η^7-Cycloheptatrienylmolybdenum Complexes. Part 1. Formation and Oxidation of Mixed-valence Dimolybdenum Complexes

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Tricarbonyl(η^7-cycloheptatrienyl)molybdenum tetrafluoroborate reacts with halogenotrimethylsilanes to give initially the complexes $[MoX(\eta^7-C_7H_7)(CO)_2]$ (X = Cl, Br, or I). These complexes undergo further reaction to yield the dimolybdenum species $[Mo_2X_3(\eta^7-C_7H_7)_2]$. The tri-iodo-complex has also been obtained by treating $[Mo(\eta^6-C_6H_5Me)(\eta^7-C_7H_7)][BF_4]$ with $SiMe_3I$. Electrochemical studies suggest the existence of cationic complexes $[Mo_2X_3(\eta^7-C_7H_7)_2]^+$, and this has been chemically accomplished with the mild oxidising agents $p-NO_2C_6H_4N_2BF_4$, PhN_2PF_6, and I_2. Moreover, $[Mo(\eta^7-C_7H_7)(CO)_3][BF_4]$ reacts with iodine to give $[Mo_2(\mu-I)_3(\eta^7-C_7H_7)_2][I_3]$.

HALIDE ions react with $[Mo(\eta^7-C_7H_7)(CO)_3][BF_4]$ to afford the synthetically useful complexes $[MoX(\eta^7-C_7H_7)(CO)_2]$ (X = Cl, Br, or I).[1-5] During extensive studies on cycloheptatrienylmolybdenum complexes we have observed [6] an interesting reaction between the salt $[Mo(\eta^7-C_7H_7)(CO)_3][BF_4]$ and organo-silicon or -germanium halides to afford initially the species $[MoX(\eta^7-C_7H_7)(CO)_2]$ and subsequently binuclear molybdenum complexes $[Mo_2X_3(\eta^7-C_7H_7)_2]$. This paper is concerned with some properties of these new complexes and their mode of formation.

RESULTS AND DISCUSSION

In tetrahydrofuran (thf) at 40—50 °C, $[Mo(\eta^7-C_7H_7)(CO)_3][BF_4]$ reacted with $SiXMe_3$ (X = Cl, Br, or I) to give the known[1] complexes $[MoX(\eta^7-C_7H_7)(CO)_2]$.

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[1] R. B. King and M. B. Bisnette, *Inorg. Chem.*, 1964, **3**, 785 and refs. therein.

[2] G. Hoch, R. Panter, and M. L. Ziegler, *Z. Naturforsch.*, 1976, **B31**, 294.

[3] M. L. Ziegler, H. E. Sasse, and B. Nuber, *Z. Naturforsch.*, 1975, **B30**, 22, 26.

[4] T. W. Beall and L. W. Houk, *Inorg. Chem.*, 1972, **11**, 915; 1973, **12**, 1979.

[5] M. D. Rausch, A. K. Ignatowicz, M. R. Churchill, and T. A. O'Brien, *J. Amer. Chem. Soc.*, 1968, **90**, 3242.

[6] M. Bochmann, M. Cooke, M. Green, H. P. Kirsch, F. G. A. Stone, and A. J. Welch, *J.C.S. Chem. Comm.*, 1976, 381.

Evolution of CO was observed and trace amounts of $[Mo(CO)_6]$ were also formed. Possibly $SiMe_3(BF_4)$ is produced in the reaction which may then decompose rapidly to $SiMe_3F$ and thf·BF_3.[7] No attempt was made to identify non-molybdenum-containing products. It has been recently reported[8] that molybdenum hexacarbonyl reacts with $SiMe_2I_2$ to give $[Mo_2I_2(CO)_8]$. Hence it appears that organosilicon halides can act as sources of halide ion in reactions with molybdenum carbonyl species, suggesting that in the reactions described herein process (1) occurs.

