Di-iodine Oxidation of Molybdenum(0)–η^6-Arene Complexes. New Results on Molybdenum(II) and Tungsten(II) Carbonyl Derivatives; Crystal Structures of $[MI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][M_2I_5(CO)_6]$ (M = Mo or W) and $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$†

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The reactions of molybdenum(0) complexes with I_2 have been investigated under a variety of reaction conditions and stoicheiometry of the reagents, and shown to be more complicated than previously suggested. Although the $[MoI(CO)_3(\eta^6\text{-arene})]^+$ cation is always formed, the counter anion can vary depending on the reaction time and on the molar ratio of the reagents. Some of the isolated compounds were studied by *X*-ray diffractometric methods: $[MoI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][Mo_2I_5(CO)_6]$, (**3**) [monoclinic, space group $P2_1/c$, a = 13.632(2), b = 13.758(2), c = 17.246(3) Å, β = 96.02(2)°, and Z = 4], the new $[Mo_2I_5(CO)_6]^-$ anion has approximately C_{2v} symmetry, the central metal atoms being seven-co-ordinated by three bridging iodides, one terminal iodide and three carbonyl groups; $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$, (**5**) [monoclinic, space group $P2_1/a$, a = 24.013(3), b = 13.681(3), c = 8.797(3) Å, β = 97.86(2)°, and Z = 4]. When the reaction between $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$ and di-iodine was carried out in a 1 : 2 molar ratio, the tri-iodide complex $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3$ was isolated, while the reaction of $[W(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$ with di-iodine in a 1 : 1 molar ratio gave the tungsten(II) derivative $[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$, (**8**) [monoclinic, space group $P2_1/c$, a = 13.602(2), b = 13.720(2), c = 17.204(3) Å, β = 95.99(2)°, and Z = 4]. Compounds (**3**) and (**8**) are isostructural. The problem of the arene orientation in the $[MI(CO)_3(\eta^6\text{-arene})]^+$ cations is discussed.

Arene–carbonyl derivatives of Group 6 metals,[1] $[M(CO)_3(\eta^6\text{-arene})]$ (M = Cr, Mo, or W), have attracted considerable interest in view of their outstanding chemical properties. Four main reaction types have been identified, namely: (*a*) substitution of the carbonyl groups upon u.v. irradiation;[2] (*b*) arene substitution[3d] or exchange;[3a–c] (*c*) ring substitution by both electrophilic[4] and nucleophilic[5] reagents; and (*d*) metal oxidation.[6] Substitution and exchange of the arene ligand were found to be promoted by Lewis bases.[3c] More recently, chemical[7] and electrochemical[8] oxidation of organometallic compounds have been found to promote substitution reactions and, while this work was in progress, a report[9] appeared concerning the I_2-catalysed arene exchange in $[Cr(CO)_3(\eta^6\text{-arene})]$ derivatives.

Concerning (*d*), the oxidation of $[Cr(CO)_3(\eta^6\text{-arene})]$ by I_2 is known[3a] to produce CrI_3, no isolation of carbonyl derivatives of intermediate oxidation states being possible. Presumably due to the higher M–CO bond energies[10] and to the greater size of the central metal atom which favours a co-ordination number higher than six, metal carbonyl derivatives of molybdenum and tungsten in oxidation states higher than zero are expected to be relatively stable and isolable. Indeed, a large number of seven-co-ordinate carbonyl complexes of molybdenum(II) and tungsten(II)[11,12] have been reported. The iodination of molybdenum(0)– and tungsten(0)–η^6-arene derivatives has been reported,[13] and the existence of the $[WI(CO)_3(\eta^6\text{-}C_6Me_6)]^+$ cation was established by *X*-ray diffraction methods. On the other hand, the authors suggested that '*the complex spectra and variable analyses are most probably due to the presence of both iodide and triiodide salts of the cation*' and the stoicheiometry of the reaction could not be established conclusively, mainly due to the low solubility of the products.

In the course of a research programme dealing with the oxidation of $[M(CO)_3(\eta^6\text{-arene})]$ complexes of molybdenum and tungsten and aimed at detecting carbonyl compounds of intermediate oxidation states, which required the use of sub-stoicheiometric amounts of di-iodine, we discovered that I_2 catalyses the carbonylation of tricarbonyl complexes of molybdenum(0) to $[Mo(CO)_6]$.[14] In order to clarify this rather surprising effect which has no equivalent in the chemistry of chromium(0)–arene derivatives, we decided to reinvestigate the oxidation of molybdenum(0) complexes by di-iodine, which had been the subject of pioneering work by Snow *et al.*[13] We have thus isolated new molybdenum(II)–η^6-arene complexes and report the crystal and molecular structures of some of them, together with their chemical properties.

Experimental

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified nitrogen or argon. Solvents were carefully dried by conventional methods prior to use. The

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† Tricarbonyliodo(η-mesitylene)molybdenum(II) tri-μ-iodo-bis[tricarbonyliodomolybdate(II)], tricarbonyliodo(η-mesitylene)tungsten(II) tri-μ-iodo-bis[tricarbonyliodotungstate(II)], and tricarbonyl(η-hexamethylbenzene)iodomolybdenum(II) tetracarbonyltri-iodomolybdate(II).

Supplementary data available (No. SUP 56615, 6 pp.): thermal parameters, H-atom co-ordinates for compound (**3**). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1986, Issue 1, pp. xvii—xx. Structure factors are available from the editorial office.

Table 1. Analytical data for the $[MI(CO)_3(\eta^6\text{-arene})]^+$ derivatives

Compound	Formula	Analytical data[a] (%) C	H	Other
(1) $[MoI(CO)_3(\eta^6\text{-}C_6H_5Me)][Mo_2I_5(CO)_6]$	$C_{16}H_8I_6Mo_3O_9$	13.6[b] (13.8)	0.5[b] (0.6)	Arene:[c] 6.3 (6.6)
(2) $[MoI(CO)_3(\eta^6\text{-}C_6H_4Me_2\text{-}1,4)][Mo_2I_5(CO)_6]$	$C_{17}H_{10}I_6Mo_3O_9$	14.9[b] (14.5)	0.7[b] (0.7)	
(3) $[MoI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5][Mo_2I_5(CO)_6]$	$C_{18}H_{12}I_6Mo_3O_9$	15.3[b] (15.2)	0.8[b] (0.8)	Arene:[c] 8.6 (8.5)
(4) $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][Mo_2I_5(CO)_6]$	$C_{21}H_{18}I_6Mo_3O_9$	17.5 (17.2)	1.2 (1.2)	
(5) $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$	$C_{19}H_{18}I_4Mo_2O_7$	21.4 (21.6)	1.7 (1.7)	
(6) $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3$	$C_{15}H_{18}I_4MoO_3$	21.3 (21.2)	2.0 (2.1)	
(7) $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]BPh_4$	$C_{39}H_{38}BIMoO_3$	59.2 (59.4)	4.6 (4.9)	
(8) $[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$	$C_{18}H_{12}I_6O_9W_3$	13.5 (12.8)	0.6 (0.7)	

