(1)	61(3)
C(12)	174(2)	104(2)	327(1)	61(3)
C(13)	306(3)	39(3)	382(2)	93(6)
C(20)	284(3)	431(3)	68(2)	92(5)
C(21)	157(2)	341(2)	128(1)	57(3)
C(22)	−12(2)	247(2)	112(1)	66(4)
C(23)	−185(3)	150(3)	20(2)	99(6)
F(101)	−167(2)	−207(1)	221(2)	†
F(102)	−329(2)	−73(2)	224(2)	†
F(103)	−194(4)	−121(3)	363(2)	†
F(131)	230(3)	−104(2)	397(2)	†
F(132)	425(2)	125(2)	472(1)	†
F(133)	411(3)	28(3)	319(2)	†
F(201)	382(2)	576(1)	114(1)	†
F(202)	403(2)	368(2)	60(2)	†
F(203)	194(3)	438(3)	−31(1)	†
F(231)	−214(2)	−5(2)	11(2)	†
F(232)	−168(2)	190(3)	−74(1)	†
F(233)	−334(2)	160(2)	33(1)	†
H(1)	68	593	244	‡
H(2)	308	604	430	
H(3)	150	366	511	
H(4)	−171	206	388	
H(5)	−242	345	299	

* The isotropic thermal parameter is given by $\exp[-8\pi^2 U_j(\sin^2\theta)/\lambda^2]$. † These atoms refined anisotropically according to $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)$. ‡ $U_j = 50$. U_{ii} and U_{ij} values (Å^2 × 10^2; Cl, × 10^3; W, × 10^4) are as follows:

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	405(3)	389(3)	412(3)	145(2)	36(2)	−28(2)
Cl	42(2)	79(3)	79(2)	11(2)	0(2)	−6(2)
C(1)	16(2)	6(1)	8(1)	7(1)	4(1)	1(1)
C(2)	8(1)	5(1)	10(1)	2(1)	2(1)	−2(1)
C(3)	12(2)	11(2)	4(1)	8(1)	2(1)	0(1)
C(4)	7(1)	9(1)	11(2)	3(1)	4(1)	−2(1)
C(5)	7(1)	12(2)	9(1)	7(1)	−1(1)	−3(1)
F(101)	12(1)	6(1)	27(2)	1(1)	5(1)	−4(1)
F(102)	6(1)	10(1)	35(3)	0(1)	4(1)	1(1)
F(103)	23(2)	18(2)	20(2)	−2(2)	11(2)	7(2)
F(131)	15(1)	9(1)	36(3)	4(1)	−4(2)	9(2)
F(132)	17(1)	11(1)	14(1)	7(1)	−6(1)	1(1)
F(133)	16(2)	26(2)	19(2)	16(2)	4(1)	4(2)
F(201)	17(1)	7(1)	11(1)	−1(1)	4(1)	1(1)
F(202)	16(1)	14(1)	17(2)	4(1)	11(1)	4(1)
F(203)	19(2)	18(2)	8(1)	4(1)	3(1)	7(1)
F(231)	15(1)	11(1)	21(2)	4(1)	−9(1)	−9(1)
F(232)	15(1)	24(2)	6(1)	2(1)	−2(1)	−1(1)
F(233)	7(1)	14(1)	15(1)	3(1)	−3(1)	−1(1)

Important interatomic distances (uncorrected for thermal effects) and interbond angles are presented in Table 4. The co-ordination geometry of the metal approximates to octahedral, with three facial sites occupied by an (η^5-C_5H_5) ligand, one site by a (Cl) ligand, and the fifth and sixth sites by η^2-bonded $CF_3C_2CF_3$ ligands. The carbon–carbon axes C(11) ··· C(12) and C(21) ··· C(22) of the co-ordinated acetylenes lie approximately parallel to the W–Cl direction. As shown in Figure 3, carbon atoms C(11) and C(22) are tilted towards each other; however, this is thought to be a solid-state effect.