TABLE 1

Analytical (%) [a] and spectroscopic data for the complexes $[MoX(\eta^7\text{-}C_7H_7)(CO)_2]$

X	M.p.[b] (θ_c/°C)	C	H	^{1}H n.m.r. (τ) [c]	I.r. bands (cm^{-1}) [d]
Cl	*ca.* 185	37.9 (38.8)	2.8 (2.5)	4.55	3 040w; 2 019vs, 1 971s [ν(CO)]; 1 527w, 1 485w (sh), 1 478m, 1 430m, 1 384vw, 1 260w, 1 248w, 1 166w, 940vw, 892vw, 867m, 854m, 797s, 698w, 550s, 509m, 492s, 465m, 413s, 399s, 356w, 331m, 291m (sh), 286s, 270vs [ν(MoCl)]
Br [e]	*ca.* 178	33.2 (33.5)	2.3 (2.2)	4.54	3 040w; 2 020vs, 1 972s [ν(CO)]; 1 528vw, 1 485w (sh), 1 479m, 1 431m, 1 387vw, 1 263w, 1 247m, 1 166vw, 940w, 892vw, 867m, 854m, 798s, 548s, 508m, 491s, 466m, 413s, 399s, 355vw, 328m, 295s, 288s, 196s [ν(MoBr)]
I	*ca.* 180	29.0 (29.2)	1.9 (1.9)	4.48	3 045w; 2 017vs, 1 969s [ν(CO)]; 1 496vw, 1 483w (sh), 1 478m, 1 435m, 1 383w, 1 366vw, 1 262w, 1 252w, 1 244vw, 1 184w, 1 171w, 982w, 959m, 934m, 894w, 863w, 852m, 795s (sh), 791s, 698w, 557s, 509m, 494s, 464m, 418s, 328m, 325m, 292s (sh), 287s, 165m [ν(MoI)]

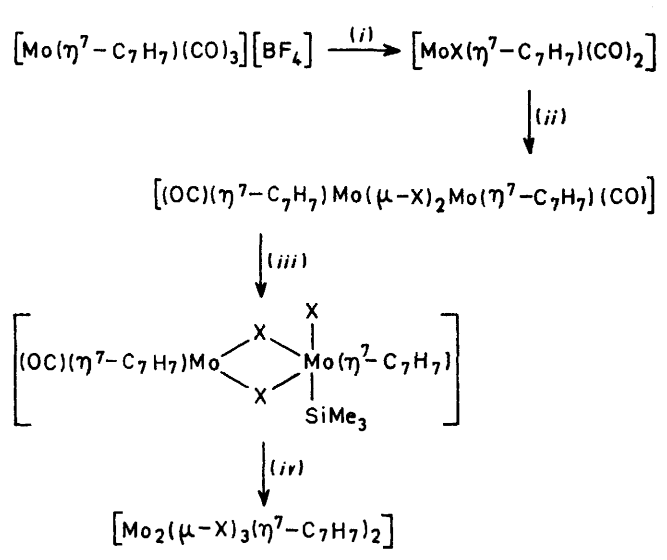
[a] Calculated values are given in parentheses. [b] With decomposition. [c] Measured in $CDCl_3$ on a Varian HA100 spectrometer. [d] Nujol and hexachlorobutadiene mulls, except for ν(CO) which were measured in CH_2Cl_2. [e] Found: Br, 24.2. Calc.: 24.7%.

$$[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4] + SiXMe_3 \longrightarrow [MoX(\eta^7\text{-}C_7H_7)(CO)_2] + CO + SiMe_3F + \text{thf}\cdot BF_3 \quad (1)$$

Spectroscopic data for the complexes $[MoX(\eta^7\text{-}C_7H_7)(CO)_2]$ are given in Table 1 since they have not been reported previously. The mass spectra of the three complexes showed parent ions; however, additional peaks occurred in the spectra corresponding to species $[Mo_2X_3(\eta\text{-}C_7H_7)_2]^+$ (see below) and are presumably ions formed by recombination reactions in the spectrometer.

Treatment of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$, $[MoX(\eta^7\text{-}C_7H_7)(CO)_2]$, or $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)][BF_4]$ with an excess of halogenotrimethylsilane in refluxing thf afforded dimolybdenum complexes $[Mo_2(\mu\text{-}X)_3(\eta^7\text{-}C_7H_7)_2]$. A qualitative estimate of reaction times suggests that the rate of formation of the trihalogeno-complexes follows the order of Mo–X bond strength, *viz.* Mo–Cl > Mo–Br > Mo–I. The chloro-complex has been prepared previously by treating $[Mo_2(\mu\text{-}OMe)_3(\eta^7\text{-}C_7H_7)_2]$ with hydrogen chloride.[9] The complexes were characterised by analysis and mass spectrometry (Table 2), and by i.r. spectroscopy (Table 3).

