

Interaction of Tricarbonyl(π -cyclopentadienyl)molybdenum Halides and Acetylenes †

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Tricarbonyl(π -cyclopentadienyl)molybdenum halides, $[(\text{cp})\text{Mo}(\text{CO})_3\text{X}]$ (X = Cl, Br, or I), ($\text{cp} = \eta^5\text{-C}_5\text{H}_5$) react with $\text{MeC}\equiv\text{CMe}$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ to give the 16-electron bisalkyne complexes $[(\text{cp})\text{Mo}(\text{RC}_2\text{R})_2\text{X}]$ whilst $\text{PhC}\equiv\text{CPh}$ gives $[(\text{cp})\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}]$ and the cyclobutadiene complexes $[(\text{cp})\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})_2\text{X}]$.

THE reactions of acetylenes with molybdenum and tungsten species have received comparatively little attention to date. Essentially they have been confined to the reactions of $\text{Mo}(\text{CO})_6$, $[\text{CH}_3\text{CNM}(\text{CO})_5]$, $[(\text{CH}_3\text{CN})_3\text{-M}(\text{CO})_3]$, $[\text{MoR}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ (R = H, Me, or Et), and $[\text{WPh}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_5)]$ with various acetylenes.¹ We have reported briefly² on the reactions of molybdenum and tungsten cyclopentadienyl carbonyl halides with some acetylenes and describe in the present paper some details of the reactions involving $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}]$ (X = Cl, Br, or I). Further work on these complexes has been carried out at the University of Bristol³ and will be described in a separate publication.

Tricarbonyl(π -cyclopentadienyl)molybdenum halides, $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}]$ (X = Cl, Br, or I) react with but-2-yne and hexafluorobut-2-yne with complete decarbonylation to give coloured crystalline solids of stoichiometry $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{RC}_2\text{R})_2\text{X}]$ (R = Me or CF_3 , X = Cl, Br, or I) and when R = Me duroquinone is also formed. The reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{I}]$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ gives only poor yields of the bisalkyne complex. In this reaction an intermediate giving a single CO stretching mode above 2000 cm^{-1} was detected in solution but it was not possible to isolate this species. $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$ is isostructural with $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$ and this latter complex has the cyclopentadienyl group, chloride, and two unlinked acetylenes bonded to the metal.³ The mass spectrum in all cases shows a molecular ion, which undergoes stepwise loss of acetylene units. The n.m.r. spectra (Table 1)‡ will be discussed in detail later but are in accordance with the structure as are the i.r. spectra.‡

Tricarbonyl(π -cyclopentadienyl)molybdenum chloride and bromide react with diphenylacetylene at temperatures below 320 K to give high yields of the green solids $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}]$. The bromo-derivative is formed more slowly than the chloro-derivative and the iodo-derivative is not formed thermally although $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{I}]$ may be prepared by photolysis. Reaction between $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}]$ and

$\text{PhC}\equiv\text{CPh}$ at higher temperatures gives complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})_2\text{X}]$ as methylene chloride solvates. In the case of the chloride and bromide these are solvates of the tetraphenylcyclobutadiene complexes formed in low yield from reactions of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}]_2$ with the cyclobutadiene-derivatives $[(\text{PhC}_2\text{Ph})_4\text{PdX}_2]$.⁴ On

TABLE 1

Coalescence data on $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{RC}_2\text{R})_2\text{X}]$ complexes derived from variable-temperature n.m.r. studies

Complex	T_c	$\Delta\nu_c/\text{Hz}$	h_c/s^{-1}	$\Delta G_c/\text{kcal mol}^{-1}$
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{MeC}_2\text{Me})_2\text{X}]$				
X = Cl	286.5	52.23	116	9.3
Br	292	43.4	96	14.4
I	289.4	29.53	6	12.7
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{X}]$				
X = Cl	243.3	159	35	11.2
Br	249	179	398	11.5
I	240.5	186	413	11.1

heating the solvate of the chloride, CH_2Cl_2 is lost to form the unsolvated species. The tetraphenylcyclobutadiene complexes are apparently formed by way of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}]$ monocarbonyls as intermediates since these latter derivatives react with diphenylacetylene at higher temperatures to give the cyclobutadiene complexes.