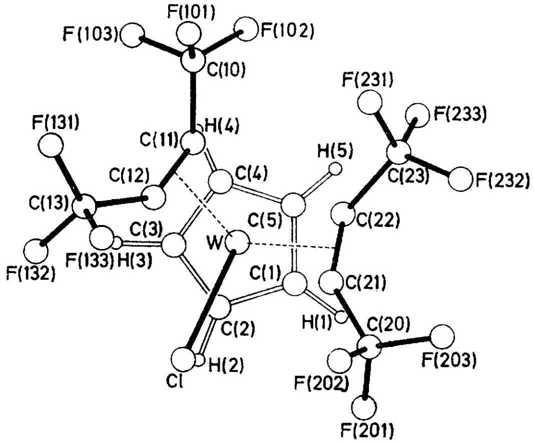


FIGURE 2 The complex $[WCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ (II)

TABLE 4

Molecular geometry in (II)

(*a*) Metal co-ordination sphere (Å)

W–Cl	2.417(3)	W–C(1)	2.35(3)
W–C(11)	2.071(15)	W–C(2)	2.36(2)
W–C(12)	2.049(18)	W–C(3)	2.33(2)
W–C(21)	2.064(16)	W–C(4)	2.29(3)
W–C(22)	2.068(16)	W–C(5)	2.38(3)

(*b*) Mean distances (Å)

		N			*N*
W–C(alkyne)	2.063(10) [a]	4	C–CF_3	1.47(2)	4
W–C(C_5H_5)	2.34(3)	5	F_3CC–CCF_3	1.27(2)	2
C–C(C_5H_5)	1.38(3)	5	C–F	1.30(3)	12

(*c*) Mean angles (°)

		N
C(alkyne)–W–C(alkyne)	36.0(6) [b]	2
$C_{(C_5H_5)}$–W–$C_{(C_5H_5)}$	34.4(7)	5
C–C–$C_{(C_5H_5)}$	108(1)	5
C–C–$C_{(alkyne)}$	139(2)	4
C–C–F	112(2)	12
F–C–F	106.₅(3)	12

[a] The estimated standard deviation of the mean of *N* values is calculated from $\sigma^2 = |\sum_{i=1}^{i=N}(\chi_i - \bar{\chi})^2|/(N-1)$, where χ_i is the i^{th} and $\bar{\chi}$ the mean value. [b] Same alkyne molecule.

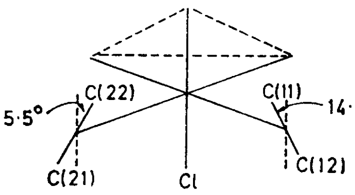


FIGURE 3

The difference in bond lengths between the tungsten and the acetylenic carbon atoms is not significant, and it is clear that the $CF_3C_2CF_3$ ligands are symmetrically bonded as 2-electron donors, and therefore the molecule can be described as a 16-electron complex. In the absence of an accurate C–C bond length [1.22(9) Å] [5] for unco-ordinated hexafluorobut-2-yne a detailed discussion is not merited; however, a mean value for C≡C in complex (II) of $1.27_5(2)$ Å suggests a small and possibly significant bond-lengthening on co-ordination.* As has been observed with complexes containing co-ordinated $CF_3C_2CF_3$,[4,6] the C·C⋮C·C sequence is non-linear, and, as expected, the CF_3 groups bend away from the metal.

The variable-temperature ^1H and ^{19}F n.m.r. spectra of the complexes $[MoX(RC_2R)_2(\eta^5\text{-}C_5H_5)]$ (R = Me or CF_3; X = Cl, Br, or I) have been briefly discussed [3] in terms of two kinds of fluxional behaviour, a polytopal inversion and propeller rotation of the acetylene about an axis perpendicular to the C–C bond and passing through the molybdenum atom. Knowledge of the molecular structure of (II) and n.m.r. data for a wider range of complexes allows a more definitive discussion of this question.