A plausible mode of formation is indicated in the Scheme, and is related to that proposed[10] for the formation of the tri-μ-chloro-bridged mixed-valence diruthenium complex $[Ru_2(\mu\text{-}Cl)_3(SnCl_3)(CO)_5]$ from the reaction of $[Ru_3(CO)_{12}]$ with $SnCl_4$. We have observed that if the halides $[MoX(\eta^7\text{-}C_7H_7)(CO)_2]$ are heated in thf there is loss of CO and a very reactive complex is produced which could not be characterised, but which may be a halogen-bridged dimeric species able to undergo an oxidative-addition reaction with a trimethylsilicon halide as shown. Loss of the trimethylsilyl group could be followed by intramolecular attack of the terminal halide group on the other molybdenum atom, with concomitant displacement of CO. Unfortunately it was not possible to establish the fate of the trimethylsilyl groups in these reactions.



SCHEME (*i*) +SiXMe$_3$, −SiMe$_3$(BF$_4$), −CO; (*ii*) heat, −CO; (*iii*) SiXMe$_3$; (*iv*) −SiMe$_3$·, −CO

However, no di-molybdenum compounds could be obtained from reactions of KI, MeI, or CCl_4 with $[MoX(\eta^7\text{-}C_7H_7)(CO)_2]$ under similar conditions of reflux. In contrast, $SiMe_2Cl_2$ and $GeMe_3Br$ reacted with $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ to afford the corresponding bridged species.

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[7] G. R. John and L. A. P. Kane-Maguire, *J.C.S. Chem. Comm.*, 1975, 481.

[8] G. Schmid, R. Boese, and E. Welz, *Chem. Ber.*, 1975, **108**, 260.

[9] E. F. Ashworth, M. L. H. Green, and J. Knight, *J.C.S. Chem. Comm.*, 1974, 5.

[10] R. K. Pomeroy, M. Elder, D. Hall, and W. A. G. Graham, *Chem. Comm.*, 1969, 381.

Mixed-halogen triply-bridged complexes $[Mo_2(\mu\text{-}X)_2(\mu\text{-}X')(\eta^7\text{-}C_7H_7)_2]$ have also been prepared (Tables 2 and 3). Thus $SiMe_3Cl$ reacts with $[MoI(\eta^7\text{-}C_7H_7)(CO)_2]$ to give *$[Mo_2(\mu\text{-}Cl)(\mu\text{-}I)_2(\mu^7\text{-}C_7H_7)_2]$*.