Attempts were made to form mixed acetylene complexes by allowing $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}]$ to react with $\text{MeC}\equiv\text{CMe}$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ but the products were $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{MeC}_2\text{Me})_2\text{X}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{X}]$ respectively; similarly, $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{MeC}_2\text{Me})_2\text{Cl}]$ gave only $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$ with $\text{CF}_3\text{C}\equiv\text{CCF}_3$. These results illustrate the stronger bonding of fluoroacetylene complexes as compared with dimethyl and diphenylacetylene complexes.⁵ It has been shown³ that under suitable conditions mixed acetylene complexes may be formed.

Irradiation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$ in pentane gives a small yield of slightly soluble red crystals which are formulated as $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]_2$ on the basis of the mass spectrum. The ¹H and ¹⁹F n.m.r. spectra each show single peaks only. The i.r. spectrum shows weak bands at 1550 and 1521 cm^{-1} which are close to those observed in the spectra of complexes, e.g.

* 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, and F. G. A. Stone, personal communication.

‡ P. M. Maitlis and A. Efraty, *J. Organometallic Chem.*, 1965, 4, 172.

§ J. L. Boston, D. W. A. Sharp, and G. Wilkinson, *J. Chem. Soc.*, 1962, 3488.

† No reprints available.

‡ See Supplementary Publication No. SUP 21619 (5 pp.). For details of the Supplementary publications scheme see *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

¹ W. Hübel and R. Merenyi, *J. Organometallic Chem.*, 1964, 2, 213; A. Nakamura and N. Hagihara, *Nippon Kagaku Zasshi*, 1963, 344 (*Chem. Abs.*, 1963, 59, 14021); N. G. Boki, Yu. V. Gatilov, Yu. T. Struchkov, and N. A. Ustynyuk, *J. Organometallic Chem.*, 1973, 54, 213; for review of earlier work see F. L. Bowden and A. B. P. Lever, *Organometallic Chem. Rev. (A)*, 1968, 3, 227.

$[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ni}_2(\text{CF}_3\text{C}_2\text{CF}_3)]$ and $[\text{Co}_2(\text{CO})_6(\text{CF}_3\text{C}_2\text{CF}_3)]$, known to contain bridging acetylene groups.⁵ The complex is thus considered to contain two bridging acetylenes and a metal-metal double-bond as is found for $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Nb}(\text{CO})(\text{PhC}_2\text{Ph})]\}_2$.^{6,7}

Irradiation of $\{[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]\}_2$ in the presence of an excess of $\text{CF}_3\text{C}\equiv\text{CCF}_3$ gives a complex which, upon the basis of i.r. and mass spectrometric evidence, is an isomer of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$ and may contain an $\eta^4\text{-C}_4(\text{CF}_3)_4$ group.

The n.m.r. spectra provide very useful information on the geometries of the complexes formed in the present work. Although the ^1H shifts of the cyclopentadienyl protons in $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{RC}_2\text{R})_2\text{X}]$ ($\text{R} = \text{Me}$, $\tau = 4.59$; $\text{R} = \text{CF}_3$, $\tau = 3.94$), $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}]$ ($\tau = \sim 2.42$), and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})_2\text{X}]$ ($\tau = 4.50$) are virtually independent of the halogen, they depend markedly upon the type and substituents of the other groups present which clearly exercise a major influence upon the electron density at the cyclopentadienyl ring. Similar observations have been previously made on $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}]$ and $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\text{R}_4\text{C}_4\text{CO})]$ complexes.⁸

The ^1H n.m.r. spectra of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CH}_3\text{C}_2\text{CH}_3)_2\text{X}]$ complexes at room temperature show a broad singlet near $\tau = 7$ from the methyl protons (the chemical shift is also fairly insensitive to the halogen) which at low temperatures (Table 1) splits into two slightly coupled resonances which are probably quartets with only the splitting of the central peaks resolved fully because of the small coupling constant ($J_{\text{HH}} = 0.7$ Hz). The ^{19}F spectra of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{X}]$ complexes are similar although distinct coupling cannot be observed in the low-temperature spectra.

These n.m.r. spectra are consistent with species in solution having a geometry similar to that found for $[(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$ in the solid state with non-equivalent substituents in the RCCR acetylenes at low temperatures.