[a] Calculated values in parentheses. [b] Average for several samples from different preparations (standard deviation <0.2). [c] Determined by ^1H n.m.r. spectroscopy, after reaction with CD_3CN, see equation (1), using $[Fe(cp)_2]$ (δ 4.3 p.p.m.) as internal standard in the neat solvent.

instrumentation used was as follows: ^1H n.m.r. (JEOL JNM-PS-100); ^{13}C n.m.r. (Varian XL-100); mass spectra (VG-MM 16 F); and i.r. (Perkin-Elmer 283 or 283 B). Each solution i.r. spectrum in the carbonyl stretching region was calibrated with both CO and water vapour and the wavenumber values are believed to be accurate to within ± 1 cm^{-1}. Magnetic susceptibilities were measured with a magnetic balance equipped for the Faraday method, using $CuSO_4{\cdot}5H_2O$ as calibrant. Gas-volumetric experiments were carried out in a burette equipped with a thermostat. Elemental analyses were by Istituto di Chimica Farmaceutica, Universitá di Pisa, and by Dipartimento di Chimica e Chimica Industriale, Sezione Chimica Analitica, Università di Pisa. Analytical data for the new compounds are collected in Table 1, solution i.r. spectroscopic data in Table 8.

The metal(0) complexes, $[Cr(CO)_3(\eta^6\text{-}C_6H_5Me)]$,[3a] $[Mo(CO)_3(\eta^6\text{-arene})]$ (arene = C_6H_5Me,[15] $C_6H_4Me_2$-1,4,[16] or $C_6H_3Me_3$-1,3,5[16]), $[W(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$,[17] and $[M(CO)_3(MeCN)_3]$ (M = Mo or W),[18] were prepared according to published procedures. The hexamethylbenzene derivative of molybdenum(0) was prepared according to a slightly modified literature[16] procedure. Hexacarbonylmolybdenum (4.87 g, 18.45 mmol) was refluxed in n-heptane (100 cm^3) with hexamethylbenzene (4.03 g, 24.83 mmol) in the presence of MeCN (1 cm^3). After reflux for 48 h the yellow product was collected by filtration from the hot solution, washed with hot n-heptane, and dried *in vacuo* (79% yield). No formation of black powders[16] was noted under these conditions and the product was analytically and spectroscopically pure. The complex $[MoI_2(CO)_3(MeCN)_2]$ was prepared by I_2 oxidation of $[Mo(CO)_3(MeCN)_3]$. In a typical experiment, $[Mo(CO)_3(MeCN)_3]$ (1.09 g, 3.60 mmol) was suspended in n-heptane (30 cm^3) and treated with a solution of I_2 (0.92 g, 3.62 mmol) in the same solvent (100 cm^3) at room temperature. At the end of the addition, a red-brown precipitate of the di-iodo complex was present. The suspension was then stirred for 2 h and the product was recovered by filtration and dried *in vacuo* (82% yield) (Found: C, 16.5; H, 1.1; N, 5.2. Calc. for $C_7H_6I_2MoN_2O_3$: C, 16.3; H, 1.2; N, 5.4%). The i.r. spectrum has bands (toluene solution) at 2 030s, 1 960s, and 1 947 (sh) cm^{-1}, due to the carbonyl stretching vibrations. Two CN stretchings were observed at 2 311w and 2 288w cm^{-1} in the same solvent.

Reaction of $[Mo(CO)_3(\eta^6\text{-arene})]$ (*arene* = C_6H_5Me, $C_6H_4Me_2$-1,4, *or* $C_6H_3Me_3$-1,3,5) *with* I_2. *Preparation of* $[MoI(CO)_3(\eta^6\text{-arene})][Mo_2I_5(CO)_6]$ [*arene* = C_6H_5Me (**1**), $C_6H_4Me_2$-1,4 (**2**), *or* $C_6H_3Me_3$-1,3,5 (**3**)].—A solution of I_2 (0.56 g, 2.21 mmol) in toluene (25 cm^3) was added dropwise within 20 min at room temperature to a well stirred solution of $[Mo(CO)_3(\eta^6\text{-}C_6H_5Me)]$ (0.59 g, 2.17 mmol) in the same solvent (25 cm^3). At the end of the addition, the brown precipitate was quickly filtered off, washed with toluene (10 cm^3), then with n-pentane (2 × 10 cm^3), and finally dried *in vacuo* to yield 0.84 g (83%) of complex (**1**). The mother-liquor showed no i.r. carbonyl bands of appreciable intensity.

Using a procedure similar to that described above for the toluene derivative, $[Mo(CO)_3(\eta^6\text{-}C_6H_4Me_2\text{-}1,4)]$ and $[Mo(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$ were treated with an equimolar amount of I_2 in the corresponding arene as solvent. Brown complex (**2**) (88% yield) and red-brown (**3**) (87% yield) were obtained respectively.

A single crystal of compound (**3**) was obtained by slowly adding, without stirring, a solution of I_2 (60 mg, 0.24 mmol) in toluene (about 80 cm^3) to a solution of $[Mo(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$ (72 mg, 0.24 mmol) in the same solvent (100 cm^3). The resulting clear solution was left overnight at 5 °C to give well formed crystals, whose spectroscopic properties were identical to those of the specimen prepared as described above.

Reaction of $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$ *with* I_2 (1:1 *molar ratio*).—(*a*) *Preparation of* $[\{[MoI_2(CO)_3]_2C_6Me_6\}_n]$. The molybdenum(0) complex (0.47 g, 1.37 mmol) was stirred with I_2 (0.36 g, 1.42 mmol) in toluene (25 cm^3) at room temperature for a few minutes. The red precipitate was promptly filtered off, washed with toluene, then with n-pentane, and finally dried under reduced pressure (78% yield) (Found: C, 21.3; H, 1.9. Calc. for $C_{18}H_{18}I_4Mo_2O_6$: C, 21.0; H, 1.8%). The i.r. spectrum (Nujol) has bands at 2 063s, 2 014s, 2 006s, 1 997s, 1 944s, 1 897m—s, 1 280w, 1 065w, 1 015vw, 990w, 580m, 560m, 510m—s, 460m, 425w, and 400vw cm^{-1}. An i.r. spectrum in dichloromethane in the carbonyl stretching region was identical to that of $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][Mo_2I_5(CO)_6]$, see next paragraph.

(*b*) *Preparation of* $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][Mo_2I_5(CO)_6]$, (**4**). For the preparation of this compound, the following procedure was found to be best. The molybdenum(0) complex (0.44 g, 1.29 mmol) and I_2 (0.33 g, 1.29 mmol) were dissolved in dichloromethane (25 cm^3) and the solution was stirred for about 15 min at room temperature. The reaction mixture was then filtered and the filtrate was cooled to about −30 °C. Dark crystals of the product separated out, and were collected by filtration, washed with n-pentane, and dried *in vacuo* (9% yield). The i.r. spectrum (Nujol) has bands at 2 065m, 2 028m, 2 005s, 1 956s, *ca.* 1 940s, 1 924s, 1 280w, 1 265w, 1 070w, 1 020vw, 995w, 560m, 510m, 460m, 440w, 430w, and 405w cm^{-1}.