TABLE 2

Analytical data [a] for the dimolybdenum complexes

Complex	Colour	Analysis (%) C	H	Halogen	M [b]
$[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2]$ (1)	Green	34.9 (35.0)	3.1 (2.9)		483
$[Mo_2(\mu\text{-}Br)_3(\eta^7\text{-}C_7H_7)_2]$ (2)	Dark green	27.3 (27.4)	2.4 (2.3)	37.3 (39.1)	615
$[Mo_2(\mu\text{-}I)_3(\eta^7\text{-}C_7H_7)_2]$ (3)	Black-brown	22.2 (22.3)	1.9 (1.9)	48.4 (50.4)	759
$[Mo_2(\mu\text{-}Br)(\mu\text{-}Cl)_2(\eta^7\text{-}C_7H_7)_2]$ (4)	Dark green	32.7 (32.0)	2.7 (2.7)		527
$[Mo_2(\mu\text{-}Br)_2(\mu\text{-}Cl)(\eta^7\text{-}C_7H_7)_2]$ (5)	Dark green	30.3 (29.5)	2.7 (2.5)	28.3 (28.1) [c]	571
$[Mo_2(\mu\text{-}Cl)(\mu\text{-}I)_2(\eta^7\text{-}C_7H_7)_2]$ (6)	Dark green	26.6 (25.4)	2.4 (2.1)	35.0 (38.3) [d]	667
$[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2][BF_4]$ (7)	Pale green	30.0 (29.6)	2.5 (2.5)	18.4 (18.6)	
$[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2][PF_6]$ (8)	Pale green	27.2 (26.7)	2.3 (2.3)		
$[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2][I_3]$ (9)	Dark grey	19.4 (19.5)	1.6 (1.6)	44.0 (44.2)	
$[Mo_2(\mu\text{-}Br)_3(\eta^7\text{-}C_7H_7)_2][BF_4]$ (10)	Ochre	23.7 (24.0)	2.0 (2.0)	34.8 (34.2)	
$[Mo_2(\mu\text{-}Br)_3(\eta^7\text{-}C_7H_7)_2][PF_6]$ (11)	Yellow-ochre	22.7 (22.2)	2.0 (1.9)	28.4 (31.6)	
$[Mo_2(\mu\text{-}Br)_3(\eta^7\text{-}C_7H_7)_2][I_3]$ (12)	Red-brown	17.1 (16.9)	1.4 (1.4)	38.5 (38.3) [d]	
$[Mo_2(\mu\text{-}I)_3(\eta^7\text{-}C_7H_7)_2][BF_4]$ (13)	Purple-brown	19.8 (20.0)	1.9 (1.7)	45.7 (45.2)	
$[Mo_2(\mu\text{-}I)_3(\eta^7\text{-}C_7H_7)_2][PF_6]$ (14)	Purple-brown	19.2 (18.7)	1.8 (1.6)	43.0 (42.3)	
$[Mo_2(\mu\text{-}I)_3(\eta^7\text{-}C_7H_7)_2][I_3]$ (15)	Dark brown	15.0 (14.8)	1.4 (1.2)	67.1 (69.5)	
$[Mo_2(\mu\text{-}Br)(\mu\text{-}Cl)_2(\eta^7\text{-}C_7H_7)_2][BF_4]$ (16)	Pale green	28.9 (27.5)	2.8 (2.3)		
$[Mo_2(\mu\text{-}Br)_2(\mu\text{-}Cl)(\eta^7\text{-}C_7H_7)_2][BF_4]$ (17)	Yellow-green	27.1 (25.6)	2.7 (2.2)		
$[Mo_2(\mu\text{-}Cl)(\mu\text{-}I)_2(\eta^7\text{-}C_7H_7)_2][BF_4]$ (18)	Rust-red	25.3 (22.4)	2.4 (1.9)		

[a] Calculated values are given in parentheses. [b] Molecular ion; ^{98}Mo, ^{35}Cl, and ^{79}Br isotopes. Mass spectra were determined on an A.E.I. MS902 instrument operating at 70 eV (1 eV ≈ 1.60×10^{-19} J). [c] Br. [d] I.

TABLE 3

Infrared spectra (cm^{-1}) of the dimolybdenum complexes [a,b]

$[Mo_2(\mu\text{-}X)_3(\eta^7\text{-}C_7H_7)_2]$ X = Cl	Br	I	$[Mo_2(\mu\text{-}X)_2(\mu\text{-}X')(\eta^7\text{-}C_7H_7)_2]$ X = Cl, X′ = Br	Br, Cl	I, Cl
3 040w	3 030w	3 030w	3 040w	3 040w	3 030w
1 432m	1 430m	1 430m	1 430m	1 430m	1 430m
1 240m	1 240vw	1 240w	1 245w	1 243w	1 260w
1 176m	1 170w		1 173m	1 170w	1 170w
965m	965m	966m	965s	966s	964m
910vw	923w, br	928w		923w	920w, br
858m	856m	855m	858s	857s	855m
820s	814s	813s	820s	814s	812s
362m	362m,	360m	363m	364m	361m
	356m (sh)				
282w, br			275m (sh)	268m	263m (sh)
261s	190m (sh)	162s	259s [c]	252m [c]	255m (sh)
	183s				248m [c]
115w, br	125w,	113m			
	122w	107m			
97w		69w			

[a] Recorded on a Perkin-Elmer 225 grating spectrophotometer using Nujol and hexachlorobutadiene mulls and NaCl plates (700—4 000 cm^{-1}), or CsI-supported Polythene discs (200—700 cm^{-1}). A Grubb–Parsons I.R.I.S. interferometer, Nujol–vaseline mulls, and high-density Polythene cells were used for Fourier-transform spectra (60—400 cm^{-1}) measured to ±1 cm^{-1} [b] Bands from 162 to 282 cm^{-1} are assigned to ν(M–X). [c] Limit of measurement, 200 cm^{-1}.