The fluxional behaviour observed at room temperature could be consistent with acetylene exchange or rapid rotation of the acetylene molecules about the metal-acetylene axis. Addition of varying amounts of but-2-yne to a CD_2Cl_2 solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{MeC}_2\text{Me})_2\text{I}]$ produced no effect on the n.m.r. spectrum above or below the coalescence temperature; the latter was not affected so that acetylene exchange by a dissociative mechanism is ruled out in this case. Rotation of co-ordinated acetylenes has been previously established in a number of chromium and osmium complexes.⁹ The

⁶ A. N. Nesmeyanov, A. I. Gusev, A. A. Pasynskii, K. N. Anisimov, N. E. Kolobova, and Yu. T. Struchkov, *Chem. Comm.*, 1968, 1365.

⁷ Cf. J. H. Nelson, K. S. Wheelock, L. C. Cusachs, and H. B. Jonassen, *J. Amer. Chem. Soc.*, 1969, **91**, 7005; L. J. Guggenberger and R. C. Cramer, *ibid.*, 1972, **94**, 3779; J. A. Evans and D. R. Russell, *Chem. Comm.*, 1971, 197.

⁸ A. N. Nesmeyanov, I. F. Leshcheva, I. V. Polovnyanyuk, Yu. A. Ustynyuk, and L. G. Makarova, *J. Organometallic Chem.*, 1972, **37**, 159; R. S. Dickson and G. R. Tailby, *Austral. J. Chem.*, 1970, **23**, 1531.

present results indicate lower barriers to equivalence in the $\text{CF}_3\text{C}\equiv\text{CCF}_3$ complexes than in the $\text{MeC}\equiv\text{CMe}$ complexes whereas in olefin complexes the presence of fluorine in the ligand increases the barrier to rotation.¹⁰ It is not possible to distinguish between rotation and a polytopal intramolecular exchange of acetylenes from the present data although further studies³ on $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{PhC}_2\text{Me})(\text{CF}_3\text{C}_2\text{CF}_3)\text{Cl}]$ show differing coalescence temperatures for the ^1H and ^{19}F spectra which would be consistent with onset of rotation of the two acetylenes at different temperatures. The orders of the ΔG_c values for both the but-2-yne and the hexafluorobut-2-yne complexes follow a similar trend with the maximum at the bromo-complex. The trend is not uniform and may reflect opposing effects of size and electronegativity. The values of ΔG_c for the but-2-yne complexes vary by over 4 kcal mol⁻¹ over the range of halides whereas the hexafluorobut-2-yne complexes all have very similar values. The values of k_c show opposite trends on changing the halogens and, as previously mentioned, hexafluorobut-2-yne complexes interchange trifluoromethyl groups much more rapidly than the rate of methyl interchange of co-ordinated but-2-yne groups.

The ^1H n.m.r. spectra of the $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}]$ complexes show a broad resonance near $\tau = 2.4$ arising from the phenyl protons. With the chloro- and bromo-complexes the signals are fairly symmetric at room temperature but the iodide shows a grossly distorted signal. Low-temperature studies on $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{Cl}]$ show a very different spectrum for the phenyl groups from that observed at room temperature. This spectrum and that of the iodide could indicate strong steric hindrance to rotation about the Mo-acetylene bond. The ^1H n.m.r. spectra of the tetraphenylcyclobutadiene complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})_2\text{X}]$ show broad signals near $\tau = 2.8$ at room temperature but at 213 K the signal splits; it is considered likely that this is due to freezing out of preferred reformation(s) at low temperature although polytopal rearrangements at room temperature cannot be ruled out.

The bis(alkyne) complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{RC}_2\text{R})_2\text{X}]$ described in this paper are formally 16-electron species if each acetylene is considered to contribute two electrons only to the metal. For the tris(alkyne)tungsten species $[(\text{RC}=\text{CR})_3\text{WL}]$, however, it has been pointed out that two acetylenes could each donate four electrons to the metal.¹¹ By similar bonding formally involving one of the acetylenes the present bis(alkyne) complexes could achieve a noble-gas electronic configuration. In the $[(\text{RC}=\text{CR})_3\text{WL}]$ complexes the $\text{C}\equiv\text{C}$ stretching mode occurs near to 1700 cm⁻¹,¹² lower than the values

⁹ M. Herberhold, H. Alt, and C. G. Kreiter, *J. Organometallic Chem.*, 1972, **42**, 413; J. Ashley-Smith, B. F. G. Johnson, and J. A. Segal, *ibid.*, 1973, **49**, C38.