(*c*) *Preparation of* $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$, (**5**). The molybdenum(0) complex (0.20 g, 0.58 mmol) was stirred at room temperature with I_2 (0.15 g, 0.59 mmol) in dichloromethane (50 cm^3) for about 3 h. By this time a fine dark precipitate was present, while the solution had an i.r. spectrum in the carbonyl stretching region in agreement with the presence of compound (**5**). The solution was filtered, concentrated to about half its original volume, and cooled to about −30 °C. The

Table 2. Fractional atomic co-ordinates of $[MoI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][Mo_2I_5(CO)_6]$, (**3**), with estimated standard deviations (e.s.d.s) in parentheses referring to the last digit

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	0.345 8(2)	−0.073 3(2)	0.117 2(2)	C(1)	0.467 2(26)	−0.153 0(22)	0.155 7(21)
Mo(2)	0.054 5(2)	0.425 9(2)	0.178 7(2)	C(2)	0.456 8(28)	0.025 5(24)	0.130 2(22)
Mo(3)	0.292 0(2)	0.429 1(2)	0.069 9(2)	C(3)	0.359 8(31)	−0.151 0(27)	0.023 7(25)
I(1)	0.323 6(2)	0.057 4(2)	−0.010 4(2)	C(4)	−0.062 3(25)	0.508 2(22)	0.156 7(20)
I(2)	0.130 7(2)	0.566 6(2)	0.073 7(1)	C(5)	−0.057 6(26)	0.338 9(22)	0.144 5(22)
I(3)	0.122 0(2)	0.302 6(2)	0.059 9(1)	C(6)	0.028 1(27)	0.345 0(23)	0.269 9(22)
I(4)	0.260 7(2)	0.403 1(1)	0.232 4(1)	C(7)	0.316 6(26)	0.515 4(25)	−0.019 6(23)
I(5)	0.050 9(2)	0.563 1(2)	0.301 8(1)	C(8)	0.303 1(28)	0.343 3(23)	−0.024 2(22)
I(6)	0.439 8(2)	0.565 2(2)	0.124 1(2)	C(9)	0.411 1(31)	0.347 9(28)	0.095 2(25)
O(1)	0.528 3(20)	−0.206 4(17)	0.174 7(15)	C(10)	0.273 4(16)	−0.158 0(12)	0.217 1(12)
O(2)	0.520 2(22)	0.076 4(19)	0.147 4(17)	C(11)	0.299 5(16)	−0.065 3(12)	0.244 7(12)
O(3)	0.358 1(21)	−0.203 2(19)	−0.028 7(18)	C(12)	0.261 1(16)	0.016 6(12)	0.204 6(12)
O(4)	−0.129 1(18)	0.556 8(15)	0.138 0(14)	C(13)	0.196 5(16)	0.005 8(12)	0.136 9(12)
O(5)	−0.123 8(20)	0.292 8(17)	0.115 9(16)	C(14)	0.170 4(16)	−0.086 9(12)	0.109 3(12)
O(6)	0.028 0(20)	0.296 2(18)	0.319 0(16)	C(15)	0.203 9(16)	−0.168 8(12)	0.149 3(12)
O(7)	0.322 0(18)	0.566 1(18)	−0.068 9(15)	C(16)	0.315 5(24)	−0.243 1(21)	0.263 6(19)
O(8)	0.307 8(18)	0.301 3(16)	−0.074 7(15)	C(17)	0.283 0(26)	0.126 3(21)	0.233 3(21)
O(9)	0.478 4(19)	0.302 4(17)	0.113 2(15)	C(18)	0.100 7(30)	−0.106 4(28)	0.034 9(24)

Table 3. Fractional atomic co-ordinates of $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$, (**5**), with e.s.d.s in parentheses

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mo(1)	0.163 87(5)	0.263 02(8)	0.047 9(1)	C(4)	0.335 7(6)	0.138 4(11)	0.443 9(16)
Mo(2)	0.373 36(5)	0.251 24(8)	0.555 7(1)	C(5)	0.223 9(6)	0.342 3(11)	−0.023 6(17)
I(1)*	0.180 08(9)	0.423 4(2)	0.253 3(3)	C(6)*	0.186 5(11)	0.211 7(18)	0.256 6(13)
I(2)	0.458 40(5)	0.396 64(9)	0.628 4(2)	C(7)	0.221 2(6)	0.163 7(10)	0.0269(16)
I(3)	0.459 29(5)	0.110 63(9)	0.534 5(1)	C(8)	0.068 9(4)	0.215 1(6)	0.061 7(8)
I(4)	0.366 71(5)	0.296 84(9)	0.237 0(1)	C(9)	0.090 8(4)	0.150 2(6)	−0.037 1(8)
O(1)	0.421 5(6)	0.200 7(10)	0.892 2(17)	C(10)	0.111 4(4)	0.185 3(6)	−0.167 4(8)
O(2)	0.268 3(5)	0.212 7(8)	0.713 5(14)	C(11)	0.110 2(4)	0.285 3(6)	−0.198 9(8)
O(3)	0.306 2(5)	0.451 0(10)	0.529 3(15)	C(12)	0.088 3(4)	0.350 2(6)	−0.100 0(8)
O(4)	0.311 1(5)	0.072 2(8)	0.384 3(12)	C(13)	0.067 6(4)	0.315 1(6)	0.030 3(8)
O(5)	0.256 8(5)	0.387 0(8)	−0.078 7(13)	C(14)	0.040 5(7)	0.176 9(12)	0.194 7(19)
O(6)*	0.197 6(11)	0.181 4(19)	0.378 8(13)	C(15)	0.093 1(7)	0.040 3(11)	−0.001 5(18)
O(7)	0.254 2(5)	0.103 4(8)	0.010 9(13)	C(16)	0.130 4(6)	0.114 6(11)	−0.287 0(18)
C(1)	0.403 8(8)	0.224 8(13)	0.766 7(23)	C(17)	0.127 7(6)	0.323 2(11)	−0.350 3(18)
C(2)	0.308 7(6)	0.229 1(11)	0.656 5(17)	C(18)	0.091 3(7)	0.463 5(11)	−0.131 0(18)
C(3)	0.332 0(7)	0.375 1(13)	0.535 3(20)	C(19)	0.035 1(7)	0.384 6(11)	0.126 7(19)

* Occupancy factor 0.77. In the alternative orientation, with occupancy factor 0.23, atoms I(1), O(6), and C(6) have the following positions: 0.180 1(3), 0.175 3(7), 0.322 5(8); 0.190(3), 0.438(3), 0.282(8); 0.191(2), 0.371(3), 0.187(7).

resulting red crystalline product was separated by filtration and dried under reduced pressure (19% yield). Its spectroscopic properties were identical to those of the compound, analytically and crystallographically characterized, prepared according to the procedure described below.