In the mass spectra of the mixed halogen bridge complexes, ions are observed consistent with halide ligand exchange. However, i.r. data in the metal-halogen stretching region show little evidence for these compounds being formed as mixtures. Thus for example, in the spectra of (4) and (5) there are no bands attributable to $[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2]$ (1). However, in the spectra of (16), (17) and (18) there is some evidence for the presence of $[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2][BF_4]$ (7), and this may account for analyses for these species being somewhat outside the acceptable limits. Hence the existence in the mass spectra of ions corresponding to halide bridge scrambling is probably caused by recombination reactions within the mass spectrometer.

It is reasonable to propose that the dimolybdenum complexes are mixed-valence compounds and that the metal ions differ by one electron in their configurations. ESCA studies confirm the presence of two distinct oxidation states for the molybdenum atoms,[11] and cyclic voltammetric measurements show that the species readily undergo oxidation (Table 4). The compounds were not reduced to a potential of −1.5 V, there thus

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[11] G. C. Allen, M. Green, H. P. Kirsch, B. J. Lee, and F. G. A. Stone, *J.C.S. Chem. Comm.*, 1976, 794.

being no evidence for mono-anions $[Mo_2(\mu\text{-}X)_3(\eta^7\text{-}C_7H_7)_2]^-$ analogous to the species $[M_2(\mu\text{-}X)_3(CO)_6]^{3-}$ (M = Cr, Mo, or W).[12-14]

The trend in oxidation potentials (E_p), I > Br > Cl, may be explained if it is assumed that the electron is removed from an anti-bonding orbital. This would lead to a decrease in the metal–metal distance, but single crystal *X*-ray diffraction studies are required to establish this point. In accord with the electrochemical studies, the species $[Mo_2(\mu\text{-}X)_3(\eta^7\text{-}C_7H_7)_2]$ are readily oxidised with diazonium salts or iodine, the monocations so produced being isolated as BF_4^-, PF_6^-, or I_3^- salts (Table 2). Although these salts are presumably diamagnetic, n.m.r. spectra could not be obtained because of low solubility. Infrared spectral bands are listed in Table 5.

TABLE 4

Electrochemical data [a] for $[Mo_2(\mu\text{-}X)_3(\eta^7\text{-}C_7H_7)_2]^z$

X	z	E_p [b]/V	$(E_p)_c - (E_p)_a$ [c]/mV
Cl	0	−0.15	125
Cl [d]	+1	−0.15	140
Br	0	−0.12	135
Br [e]	+1	−0.13	140
I [f]	0	−0.11	135

[a] From cyclic voltammetry in CH_2Cl_2 at a stationary platinum-wire electrode using a Beckmann Electroscan 30 instrument with $[NEt_4][ClO_4]$ (0.05 mol dm^{-3}) as base electrolyte. [b] *versus* the saturated calomel electrode (1 mol dm^{-3} in LiCl), ±10 mV [c] For the reversible one-electron oxidation of $[Ni\{S_2C_2(CN)_2\}_2]^{2-}$: $(E_p)_c - (E_p)_a$ = 150 mV. [d] $[BF_4]^-$ Anion. [e] $[PF_6]^-$ Anion. [f] $z = +1$ was not measured as the cations decompose.

TABLE 5

Infrared spectral bands (cm^{-1}) for the cationic dimolybdenum complexes [a,b]