In general the aromatic proton region of the ^1H spectra of the diphenyl- and methylphenyl-acetylene complexes, although in most cases showing temperature dependence, gives little information about the fluxional process. However, with (II), (XIV), and (XV) the ^1H or ^{19}F spectra show two peaks at −80 °C due to CF_3 or Me groups. At higher temperatures (Table 2) coalescenc occurs, and eventually a sharp singlet is obtained as the temperature is further increased. This is consistent with the presence in solution at low temperature of one isomer, presumably with the structure established in the solid state for (II). The methyl group region of the ^1H spectrum of (VI) and (VII) showed at low temperature four singlet resonances, two of equal intensity, indicating the presence of three isomers. Similarly, the ^{19}F and ^1H spectra of (XVI) also revealed the presence of isomers at low temperatures, and in this case it was possible to observe the coalescence of signals in both the ^1H and ^{19}F spectra at the same temperature (Table 2). However, only two ($CF_3C{\equiv}C$) and (HC≡C) resonances were observed, suggesting that possibly isomer (XVIc) is unstable. The ^{19}F spectrum of (XVII) is independent of temperature over the range −90 to +20 °C, unlike the hexafluorobut-2-yne analogue (XV), again suggesting one isomer to be unstable although two are possible. No change in the trifluoropropyne proton resonance was observed over the temperature range, but the C_6H_5 resonances of the (PhC⋮CPh) ligand gave temperature-dependent resonances. This compares with $[Mo(SC_6F_5)(CO)(CF_3C_2H)(\eta^5\text{-}C_5H_5)]$ where the presence of two isomers was detected, but interchange of isomers was slow on the n.m.r. time scale.[1]

The ^1H spectrum of (XIII) also shows the maximum possible two methyl group environments at −90 °C. At −70 °C coalescence occurs. The ^{19}F spectrum shows two sets of two peaks at −90 °C, which coalesce to two signals at −70 °C and finally to a singlet at +30 °C. This behaviour can be explained in terms of both acetylenes having fixed orientations at −90 °C. At −70 °C onset of rotation of PhC_2Me has occurred leading to coalescence of isomer signals. The trifluoromethyl resonances of the co-ordinated hexafluorobut-2-yne remain distinct, however, until rotation of $CF_3C_2CF_3$ becomes important at +30 °C. It is not possible to explain these observations in terms of an intramolecular polytopal rearrangement, since such a process would lead to equilibration of each set of acetylene signals simultaneously.

Complex (IV), like its molybdenum analogue, also gives temperature-dependent n.m.r. spectra, whereas, in contrast (V) and (IX) give spectra which do not change over the temperature range −90 to +20 °C. There is no obvious explanation for this apparently conflicting result, but it is possibly significant that the complexes $[M(SR')(CO)(RC_2R)(\eta^5\text{-}C_5H_5)]$ (M = Mo or W, R = CF_3, CH_3, or Ph, R′ = CF_3 or C_6F_5) are stereochemically rigid.

Examination of the variable-temperature n.m.r. data for the bis-acetylene complexes reveals three trends. Since back donation from filled metal *d*-orbitals to π*-antibonding orbitals of the co-ordinated acetylene must result in an increase in the barrier to propeller-like rotation, it is expected, and was observed, that the presence of electron-withdrawing substituents on the acetylenes would lead to higher coalescence points. The nature of the metal atom would also be expected to influence the barrier to rotation. Higher coalescence temperatures (t_c) are found with the tungsten complexes as illustrated for the systems $[MCl(CF_3C_2CF_3)_2(\eta^5\text{-}C_5H_5)]$ [t_c = −28 °C for M = Mo, t_c = −22 °C for M = W] and $[MCl(CF_3C_2CF_3)(PhC_2Ph)(\eta^5\text{-}C_5H_5)]$ [t_c = +8 °C for M = Mo, t_c = +40 °C for M = W]. It is also significant that the coalescence temperature for a particular acetylene is dependent on the nature of the other coordinated acetylenes. Thus for $CF_3C_2CF_3$ in the complexes $[MoCl(CF_3C_2CF_3)(RC_2R)(\eta^5\text{-}C_5H_5)]$ t_c = −28 °C when R = CF_3, and +8 °C when R = Ph. Similarly, for the acetylene PhC_2Me in the complexes $[MoCl(PhC_2Me)(RC_2R')(\eta^5\text{-}C_5H_5)]$ the coalescence temperatures for PhC_2Me are t_c = −20 to −45 °C when R = Ph and R′ = Me; and t_c = −70 °C when R = R′ = CF_3.