Crystals for the *X*-ray diffractometric study were grown by the following procedure. A solution of I_2 (0.042 g, 0.17 mmol) in toluene (35 cm^3) was slowly added to a solution of $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$ (0.050 g, 0.15 mmol) in the same solvent. The resulting clear solution was left overnight at 5 °C to give well formed crystals of complex (**5**). I.r. (Nujol): 2 066s, 2 009s, 1 990s, 1 933s, 1 280w, 1 065w, 1 015vw, 990w, 575w, 560w, 530m, 510m, 495w, 480m, 460w, 420w, and 400vw cm^{-1}.

Reaction of $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$ *with* I_2 *(1:2 molar ratio). Preparation of* $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3$, (**6**).—A solution of I_2 (1.10 g, 4.33 mmol) in toluene (100 cm^3) was treated with $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$ (0.74 g, 2.16 mmol). Upon stirring at room temperature, red-brown crystals quickly formed, which were separated by filtration, washed with toluene (2 × 5 cm^3), then with n-pentane (2 × 5 cm^3), and finally dried *in vacuo*. Yield 1.40 g (76%). The compound was indefinitely stable at room temperature under a dinitrogen atmosphere. I.r. (Nujol): 2 057s, 2 051s, 2 007m, 1 948vs, 1 275w, 1 065w, 1 015vw, 995w, 575w, 560m, 545w, 515m, 465m, 440w, and 420w cm^{-1}.

Metathetical Reactions on $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3$.—*Preparation of* $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]BPh_4$, (**7**).—The tri-iodide derivative (**6**) (0.66 g, 0.78 mmol) was treated with a solution of NBu_4BPh_4 (0.47 g, 0.84 mmol) in dichloromethane (25 cm^3). The resulting solution was immediately filtered and then treated with toluene (40 cm^3). Red crystals of the product formed, which were collected by filtration and washed with CH_2Cl_2 (2 × 10 cm^3). Yield 0.35 g (56%).

Preparation of $[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$, (**8**).—A solution of I_2 (0.064 g, 0.25 mmol) in toluene (25 cm^3) was slowly added to a solution of $[W(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$ (0.095 g, 0.24 mmol) in the same solvent (50 cm^3). The formation of a precipitate was observed, but this redissolved within 1 min. The resulting clear solution was left overnight at about −30 °C. The red crystals which formed were decanted, washed with n-pentane, and dried. Yield 25%. The compound has i.r. bands (Nujol) at 2 071s, 2 019vs, 2 001s, 1 947s, 1 931s, 1 926s, 1 911s, 1 520w, 1 300w, 1 155w, 1 030w, 690vw, 650w, 575m, 550m, 530m, 510w—m, 500w—m, 480m, 460w—m, and

Table 4. Fractional atomic co-ordinates of $[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$ (**8**) with e.s.d.s in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
W(1)	0.345 7(6)	−0.071 8(9)	0.116 5(5)	C(1)	0.461 0(75)	−0.163 6(84)	0.136 1(90)
W(2)	0.051 4(5)	0.425 7(10)	0.177 9(5)	C(2)	0.464 1(85)	0.016 4(103)	0.124 9(78)
W(3)	0.292 6(5)	0.428 8(8)	0.069 2(4)	C(3)	0.349 4(122)	−0.159 0(110)	0.024 8(67)
I(1)	0.322 5(13)	0.057 1(15)	−0.010 6(10)	C(4)	−0.059 7(61)	0.520 8(75)	0.142 1(99)
I(2)	0.131 9(9)	0.566 4(14)	0.076 1(7)	C(5)	−0.068 2(87)	0.346 2(96)	0.141 7(83)
I(3)	0.122 9(10)	0.305 9(11)	0.059 1(8)	C(6)	0.024 3(110)	0.335 6(107)	0.264 9(59)
I(4)	0.258 5(10)	0.399 5(9)	0.231 2(9)	C(7)	0.312 9(142)	0.509 7(85)	−0.025 5(62)
I(5)	0.053 7(11)	0.562 8(16)	0.300 6(9)	C(8)	0.311 4(124)	0.349 2(100)	−0.025 0(66)
I(6)	0.436 7(10)	0.568 6(15)	0.126 1(9)	C(9)	0.408 4(69)	0.345 5(104)	0.106 1(86)
O(1)	0.536 2(55)	−0.189 8(72)	0.169 9(68)	C(10)	0.232 5(85)	−0.163 9(71)	0.208 2(65)
O(2)	0.524 4(60)	0.073 0(80)	0.149 6(58)	C(11)	0.281 3(85)	−0.085 4(71)	0.246 6(65)
O(3)	0.359 1(86)	−0.207 4(76)	−0.030 2(52)	C(12)	0.274 7(85)	0.007 2(71)	0.213 0(65)
O(4)	−0.144 1(51)	0.544 9(67)	0.141 0(65)	C(13)	0.219 4(85)	0.021 3(71)	0.140 9(65)
O(5)	−0.124 9(60)	0.281 5(67)	0.134 6(67)	C(14)	0.170 6(85)	−0.057 2(71)	0.102 5(65)
O(6)	0.026 7(84)	0.299 0(83)	0.327 1(47)	C(15)	0.177 2(85)	−0.149 8(71)	0.136 1(65)
O(7)	0.332 6(71)	0.578 0(70)	−0.062 0(50)	C(16)	0.293 9(133)	−0.262 6(79)	0.243 4(98)
O(8)	0.302 5(81)	0.296 3(74)	−0.078 8(50)	C(17)	0.279 1(136)	0.118 3(94)	0.252 6(86)
O(9)	0.483 3(52)	0.312 5(76)	0.109 3(68)	C(18)	0.093 5(101)	−0.076 2(149)	0.025 5(73)

420m cm^{-1}. A crystal from this crop was used for the *X*-ray diffractometric analysis.

Reaction of Complex (**6**) *with* $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$.—The molybdenum(0) complex $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$ (0.027 g, 0.079 mmol) was treated with compound (**6**) (0.083 g, 0.098 mmol) in dichloromethane (25 cm^3) at room temperature. Immediately after mixing the reagents, the bands of (**6**) at 2 067s and 2 011s cm^{-1} originally present in solution were accompanied by new bands at 2 025 (sh), 1 961m, and 1 940 (sh) cm^{-1}. The solution was stirred for about 2 h: during this time the i.r. spectrum changed, while a small amount of a dark precipitate was observed. The final i.r. spectrum (2 067m, 2 010s, and 1 947w cm^{-1}) was that of compound (**5**), $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$, see Table 8.

Collection and Reduction of X-*Ray Data and Structure Determinations*.—$[MoI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][Mo_2I_5(CO)_6]$, (**3**). A crystal of approximate dimensions 0.20 × 0.10 × 0.05 mm protected in a glass capillary was mounted on a computer-controlled Philips PW 1 100 single-crystal diffractometer, equipped with graphite monochromatized Mo-K_α radiation ($\lambda = 0.710\,69$ Å). The lattice parameters were determined at room temperature by a least-squares calculation based on the setting angles of 25 reflections with the 2θ ranging between 17 and 25°.