¹⁰ R. Cramer, J. B. Cline, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1969, **91**, 2519; R. Cramer and G. S. Reddy, *Inorg. Chem.*, 1973, **12**, 346.

¹¹ R. B. King, *Inorg. Chem.*, 1968, **7**, 1044.

¹² D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselli, *J. Amer. Chem. Soc.*, 1964, **86**, 3261.

(ca. 1 800 cm^{-1}) found for the bis(alkyne) complexes thus implying less donation of electron density from the C-C multiple bond to metal in the bis(alkyne) complexes than in the tris(alkyne) derivatives. The frequencies observed in the bis(alkyne) complexes are comparable with those observed in complexes such as $[(\text{Ph}_3\text{P})_2\text{M}(\text{CF}_3\text{C}_2\text{CF}_3)]$ ($\text{M} = \text{Ni}$ or Pt).¹³ Although not generally considered so, these latter complexes would need to have the acetylenes acting as four-electron donors if the central metal is to have a noble-gas electronic configuration.

Although the series of complexes $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})\text{-}(\text{PhC}_2\text{Ph})\text{X}]$ are also formally 16-electron complexes it is

the reaction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{I}]$ and $\text{CF}_3\text{C}\equiv\text{CCF}_3$ suggesting that species $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{RC}_2\text{R})\text{X}]$ may be formed initially during these reactions. Subsequent reaction of the latter leads to carbonyl expulsion with but-2-yne and hexafluorobut-2-yne but to coupling of two acetylenes with diphenylacetylene. This latter reaction possibly proceeds *via* a metallocyclopentadiene species.¹⁴ Formation of co-ordinated cyclobutadiene occurs fairly readily with diphenylacetylene and, in contrast, but-2-yne commonly gives duroquinone with metal carbonyls.¹⁵ The reactions of tricarbonyl(π -cyclopentadienyl)molybdenum halides with acetylenes

TABLE 2

Reagents	Temperature	Time/h	Products	Yield (%)
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}] + \text{MeC}\equiv\text{CMe}$ X = Cl	338 K	60	$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{MeC}_2\text{Me})_2\text{X}]$ (A) + $\text{C}_4(\text{Me})_4(\text{CO})_2$ (B)	A 40 B 11
Br	338 K	60		A 35 B 8
I	338 K	100		A 32 B 9
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}] + \text{CF}_3\text{C}\equiv\text{CCF}_3$ X = Cl	343 K	15	$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)\text{X}]$	77
Br	348 K	40		29
I	358 K	80		5
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}] + \text{PhC}\equiv\text{CPh}$ X = Cl	313 K	30	$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}]$	81
Br	293 K/hv	20		90
	328 K	40		87
I	293 K/hv	20		92
	293 K/hv	20		95
Cl	363 K	60	$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC})_4\text{X}\cdot\text{CH}_2\text{Cl}_2]$	61
Br	363 K	48		45
I	358 K	48		49
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}] + \text{CF}_3\text{C}\equiv\text{CCF}_3$ X = Cl	338 K	16	$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{X}]$	70
Br	338 K	20		65
I	338 K	8		17
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)\text{Cl}]$	293 K (u.v.)	24	$\{[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)\text{Cl}]_2\}$	10
$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)\text{Cl}] + \text{CF}_3\text{C}_2\text{CF}_3$	293 K (u.v.)	48	$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$	5

not possible to identify the C=C mode in the i.r. spectra of these species; this is unfortunate since if a noble-gas configuration is achieved by four-electron donation from the one acetylene this should lead to very low values for the C=C stretching frequency. The i.r. spectra of many of the bis(alkyne) complexes show two bands in the C=C stretching region; this may arise from coupling between the two alkynes although many mono-acetylene complexes also show two C=C stretching modes.¹⁴ It is clearly necessary to consider the formulation of complexes formed by elements in Group VI of the transition series in terms of structures which do not formally confer a noble-gas electronic configuration on the metal atom.

The different pattern of reaction when comparing diphenylacetylene with but-2-yne and hexafluorobut-2-yne suggests that steric factors are important. What is apparently a monocarbonyl species was detected during

¹³ E. O. Greaves, C. J. L. Lock, and P. M. Maitlis, *Canad. J. Chem.*, 1968, **46**, 3879.