Clearly, hexafluorobut-2-yne is a better π-acceptor than the other acetylenes, and therefore reduces the coalescence temperature of the other acetylenes present in a bis-acetylene complex. With PhC_2Me the converse is true. Similar effects have been observed with coordinated olefins where replacement of hydrogen by fluorine results in a significant increase in the barrier to rotation.[7]

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* A previous discussion [1] of the bonding in this type of complex suggested that the acetylene acted as a 4-electron donor; however, this now seems unlikely in view of the *X*-ray results.

[5] B. W. Davies, R. J. Puddephatt, and N. C. Payne, *Canad. J. Chem.*, 1972, **50**, 2276.

[6] J. A. Ibers and W. C. Hamilton, *Acta Cryst.*, 1964, **17**, 781.

[7] R. Cramer and G. S. Reddy, *Inorg. Chem.*, 1973, **12**, 346; R. Cramer, J. B. Kline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 259.

The existence of a lower coalescence temperature for [MoCl($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)] compared with [MoCl-(MeC_2Me)$_2$(η^5-C_5H_5)] appears at first sight to be anomalous. However, this phenomenon can be rationalised in terms of each co-ordinated $CF_3C_2CF_3$ ligand in [MoCl($CF_3C_2CF_3$)$_2$(η^5-C_5H_5)] competing strongly for metal *d*-electron density, but since this is limited, effectively each acetylene weakens the extent of back-bonding with the other. This effect is somewhat similar to *trans*-effects in platinum(II) complexes. In the but-2-yne complexes back donation is unlikely to be as important and the coalescence temperature is correspondingly higher.

EXPERIMENTAL

^1H and ^{19}F 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 using carbon tetrachloride or dichloromethane solutions. Solvents were dried and distilled under nitrogen, and all operations were conducted in an atmosphere of dry oxygen-free nitrogen. Analytical data are given in Table 1.

Reactions of Hexafluorobut-2-yne.—(a) *With tricarbonyl-(chloro)cyclopentadienylmolybdenum.* Hexafluorobut-2-yne (2 g, 12 mmol) was condensed (−196 °C) into a tube (80 cm^3 fitted with a Westef Stopcock) containing hexane (25 cm^3) and [MoCl(CO)$_3$(η^5-C_5H_5)] (0.50 g, 1.8 mmol). The tube and contents were warmed to room temperature and then heated (20 h, 80 °C). Orange crystals formed during the reaction. Volatile material was removed *in vacuo*, and the crystalline product was dissolved in dry diethyl ether. The orange solution was filtered and the volume of solvent reduced; when cooled it afforded yellow-brown *microcrystals* of (I) (0.46 g, 45%).

In a second reaction, the same quantities of reactants and solvent were sealed together in an identical tube. After 2 h at 80 °C, the reaction tube was cooled (−196 °C) and carbon monoxide which had formed was removed *in vacuo*. The reaction was continued, and at 2 h intervals the evolved CO was released. After 12 h reaction was complete. Volatile material was removed *in vacuo*, and the orange residue was extracted with diethyl ether. Partial removal of solvent followed by addition of hexane gave on cooling (−20 °C) of the solution yellow-orange crystals of the known [3] compound [MoCl($CF_3C_2CF_3$)$_2$-(η^5-C_5H_5)] (0.52 g, 56%).

(b) *With tricarbonyl(chloro)cyclopentadienyltungsten.* A similar reaction of [WCl(CO)$_3$(η^5-C_5H_5)] with $CF_3C_2CF_3$ using identical reaction conditions and molar quantities gave only the crystalline pale yellow complex (II) (53%).

Reaction of But-2-yne with Tricarbonyl(chloro)cyclopentadienylmolybdenum.—But-2-yne (1 g, 18.5 mmol) was condensed (−196 °C) into a reaction tube containing benzene (20 cm^3) and [MoCl(CO)$_3$(η^5-C_5H_5)] (0.40 g, 1.4 mmol). After 40 h at room temperature red-brown *crystals* formed. Volatile material was removed *in vacuo*, and the residue was dissolved in methylene chloride. Addition of hexane and cooling (−20 °C) gave red-brown *crystals* of (III) (0.38 g, 69%).

A similar reaction of but-2-yne (1 g, 18.5 mmol) with [MoCl(CO)$_3$(η^5-C_5H_5)] (0.30 g, 1.1 mmol) in hexane (25 cm^3) at 70 °C (60 h) gave on cooling to room temperature yellow crystals of [MoCl(MeC_2Me)$_2$(η^5-C_5H_5)] (0.14 g, 43%). The solvent was removed from the mother liquor and the residue sublimed *in vacuo* (40 °C) to give duroquinone (20 mg, 11%).