Crystal data. $C_{18}H_{12}I_6Mo_3O_9$, $M = 1\,421.5$, monoclinic, space group $P2_1/c$ (from systematic extinctions), $a = 13.632(2)$, $b = 13.758(2)$, $c = 17.246(3)$ Å, $\beta = 96.02(2)°$, $U = 3\,216.6$ Å^3, $Z = 4$, $D_c = 2.933$ g cm^{-3}, $\mu = 65.4$ cm^{-1}, $F(000) = 2\,544$.

Intensities were collected up to $2\theta = 40°$, using the ω—2θ scan technique, the scan range being 1.5° and the speed 0.05° s^{-1}. A total of 2 080 reflections ($\pm h,k,l$) were measured, of which, 985, having $I < 3\sigma(I)$, were considered as unobserved and excluded from the refinement. Three standard reflections, measured periodically, showed no apparent variation in intensity. The data were corrected for Lorentz and polarization factors. A semi-empirical absorption correction was applied on the basis of the variation in intensity during azimuthal scans of some reflections, according to the method of North *et al.*[19] The transmission factors were in the range 0.99—0.81. A further absorption correction was applied during the refinement, according to the empirical method of Walker and Stuart.[20] The structure was solved by direct methods and refined by full-matrix least squares with the SHELX 76[21] package of programs. The arene group was constrained to a perfect hexagon (C–C 1.395 Å) and refined as a rigid group. The hydrogen atoms (with the exception of those of the methyl groups) were included in calculated positions (C–H 1.08 Å) with an overall isotropic thermal parameter $U = 0.11$ Å^2. The methyls were refined as rigid groups starting from the staggered position. Anisotropic thermal parameters were assigned to the molybdenum and iodine atoms. The final *R* index was 0.033 for 1 095 observations and 188 parameters $\{R' = [\Sigma w(|F_o| - |F_c|)^2]^{\frac{1}{2}}/(\Sigma wF_o^2)^{\frac{1}{2}} = 0.039, \text{where } w = [\sigma^2(F_o) + 0.0128F_o^2]^{-1}\}$. The fractional atomic co-ordinates are in Table 2, relevant bond distances and angles in Tables 5 (cation) and 6 (anion).

$[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$, (**5**). A tabular crystal with dimensions 0.25 × 0.20 × 0.05 mm protected in a glass capillary was mounted on the diffractometer, as above.

Crystal data. $C_{19}H_{18}I_4Mo_2O_7$, $M = 1\,057.8$, monoclinic, space group $P2_1/a$ (from systematic extinctions), $a = 24.013(3)$, $b = 13.681(3)$, $c = 8.797(3)$ Å, $\beta = 97.86(2)°$, $U = 2\,862.9$ Å^3, $Z = 4$, $D_c = 2.453$ g cm^{-3}, $\mu = 49.1$ cm^{-1}, $F(000) = 1\,936$.

A total of 2 422 independent reflections were measured by the same technique as above, of which 512, having $I < 3\sigma(I)$ were considered as unobserved and excluded from the refinement. Crystal stability was tested as indicated above, and the data were corrected for Lorentz and polarization factors and for absorption.[19,20] The transmission factors were in the range 0.99—0.86. The structure was solved and refined as for compound (**3**). At the end of the isotropic refinement, a Fourier difference map showed a peak at a distance of about 2.8 Å from Mo(1) nearly coinciding with the C(6)–O(6) carbonyl group. This was ascribed to disorder of the co-ordination polyhedron around Mo(1), only the I(1) and the C(6)–O(6) ligands being interchanged, and was verified by refinement in each of the two positions with occupancy factors of $1 - x$ and x, and x and $1 - x$, respectively. Convergence was achieved with $x = 0.23$, *i.e.* the two statistical orientations around the metal are not equally represented. To avoid instability of the system during the refinement, the C(6)–O(6) distance was constrained to 1.15 ± 0.02 Å. The phenyl group was also constrained to a perfect hexagon (C–C 1.395 Å) and refined as a rigid group. Anisotropic thermal parameters were refined for Mo and I. The refinement converged at $R = 0.037$ and $R' = 0.040$ $\{w = [\sigma^2(F_o) + 0.0003F_o^2]^{-1}\}$ for 162 parameters and 1 910 observed reflections. The fractional atomic co-ordinates are in Table 3, relevant bond distances and angles in Tables 5 (cation) and 6 (anion).

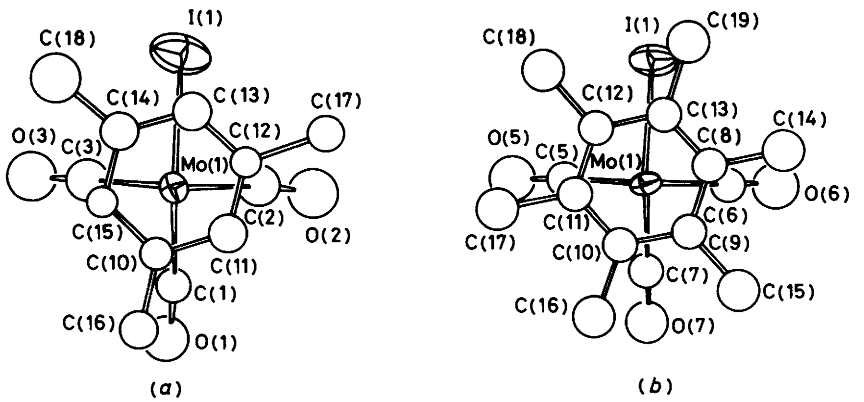

Figure 1. View of the $[MoI(CO)_3(\eta^6\text{-arene})]^+$ cations of compounds (**3**) and (**5**): arene = $C_6H_3Me_3$-1,3,5 (*a*) or C_6Me_6 (*b*). The cation of compound (**8**),$[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]^+$, has the same structure as in (*a*)

$[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$, (**8**). A crystal with dimensions 0.08 × 0.04 × 0.03 mm protected in a glass capillary was mounted on the diffractometer and treated as described for compound (**3**).

Crystal data. $C_{18}H_{12}I_6O_9W_3$, $M = 1\,685.3$, monoclinic, space group $P2_1/c$ (from systematic extinctions), $a = 13.602(2)$, $b = 13.720(2)$, $c = 17.204(3)$ Å, $\beta = 95.99(2)$, $U = 3\,193.1$ Å^3, $Z = 4$, $D_c = 3\,503$ g cm^{-3}, $\mu = 164.7$ cm^{-1}, $F(000) = 2\,928$.