Complex	Bridging ligands	Anion	
(7)	Cl	$[BF_4]^-$	3 070m, 1 436m, 1 291w, 1 254w, 1 182w, 1 098s, 1 075s (sh), 1 063s, 968m, 891vw, 858m, 850m, 817s, 663w, 527w, 357w, br, 335w, 330w, 295vs,[c] 279s,[c] 106m, br
(8)	Cl	$[PF_6]^-$	3 075m, 1 437m, 1 254vw, 1 186w, 970m, 870s, 830vs, 810s, 557s, 538w (sh), 359w, 292s,[c] 278m [c]
(9)	Cl	$[I_3]^-$	3 030m, 1 432m, 1 242m, 1 170w, 966vw, 854w, 807s, 534vw, br, 362vw, 305m,[c] 283m,[c] 156w, br, 127vs, br, 106vs, br
(10)	Br	$[BF_4]^-$	3 070m, 1 437m, 1 317w, 1 290w, 1 256m, 1 098s, 1 060vs, 968m, 935w, br, 890w, 860m, 817s, 743w, 662w, 634w, 522m, 352w, 335vw, 301w, 249w, 216vs,[c] 204s,[c] 126m, 95m, br
(11)	Br	$[PF_6]^-$	3 080m, 1 439m, 1 259m, 970w, 882m (sh), 868m (sh), 835vs, 816s, 662w, br, 636w, br, 558s, 536w, 352w, 213m,[c] 202w [c]
(12)	Br	$[I_3]^-$	3 030w, 1 433m, 1 259m, 969m, 915w, 850w, 808s, 631w, br, 533vw, 351w, 222m,[c] 207m,[c] 133vs, 126vs
(13)	I	$[BF_4]^-$	3 070m, 1 435m, 1 285vw, 1 260vw, 1 098s, 1 058vs, 1 040s, 972m, br, 850m, br, 814s, 670w, br, 646w, 522w, 354w, br, 345w, br, 190vw, br,[c] 171vw,[c] 134m, br
(14)	I	$[PF_6]^-$	3 080vw, 1 435m, 970m, br, 880m (sh), 830vs, 813s, 664w, br, 636w, br, 558s, 534w, 352w, br, 344w, br
(15)	I	$[I_3]^-$	3 025m, 1 433m, 965w, 850w, 804s, 667w, br, 637w, br, 532vw, 342w, br, 190w, br,[c] 184vw, 172w,[c] 134vs, 110m
(16)	Br, 2Cl	$[BF_4]^-$	3 069m, 1 434m, 1 288w, 1 252w, 1 180w, 1 092vs, 1 051vs, br, 966m, 891w, 857m, 848m, 812vs, 663w, 633w, br, 522m, 355w, br, 294m,[c] 279w,[c] 214w [c]
(17)	2Br, Cl	$[BF_4]^-$	3 072w, 1 435m, 1 286w, 1 257m, 1 093s, 1 056vs, 1 045s (sh), 972m (sh), 963m, 888vw, 855m (sh), 846m, 812vs, 662w, br, 636w, br, 522m, 472w, br, 353w, br, 293m, br,[c] 270w,[c] 214m [c]
(18)	Cl, 2I	$[BF_4]^-$	3 070w, 1 439m, 1 260w, 1 098s, 1 058vs, 1 044s (sh), 966w, 814s, 664w, 523m, 355w, br, 292m,[c] 279w (sh) [c]

[a] See Table 3, footnote *a*. [b] See Table 2. [c] Metal–halogen stretch.

The complexes (1)—(18) are thermally stable up to 250 °C. However, with the intensely coloured complexes, for example (3) and (15), observation of colour changes accompanying any decomposition would be difficult to note. The neutral complexes (1)—(6) are poorly soluble in non-polar and in polar organic solvents; however, the salts (7)—(18) are more soluble. As solids, with the exception of (6), all the complexes appear to be indefinitely stable in air, but in solution they are all oxidised slowly over periods of several hours with the cations being the more stable.

EXPERIMENTAL

Solvents were dried and distilled under nitrogen, and all the operations were conducted in an atmosphere of dry oxygen-free nitrogen. Analytical data are given in Tables 1 and 2. The complex $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ was prepared as described elsewhere.[15] Chlorotrimethysilane and other Group 4 halides were distilled before use.

Synthesis of the Complexes $[MoX(\eta^7\text{-}C_7H_7)(CO)_2]$ (X = Cl, Br, *or* I).—(*a*) $[MoCl(\eta^7\text{-}C_7H_7)(CO)_2]$. The salt $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (0.5 g, 1.40 mmol) and $SiMe_3Cl$ (0.18 g, 1.68 mmol) were stirred (30 min) in thf (5 cm^3) at 50 °C. Trace amounts of $[Mo(CO)_6]$, identified by i.r. spectroscopy, were sublimed out of the mixture after removal of solvent. The residue was extracted with CH_2Cl_2 and filtered. The filtrate was taken to dryness and the product was washed with light petroleum (b.p. 30—40 °C) and diethyl ether. The dark green product (Table 1) was obtained (200 mg) in 51% yield. The complex (1.6 g, 69%) was also prepared by

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[12] J. F. White and M. F. Farona, *J. Organometallic Chem.*, 1972, **37**, 119.