¹⁴ H. Yamasaki and N. Hagihara, *J. Organometallic Chem.*, 1970, **21**, 431.

¹⁵ W. Hubel, 'Organic Syntheses *via* Metal Carbonyls,' vol. 1, eds. I. Wender and P. Pino, Interscience, New York, 1968, p. 273; J. F. Helling, S. C. Rennison, and A. Merijan, *J. Amer. Chem. Soc.*, 1967, **89**, 7140.

are similar to reactions involving carbonyl(π -cyclopentadienyl)-niobium and -tantalum species in that π -acetylene complexes are formed very readily and cyclisation occurs only rarely.⁶

EXPERIMENTAL

Tricarbonyl(η^5 -cyclopentadienyl)molybdenum halides were prepared by standard methods.¹⁶ The reactions with acetylenes were carried out by methods previously described¹⁷ under conditions given in Table 2, the following separation and purification procedures being employed.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}] + \text{CH}_3\text{C}\equiv\text{CCH}_3$.—The product mixture was sublimed at 313 K and the sublimate crystallised from pentane at 249 K to give pale yellow crystals of duroquinone $\text{C}_4\text{Me}_4(\text{CO})_2$ which was identified by its spectrum (Sadler Index) and melting point.¹⁸ Recrystallisation of the sublimation residue from CH_2Cl_2 -hexane gave yellow crystals of *bis*(but-2-yne)(π -cyclopentadienyl)-molybdenum(II) halides.

¹⁶ T. S. Piper and G. Wilkinson, *J. Inorg. Nuclear Chem.*, 1956, **8**, 104; F. A. Cotton, T. S. Piper, and G. Wilkinson, *ibid.*, 1955, **1**, 165.

¹⁷ J. L. Davidson and D. W. A. Sharp, *J.C.S. Dalton*, 1975, 2283.

¹⁸ H. M. van Dort and H. J. Geursen, *Rec. Trav. chim.*, 1967, **86**, 520.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}] + \text{CF}_3\text{C}\equiv\text{CCF}_3$.—Repeated recrystallisation of the product from CH_2Cl_2 -hexane gave yellow, X = Cl, orange, X = Br, or red-brown, X = I, crystals of $(\pi\text{-cyclopentadienyl})\text{bis}(\text{hexafluorobut-2-yne})\text{-molybdenum(II) halides}$. Very poor yields of the iodide were obtained, mainly insoluble decomposition material being produced. The reactions were followed by i.r. spectroscopy and in the case of the iodide a species giving a single CO stretching mode above 2000 cm^{-1} was detected, but attempted isolation by recrystallisation and chromatography was unsuccessful.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}] + \text{PhC}\equiv\text{CPh}$ (*Low Temperature or U.V. Irradiation*).—Recrystallisation of the products from these reactions from CH_2Cl_2 /hexane gave *carbonyl(π -cyclopentadienyl)(diphenylacetylene)molybdenum(II) halides* as green powdery solids.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{X}]$ or $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})\text{X}] + \text{PhC}\equiv\text{CPh}$.—The products were recrystallised from CH_2Cl_2 -hexane to give red-brown powders $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})_2\text{X}] \cdot \text{CH}_2\text{Cl}_2$, X = Cl, Br, or I. If treated as

described in the literature ⁴ red-brown crystals of $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})(\text{PhC}_2\text{Ph})_2\text{X}]$ were obtained.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CH}_3\text{C}_2\text{CH}_3)_2\text{X}] + \text{CF}_3\text{C}\equiv\text{CCF}_3$ or $\text{MeC}\equiv\text{CMe}$.—The products of these reactions $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{X}]$, and $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{MeC}_2\text{Me})_2\text{X}]$ were isolated by repeated recrystallisation from CH_2Cl_2 -hexane.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}] + \text{CF}_3\text{C}\equiv\text{CCF}_3$ (*U.V. Irradiation*).—The pentane soluble material was removed, centrifuged, and recrystallised from CH_2Cl_2 -hexane to give a mixture of a yellow complex and starting material. Repeated recrystallisation and fractional sublimation (338 K) gave a small quantity of almost pure complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$ (see Discussion) which is slightly more volatile and soluble in organic solvents than $[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Mo}(\text{CF}_3\text{C}_2\text{CF}_3)_2\text{Cl}]$ (*U.V. Irradiation*).—The red crystals were collected and recrystallised from acetone.

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