Reaction of Diphenylacetylene with Tricarbonyl(chloro)-cyclopentadienyltungsten.—Irradiation (Hanovia 250 W u.v. lamp) (30 h) of a solution of diphenylacetylene (0.30 g, 1.7 mmol) and [WCl(CO)$_3$(η^5-C_5H_5)] (0.30 g, 0.8 mmol) in hexane (40 cm^3) afforded green crystals. Separation and recrystallisation (−20 °C) from methylene chloride–hexane gave green *crystals* of (IV) (0.26 g, 66%).

Reactions of Methylphenylacetylene.—(a) *With tricarbonyl-(chloro)cyclopentadienylmolybdenum.* A solution of [MoCl-(CO)$_3$(η^5-C_5H_5)] (0.20 g, 0.71 mmol) and MeC_2Ph (0.40 g, 3.4 mmol) in hexane (30 cm^3) was heated (40 °C) in a sealed tube for 40 h. Recrystallisation of the product from methylene chloride–hexane gave green *crystals* of (V) (0.15 g, 64%). An identical reaction but carried out at 80 °C for 40 h gave yellow *crystals* of (VI) (0.20 g, 67%).

(b) *With tricarbonyl(chloro)cyclopentadienyltungsten.* The complex [WCl(CO)$_3$(η^5-C_5H_5)] (0.25 g, 0.68 mmol) and MeC_2Ph (0.5 g, 4.3 mmol) were allowed to react (70 °C) together in hexane (25 cm^3). After 50 h the mixture was allowed to cool slowly to room temperature when yellow crystals formed. Volatile material was removed *in vacuo* and the residue was recrystallised from methylene chloride–hexane to give yellow *crystals* of (VII) (0.18 g, 53%). The orange-red mother liquor from the recrystallisation was concentrated to give a small crop of orange-brown crystals. Recrystallisation from methylene chloride–hexane gave *crystals* of (VIII) (0.01 g, 2.7%). At 35 °C the reaction gave only (VII), whereas at 130 °C (VII) (59%) and (VIII) (6%) were obtained. U.v. irradiation of the reactants gave dark blue *crystals* of (IX) (0.12 g, 41%).

Reactions of Diphenylacetylene.—(a) *With tricarbonyl-(chloro)cyclopentadienylmolybdenum (open system).* A solution of [MoCl(CO)$_3$(η^5-C_5H_5)] (0.28 g, 1.0 mmol) and diphenylacetylene (0.4 g, 2.2 mmol) in hexane (40 cm^3) was heated under reflux in a nitrogen atmosphere. After 14 h green crystals of [MoCl(CO)(PhC_2Ph)(η^5-C_5H_5)] were formed. These were filtered off to afford an orange solution which when cooled (−20 °C) gave orange *crystals* of (X) (0.12 g, 22%).

(b) *With tricarbonyl(chloro)cyclopentadienyltungsten.* A solution of [WCl(CO)$_3$(η^5-C_5H_5)] (0.25 g, 0.68 mmol) and diphenylacetylene (0.30 g, 1.7 mmol) in light petroleum (80—100 °C) (40 cm^3) was heated under reflux (5 h). The hot solution was decanted and when cooled (−20 °C) gave pale yellow *crystals* of (XI) (0.28 g, 65%). The residue remaining in the reaction flask after decantation was recrystallised from methylene chloride–hexane to give *crystals* of (XII) (0.01 g, 0.4%).

Reactions of Hexafluorobut-2-yne.—(a) *With complex* (V). Hexafluorobut-2-yne (2.0 g, 12 mmol) was condensed (−196 °C) into a reaction tube containing [MoCl(CO)-(PhC_2Me)(η^5-C_5H_5)] (V) (0.15 g, 0.44 mmol) dissolved in methylene chloride (10 cm^3). After 20 h at room temperature an orange solution was formed. The volatile material was removed under reduced pressure and the residue recrystallised from methylene chloride–hexane to give orange *crystals* of (XIII) (0.075 g, 36%).