2 062 Independent reflections were measured. Owing to the small dimensions of the crystal employed, the quality of data was quite poor. 1 410 Intensity data with $I < 3\sigma(I)$ were considered unobserved. The data were treated as for compound (**3**). Transmission factors were in the range 0.99—0.71. As inferred from a comparison between the symmetry and the lattice parameters, compounds (**3**) and (**8**) are isostructural. The structure of (**8**) was therefore refined starting from the atomic co-ordinates of (**3**). Because of the unfavourable ratio of the number of observations to the number of parameters, the W–C(carbonyl) and C–O bond lengths were constrained to two average values, which at the end of the refinement were 2.00 ± 0.02 and 1.17 ± 0.04 Å, respectively. The phenyl group was constrained to a perfect hexagon (C–C 1.395 Å), the C(methyl)–C distance to 1.56 ± 0.10 Å. Anisotropic thermal parameters were refined only for W and I. Two common isotropic thermal parameters were assigned and refined for the other atoms, one for the carbon atoms of the carbonyl groups and the other for the carbon atoms of the arene group. The parameters of the oxygen atoms and of the carbon atoms of the methyl groups were assumed to be 1.3 times greater than those of the carbon atoms to which they are bound. These values refined to 0.022 and 0.048 Å^2, respectively. The final R index was 0.065 for 552 observations and 156 parameters $\{R' = 0.067,\ w = [\sigma^2(F_o)]^{-1}\}$. The atomic co-ordinates are listed in Table 4, relevant bond distances and angles in Tables 5 (cation) and 6 (anion).

The atomic scattering factors for all compounds were taken from ref. 21 for O, C, and H and from ref. 22 for Mo, W, and I; the correction for anomalous correction was included.

Results and Discussion

Synthesis, Structure, and Reactivity.—$[MoI(CO)_3(\eta^6\text{-arene})][Mo_2I_5(CO)_6]$. The molybdenum(0) complexes $[Mo(CO)_3(\eta^6\text{-arene})]$ (arene = C_6H_5Me, $C_6H_4Me_2$-1,4, or $C_6H_3Me_3$-1,3,5) are promptly oxidized by I_2 in the parent hydrocarbon as solvent and under a dinitrogen atmosphere to microcrystalline solids of analytical composition $Mo_3I_6(CO)_9$(arene) [arene = C_6H_5Me (**1**), $C_6H_4Me_2$-1,4 (**2**), or $C_6H_3Me_3$-1,3,5 (**3**)]. Reproducible analytical results and good yields were obtained by prompt separation of the compounds from the reaction mixtures as precipitates. The C_6Me_6 derivative, (**4**), was obtained by a similar reaction carried out in dichloromethane as solvent. Gas-volumetric measurements established that no CO evolution had occurred during the formation of the new compounds. Furthermore, by i.r. spectrophotometric monitoring, it was found that 2 equivalents of iodine were used per molybdenum atom and no soluble compounds of intermediate oxidation state had any appreciable lifetime under these conditions: the original molybdenum(0) disappeared only when 2 equivalents of iodine had been used. The relatively high thermal stability of the compounds {they decompose at about 70 °C under reduced pressure with evolution of the arene, carbon monoxide, and formation of some $[Mo(CO)_6]$} indicates that the arene is chemically bonded to the metal, thus excluding the possibility of it being part of a clathrate structure. Elemental analyses suggested a composition with three molybdenum atoms per arene, but in view of the low C,H content and of the subsequent low sensitivity of this analytical method it was decided to determine the arene directly. The elevated reactivity of these compounds towards Lewis bases offered the possibility of measuring the arene content by ^1H n.m.r. spectroscopy of the solutions obtained after attack on the complex by CD_3CN, see equation (1) where L = MeCN, tetrahydrofuran (thf), Et_2O, or Me_2CO.

$$[Mo_3I_6(CO)_9(\text{arene})] + 6L \longrightarrow 3[MoI_2(CO)_3L_2] + \text{arene} \quad (1)$$

The arene content was established by measuring the integrated area of the corresponding proton resonances in comparison with the proton resonances of bis(η-cyclopentadienyl)iron(II) used as internal standard. Having established the analytical composition of these compounds, it was of interest that they were apparently different from the compounds reported in an earlier article[13] dealing with the reaction of molybdenum(0)–arene complexes with I_2. In fact, the resulting molybdenum(II)–arene complexes had previously been reported to have a molybdenum:arene ratio of 1:1, whereas we established a 3:1 ratio for compounds (**1**)—(**4**). Furthermore, only a few examples of organometallic compounds containing a metal:arene ratio higher than 1:1 have been reported.[23] It was therefore decided to carry out an *X*-ray diffractometric study. After several unsuccessful attempts, due to the limited solubility of these compounds in aromatic hydrocarbons and to their elevated reactivity with most organic solvents, single crystals of compound (**3**) were obtained by slow diffusion of an iodine–toluene solution into a dilute solution of the 1,3,5-trimethyl-

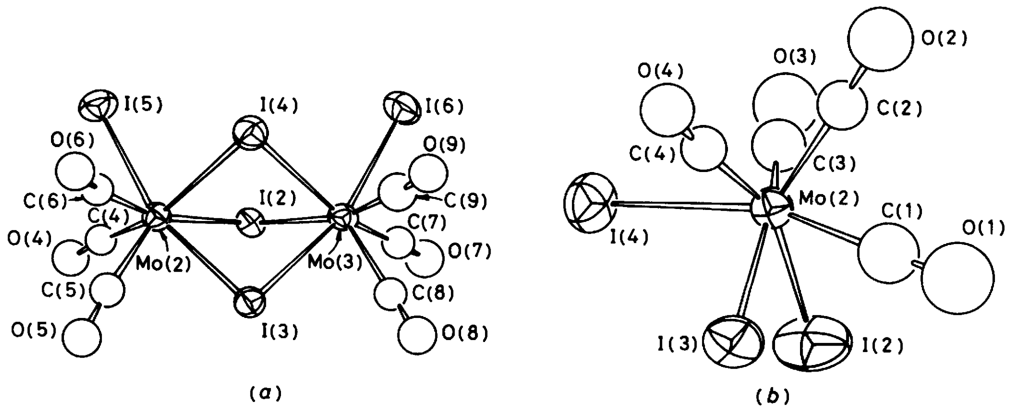

Figure 2. View of the anions of compounds (3) and (5), $[Mo_2I_5(CO)_6]^-$ (*a*) and $[MoI_3(CO)_4]^-$ (*b*). The anion of compound (8), $[W_2I_5(CO)_6]^-$, has the same structure as in (*a*)

Table 5. Selected bond distances (Å) and angles (°) for the $[MI(CO)_3(\eta^6\text{-arene})]^+$ cations of compounds (3), (5), and (8)*