[13] B. G. Albano, G. Ciani, and M. Manessero, *J. Organometallic Chem.*, 1970, **25**, C55.

[14] W. Hieber, K. Englert, and K. Rieger, *Z. anorg. Chem.*, 1959, **300**, 295.

[15] R. B. King, 'Organometallic Synthesis,' Academic Press, New York, 1965, p. 141.

treating $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (3.0 g, 8.4 mmol) in acetone (15 cm^3) with anhydrous LiCl (0.356 g, 8.4 mmol) for 5 min.

(*b*) $[MoBr(\eta^7\text{-}C_7H_7)(CO)_2]$. The salt $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (1.5 g, 4.2 mmol) and $SiMe_3Br$ (0.8 g, 5.2 mmol) were stirred (10 min) in thf (10 cm^3) at 50 °C. Following removal of trace amounts of $[Mo(CO)_6]$, the green-black product (0.95 g, 70%) was isolated. The complex (1.9 g, 90%) was also prepared from $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (2.35 g, 6.5 mmol) and anhydrous LiBr (0.57 g, 6.5 mmol) in acetone (20 cm^3).

(*c*) $[MoI(\eta^7\text{-}C_7H_7)(CO)_2]$. Similarly, reaction (1 h, 50 °C) of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (1.0 g, 2.8 mmol) with $SiMe_3I$ (1.64 g, 8.2 mmol) in thf (10 cm^3) gave the product (0.70 g, 66%).

Synthesis of Tri-μ-halogeno-bis[(η⁷-cycloheptatrienyl)molybdenum] Complexes $[Mo_2X_3(\eta^7\text{-}C_7H_7)_2]$ (X = Cl, Br, *or* I).—(*a*) *Trichloro-complexes*. To a suspension of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (2.0 g, 5.6 mmol) in thf (20 cm^3) was added $SiMe_3Cl$ (1.5 g, 13.8 mmol), and the mixture was stirred and heated under reflux for 14 h. After filtration and drying *in vacuo* a green *solid* (1) (0.9 g, 67%) was obtained. This product was also obtained using $SiMe_2Cl_2$ under the same conditions.

(*b*) *Tribromo-complex*. To a suspension of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (0.5 g, 1.4 mmol) in thf (10 cm^3) was added $SiMe_3Br$ (0.37 g, 2.4 mmol). The mixture was heated under reflux for 14 h, and after filtration and drying the *complex* (2) (0.28 g, 65%) was obtained. Complex (2) (0.4 g, 61%) was also obtained from $GeMe_3Br$ (2.0 g, 10 mmol) and $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (1.5 g, 2.1 mmol) in thf (10 cm^3).

(*c*) *Tri-iodo-complex*. Treatment of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (1.0 g, 2.8 mmol) with $SiMe_3I$ (1.27 g, 6.3 mmol) in thf (10 cm^3) afforded, after 14 h reflux, *solid* (3) (0.63 g, 60%). Alternatively, reaction of $[Mo(\eta^6\text{-}C_6H_5Me)(\eta^7\text{-}C_7H_7)][BF_4]$ (0.42 g, 1.13 mmol) with $SiMe_3I$ (0.50 g, 2.5 mmol) in refluxing (7 h) thf (10 cm^3) gave (3) in 66% (0.28 g) yield.

Synthesis of the Mixed Tri-μ-halogeno-dimolybdenum Complexes.—(*a*) $[Mo_2(\mu\text{-}Br)(\mu\text{-}Cl)_2(\eta^7\text{-}C_7H_7)_2]$. A thf (10 cm^3) solution of $[MoCl(\eta^7\text{-}C_7H_7)(CO)_2]$ (0.5 g, 1.8 mmol) was treated with $SiBrMe_3$ (0.13 g, 0.81 mmol). The mixture was heated under reflux for 43 h, and, after filtration and drying under high vacuum, *solid* (4) (0.32 g, 75%) was obtained.