(b) *With the complex* [MoCl(CO)(PhC_2Ph)(η^5-C_5H_5)]. A similar reaction between [MoCl(CO)(PhC_2Ph)(η^5-C_5H_5)] (0.2 g, 0.5 mmol) and hexafluorobut-2-yne (1 g, 6 mmol) in methylene chloride (10 cm^3) gave orange *crystals* of (XIV) (0.067 g, 25%).

Reactions of [WCl(CO)(PhC$_2$Ph)(η^5-C$_5$H$_5$)] (IV).—(a) *With hexafluorobut-2-yne*. Similarly, reaction (60 h/40 °C) of (IV) (0.3 g, 0.6 mmol) with CF$_3$C$_2$CF$_3$ (1 g, 6 mmol) gave orange *crystals* of (XV) (0.078 g, 21%).

(b) *With but-2-yne*. Reaction (120 h/55 °C) of (IV) (0.24 g, 0.5 mmol) with but-2-yne (0.5 g, 9.2 mmol) gave yellow *crystals* of (XVI) (0.11 g, 45%).

Reaction of Carbonylchlorocyclopentadienyldiphenylacetylenemolybdenum with Trifluoroprop-1-*yne*.—A similar reaction ($\frac{1}{2}$ h/ 20 °C) of CF$_3$C≡CH (1.5 g, 16 mmol) with [MoCl(CO)(PhC$_2$Ph)(η^5-C$_5$H$_5$)] (0.2 g, 0.5 mmol) in methylene chloride (10 cm^3) gave yellow crystals of (XVI) (0.067 g, 35%).

The direct reaction (45 h/ 60 °C) of [MoCl(CO)$_3$(η^5-C$_5$H$_5$)] with CF$_3$C≡CH in hexane gave a low yield (11%) of (XVI).

Reaction of [WCl(CO)(PhC$_2$Ph)(η^5-C$_5$H$_5$)] (IV) *with Trifluoroprop*-1-*yne*.—Reaction (15 h/20 °C) of (IV) (0.2 g, 0.4 mmol) with CF$_3$C≡CH (1.5 g, 16 mmol) gave yellow *crystals* of (XVII) (0.035 g, 16%).

Crystal Structure Determination of (II).—A single crystal, 0.022 × 0.014 × 0.014 cm, was chosen for study on a Syntex $P2_1$ automated diffractometer. Lattice parameters and one hemisphere of diffracted data were accurately determined according to the following details: graphite monochromated Mo-K_α radiation; 96-step θ—2θ scan procedure; variable-scan rates from 0.0337 to 0.4883° s^{-1}; $2.9 \leqslant 2\theta \leqslant 50.0°$; 3 check reflections periodically monitored; 2 390 reflections measured, 2 210 having $I \geqslant 2.5\sigma(I)$ used for solution and refinement of the structure.

Crystal Data.—C$_{13}$H$_5$ClF$_{12}$W, M = 608.5, Triclinic, a = 7.942(1), b = 9.302(1), c = 12.828(2) Å, α = 93.76(1), β = 104.76(1), and γ = 111.57(1)°, U = 841.4(2) Å^3, D_m = 2.38 (by flotation), Z = 2, D_c = 2.401, $F(000)$ = 564. Mo-K_α radiation, $\bar{\lambda}$ = 0.710 69 Å; μ(Mo-$K_{\bar{\alpha}}$) = 75.5 cm^{-1}. Space group $P\bar{1}$.

Data were corrected for X-ray absorption, Lorentz and polarisation effects, and the molecular structure was determined by conventional Patterson (W), least-squares refinement, and difference-Fourier (Cl, F, and C) techniques. Hydrogen atoms were introduced into calculated positions (assuming $r_{\text{C-H}}$ 1.0 Å, U_{H} 0.05 Å^2). Reflection intensities were weighted such that $w^{-1} = 4.91 + |F_o| + 0.011|F_o|^2$. Full-matrix least-squares refinement [W, Cl, F, C(C$_5$H$_5$) atoms anisotropic; C(alkyne) isotropic; H invariant] converged to R 0.058 and R' 0.071.

Observed and calculated structure-factor amplitudes are listed in Supplementary Publication No. SUP 21575 (11 pp., 1 microfiche).*

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.