$[MoI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]^+$, (3)		$[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]^+$, (5)		$[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]^+$, (8)	
Mo(1)–I(1)	2.833(4)	Mo(1)–I(1)	2.835(2)	W(1)–I(1)	2.80(2)
Mo(1)–C(1)	2.04(3)	Mo(1)–C(7)	1.961(13)	W(1)–C(1)	2.01(10)
Mo(1)–C(2)	2.03(3)	Mo(1)–C(6)	1.971(14)	W(1)–C(2)	2.01(12)
Mo(1)–C(3)	1.96(4)	Mo(1)–C(5)	1.974(14)	W(1)–C(3)	1.98(13)
Mo(1)–ring	1.92(2)	Mo(1)–ring	1.941(8)	W(1)–ring	1.96(10)
I(1)–Mo(1)–C(1)	127.7(9)	I(1)–Mo(1)–C(7)	124.0(7)	I(1)–W(1)–C(1)	123(2)
I(1)–Mo(1)–C(2)	71.2(10)	I(1)–Mo(1)–C(6)	71.7(7)	I(1)–W(1)–C(2)	73(3)
I(1)–Mo(1)–C(3)	73.7(11)	I(1)–Mo(1)–C(5)	74.7(4)	I(1)–W(1)–C(3)	77(4)
C(1)–Mo(1)–C(2)	75.7(13)	C(7)–Mo(1)–C(6)	74.5(8)	C(1)–W(1)–C(2)	76(4)
C(1)–Mo(1)–C(3)	80.1(14)	C(7)–Mo(1)–C(5)	78.4(5)	C(1)–W(1)–C(3)	71(5)
C(2)–Mo(1)–C(3)	108.7(15)	C(6)–Mo(1)–C(5)	111.8(8)	C(2)–W(1)–C(3)	110(5)
I(1)–Mo(1)–ring	113.7(5)	I(1)–Mo(1)–ring	116.9(2)	I(1)–W(1)–ring	102(2)
C(1)–Mo(1)–ring	118.2(10)	C(7)–Mo(1)–ring	118.9(4)	C(1)–W(1)–ring	134(3)
C(2)–Mo(1)–ring	123.8(11)	C(6)–Mo(1)–ring	125.2(8)	C(2)–W(1)–ring	122(4)
C(3)–Mo(1)–ring	126.8(12)	C(5)–Mo(1)–ring	122.8(4)	C(3)–W(1)–ring	125(5)

* Data are arranged in such a way that the numbering in the same row corresponds to the same geometrical arrangement of the atoms.

benzene complex of molybdenum(0) in the same solvent. The crystalline product was studied by *X*-ray diffraction methods and found to correspond to the ionic formulation $[MoI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][Mo_2I_5(CO)_6]$. A view of the cation is shown in Figure 1(*a*), while the anion is shown in Figure 2(*a*). Having established the molecular structure of the mesitylene derivative, the stoicheiometry of the formation of the complexes could be formulated as shown in equation (2).

$$3[Mo(CO)_3(\eta^6\text{-arene})] + 3I_2 \longrightarrow [MoI(CO)_3(\eta^6\text{-arene})][Mo_2I_5(CO)_6] + 2\,\text{arene} \quad (2)$$

The *X*-ray investigation on compound (3) and on the other systems (see below) definitely establishes that the reaction of the molybdenum(0) tricarbonyl–arene complexes with I_2 leads to ionic complexes. The assignment of one single charge to the cation of (3), which was suggested by the existence of the $[WI(CO)_3(\eta^6\text{-}C_6Me_6)]^+$ cation,[13] was definitely established by the isolation of the I_3^- and BPh_4^- derivatives, see below. Moreover, magnetic susceptibility measurements showed compounds (1)—(3) to be diamagnetic, in agreement with a closed-shell electron configuration for both the cation and the anion.

The cation of compound (3) contains a molybdenum(II) centre surrounded by three carbonyl groups, an η^6-arene ligand, and an iodo group. By considering the arene ligand as three-co-ordinated, the molybdenum atom in the cation is seven-co-ordinated. The iodide and the three carbonyl groups define an almost regular square when projected onto the arene hexagon, see Figure 1(*a*). A similar structural situation was found in the isoelectronic cyclopentadienyl (cp) derivatives $[Mo(cp)X(CO)_3]$ (X = Et,[24] C_3F_7,[25] or Cl[26]) and in the tungsten(II)[13] and vanadium(I)[27] cations $[WI(CO)_3(\eta^6\text{-}C_6Me_6)]^+$ and $[V(CO)_4(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)]^+$, respectively, having the same number of valence electrons as our cation. The problem of the orientation of the arene ring with respect to the carbonyl groups will be discussed in a subsequent section, also in relation to the other structures reported in this paper.

Concerning the $[Mo_2I_5(CO)_6]^-$ anion, which has not been reported earlier, this belongs to the class of the triply halide-bridged anions, with confacial[28] geometries, with or without metal–metal bonds, of d^3 Cr^{III} in $[Cr_2X_9]^{3-}$,[29] Mo^{III} in $[Mo_2X_9]^{3-}$,[30] and W^{III} in $[W_2X_9]^{3-}$,[31] and of the d^3–d^4 mixed-valence anion[32] $[W_2Br_9]^{2-}$, of d^4 Mo^{II},[33] W^{II},[34] and Nb^{I},[35] and of d^6 Re^{I}.[23e] Particularly relevant to our compounds are the d^4 and d^6 derivatives[23e,33–35] in which metal–metal interactions have been observed. In our case the Mo ⋯ Mo

Table 6. Selected bond distances (Å) and angles (°) for the $[M_2I_5(CO)_6]^-$ anions of compounds (**3**) and (**8**)*