(*b*) $[Mo_2(\mu\text{-}Br)_2(\mu\text{-}Cl)(\eta^7\text{-}C_7H_7)_2]$. Similarly, $[MoBr(\eta^7\text{-}C_7H_7)(CO)_2]$ (0.5 g, 1.55 mmol) with $SiMe_3Cl$ (76 mg, 0.71 mmol) gave, after refluxing in thf (10 cm^3) for 5 h, dark green *solid* (5) (0.32 g, 79%).

(*c*) $[Mo_2(\mu\text{-}Cl)(\mu\text{-}I)_2(\eta^7\text{-}C_7H_7)_2]$. As above, $[MoI(\eta^7\text{-}C_7H_7)(CO)_2]$ (0.5 g, 1.46 mmol) with $SiMe_3Cl$ (80 mg, 0.73 mmol) gave *solid* (6) (0.58 g, 60%) after reflux (16 h) in thf (10 cm^3) but the complex was not obtained pure.

Preparation of the Cationic Complexes (7)—(18).—Treatment of a suspension of $[Mo_2(\mu\text{-}Cl)_3(\eta^7\text{-}C_7H_7)_2]$ (0.1 g, 0.21 mmol) in thf (10 cm^3) with $p\text{-}NO_2C_6H_4N_2BF_4$ (50 mg, 0.21 mmol) for 0.5 h at room temperature gave, after filtration and drying *in vacuo*, light green *solid* (7) (0.1 g, 85%).

The other salts were prepared similarly using quantities of reactants as follows: (8) (125 mg, 48%) from (1) (0.2 g, 0.42 mmol) and PhN_2PF_6 (0.3 g, 1.2 mmol) in thf (20 cm^3) for 10 min; (9) (90 mg, 50%) from (1) (0.1 g, 0.21 mmol) and I_2 (90 mg, 0.36 mmol) in thf (10 cm^3) for 14 h; (10) (0.14 g, 82%) from (2) (0.15 g, 0.24 mmol) and $p\text{-}NO_2C_6H_4N_2BF_4$ (58 mg, 0.24 mmol) in thf (5 cm^2) for 15 min; (11) (0.115 g, 62%) from (2) (0.15 g, 0.24 mmol) and PhN_2PF_6 (67 mg, 0.27 mmol) in thf (10 cm^3) for 25 min; (12) (90 mg, 56%) from (2) (0.1 g 0.16 mmol) and I_2 (69 mg, 0.27 mmol) in thf (10 cm^3) for 14 h; (13) (0.1 g, 45%) from (3) (0.2 g, 0.26 mmol) and $p\text{-}NO_2C_6H_4N_2BF_4$ (63 mg, 0.26 mmol) in thf (10 cm^3) for 15 min; (14) (0.29 g, 81%) from (3) (0.3 g, 0.40 mmol) and PhN_2PF_6 (0.1 g, 0.40 mmol) in thf (20 cm^3) for 15 min; (15) (0.215 g, 45%) from (3) (0.32 g, 0.42 mmol) and I_2 (0.16 g, 0.64 mmol) in thf (10 cm^3) for 15 h; (16) (87 mg, 81%) from (4) (92 mg, 0.17 mmol) and $p\text{-}NO_2C_6H_4N_2BF_4$ (42 mg, 0.18 mmol) in thf (5 cm^3) for 2 h; (17) (60 mg, 65%) from (5) (83 mg, 0.14 mmol) and $p\text{-}NO_2C_6H_4N_2BF_4$ (35 mg, 0.15 mmol) in thf (5 cm^3) for 1 h; and (18) (70 mg, 62%) from (6) (0.1 g, 0.15 mmol) and $p\text{-}NO_2C_6H_4N_2BF_4$ (36 mg, 0.15 mmol) in thf (10 cm^3) for 0.5 h.

Complex (15) was also prepared by treating a thf (10 cm^3) suspension of $[Mo(\eta^7\text{-}C_7H_7)(CO)_3][BF_4]$ (0.5 g, 1.4 mmol) with I_2 (0.53 g, 2.10 mmol) for 42 h. After filtration and drying *in vacuo*, dark brown solid (15) (0.55 g, 69%) was isolated.

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