$[Mo_2I_5(CO)_6]^-$, (**3**)		$[W_2I_5(CO)_6]^-$, (**8**)		$[Mo_2I_5(CO)_6]^-$, (**3**)		$[W_2I_5(CO)_6]$, (**8**)	
Mo(2)–I(2)	2.915(4)	W(2)–I(2)	2.897(19)	Mo(2)–C(4)	1.96(3)	W(2)–C(4)	2.04(10)
Mo(2)–I(3)	2.884(4)	W(2)–I(3)	2.870(17)	Mo(2)–C(5)	1.98(3)	W(2)–C(5)	2.00(11)
Mo(2)–I(4)	2.883(4)	W(2)–I(4)	2.892(14)	Mo(2)–C(6)	1.99(4)	W(2)–C(6)	2.00(12)
Mo(2)–I(5)	2.845(4)	W(2)–I(5)	2.825(22)	Mo(3)–C(7)	2.00(4)	W(3)–C(7)	2.01(11)
Mo(3)–I(2)	2.907(4)	W(3)–I(2)	2.900(17)	Mo(3)–C(8)	2.02(4)	W(3)–C(8)	1.99(12)
Mo(3)–I(3)	2.889(4)	W(3)–I(3)	2.849(16)	Mo(3)–C(9)	1.98(4)	W(3)–C(9)	2.00(11)
Mo(3)–I(4)	2.901(4)	W(3)–I(4)	2.901(17)	Mo(2) ··· Mo(3)	3.909(4)	W(2) ··· W(3)	3.942(9)
Mo(3)–I(6)	2.836(4)	W(3)–I(6)	2.842(19)				
I(2)–Mo(2)–I(3)	77.8(1)	I(2)–W(2)–I(3)	76.9(4)	I(4)–Mo(2)–C(6)	86.3(9)	I(4)–W(2)–C(6)	86(4)
I(2)–Mo(2)–I(4)	82.7(1)	I(2)–W(2)–I(4)	81.8(4)	I(5)–Mo(2)–C(4)	71.6(9)	I(5)–W(2)–C(4)	76(2)
I(2)–Mo(2)–I(5)	93.3(1)	I(2)–W(2)–I(5)	91.9(4)	I(5)–Mo(2)–C(5)	123.3(9)	I(5)–W(2)–C(5)	123(3)
I(3)–Mo(2)–I(4)	77.9(1)	I(3)–W(2)–I(4)	76.3(4)	I(5)–Mo(2)–C(6)	76.3(9)	I(5)–W(2)–C(6)	81(4)
I(3)–Mo(2)–I(5)	162.2(1)	I(3)–W(2)–I(5)	159.2(4)	I(2)–Mo(3)–C(7)	79.6(9)	I(2)–W(3)–C(7)	81(5)
I(4)–Mo(2)–I(5)	85.7(1)	I(4)–W(2)–I(5)	84.9(4)	I(2)–Mo(3)–C(8)	121.2(10)	I(2)–W(3)–C(8)	124(4)
I(2)–Mo(3)–I(3)	77.8(1)	I(2)–W(3)–I(3)	77.2(4)	I(2)–Mo(3)–C(9)	165.1(11)	I(2)–W(3)–C(9)	159(2)
I(2)–Mo(3)–I(4)	82.5(1)	I(2)–W(3)–I(4)	81.6(4)	I(3)–Mo(3)–C(7)	120.6(9)	I(3)–W(3)–C(7)	117(5)
I(2)–Mo(3)–I(6)	94.3(1)	I(2)–W(3)–I(6)	92.4(4)	I(3)–Mo(3)–C(8)	74.2(10)	I(3)–W(3)–C(8)	78(4)
I(3)–Mo(3)–I(4)	77.6(1)	I(3)–W(3)–I(4)	76.5(4)	I(3)–Mo(3)–C(9)	107.9(11)	I(3)–W(3)–C(9)	107(2)
I(3)–Mo(3)–I(6)	162.8(1)	I(3)–W(3)–I(6)	161.0(4)	I(4)–Mo(3)–C(7)	150.6(9)	I(4)–W(3)–C(7)	155(5)
I(4)–Mo(3)–I(6)	86.2(1)	I(4)–W(3)–I(6)	86.3(4)	I(4)–Mo(3)–C(8)	137.2(10)	I(4)–W(3)–C(8)	139(4)
Mo(2)–I(2)–Mo(3)	84.3(1)	W(2)–I(2)–W(3)	85.7(3)	I(4)–Mo(3)–C(9)	85.3(11)	I(4)–W(3)–C(9)	79(2)
Mo(2)–I(3)–Mo(3)	85.2(1)	W(2)–I(3)–W(3)	87.1(4)	I(6)–Mo(3)–C(7)	72.1(9)	I(6)–W(3)–C(7)	76(5)
Mo(2)–I(4)–Mo(3)	85.0(1)	W(2)–I(4)–W(3)	85.8(4)	I(6)–Mo(3)–C(8)	122.6(10)	I(6)–W(3)–C(8)	120(4)
I(2)–Mo(2)–C(4)	80.3(9)	I(2)–W(2)–C(4)	73(2)	I(6)–Mo(3)–C(9)	76.2(11)	I(6)–W(3)–C(9)	78(2)
I(2)–Mo(2)–C(5)	122.0(9)	I(2)–W(2)–C(5)	121(3)	C(4)–Mo(2)–C(5)	72.9(13)	C(4)–W(2)–C(5)	73(4)
I(2)–Mo(2)–C(6)	165.4(10)	I(2)–W(2)–C(6)	167(4)	C(4)–Mo(2)–C(6)	105.4(13)	C(4)–W(2)–C(6)	116(4)
I(3)–Mo(2)–C(4)	121.1(9)	I(3)–W(2)–C(4)	116(2)	C(5)–Mo(2)–C(6)	72.5(13)	C(5)–W(2)–C(6)	72(5)
I(3)–Mo(2)–C(5)	74.1(9)	I(3)–W(2)–C(5)	78(3)	C(7)–Mo(3)–C(8)	72.3(13)	C(7)–W(3)–C(8)	67(7)
I(3)–Mo(2)–C(6)	109.3(10)	I(3)–W(2)–C(6)	106(4)	C(7)–Mo(3)–C(9)	107.7(14)	C(7)–W(3)–C(9)	114(6)
I(4)–Mo(2)–C(4)	150.5(9)	I(4)–W(2)–C(4)	147(2)	C(8)–Mo(3)–C(9)	73.7(15)	C(8)–W(3)–C(9)	77(5)
I(4)–Mo(2)–C(5)	136.5(9)	I(4)–W(2)–C(5)	140(3)				

* Data are arranged in such a way that the numbering in each row corresponds to the same geometrical arrangement of the atoms.

Table 7. Selected bond distances (Å) and angles (°) for the $[MoI_3(CO)_4]^-$ anion of compound (**5**)

Mo(2)–I(2)	2.860(2)	Mo(2)–C(2)	1.915(13)
Mo(2)–I(3)	2.846(2)	Mo(2)–C(3)	1.960(17)
Mo(2)–I(4)	2.855(1)	Mo(2)–C(4)	1.981(14)
Mo(2)–C(1)	1.934(20)		
I(2)–Mo(2)–I(3)	89.0(1)	I(4)–Mo(2)–C(1)	161.2(5)
I(2)–Mo(2)–I(4)	90.6(1)	I(4)–Mo(2)–C(2)	123.3(4)
I(3)–Mo(2)–I(4)	91.5(0)	I(4)–Mo(2)–C(3)	76.2(4)
I(2)–Mo(2)–C(1)	75.6(5)	I(4)–Mo(2)–C(4)	73.9(4)
I(2)–Mo(2)–C(2)	127.3(4)	C(1)–Mo(2)–C(2)	75.5(6)
I(2)–Mo(2)–C(3)	75.9(4)	C(1)–Mo(2)–C(3)	111.7(6)
I(2)–Mo(2)–C(4)	156.4(4)	C(1)–Mo(2)–C(4)	114.7(6)
I(3)–Mo(2)–C(1)	75.8(5)	C(2)–Mo(2)–C(3)	75.3(6)
I(3)–Mo(2)–C(2)	124.4(4)	C(2)–Mo(2)–C(4)	76.3(5)
I(3)–Mo(2)–C(3)	160.3(4)	C(3)–Mo(2)–C(4)	115.9(6)
I(3)–Mo(2)–C(4)	74.1(4)		

distance is 3.909(4) Å, to be compared with the value of 3.531 Å* found[33] in $[Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$. On the other hand, the Mo ··· Mo distance reported[36] for the $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_4]^{n+}$ cation of undefined oxidation state† for molybdenum is 3.575 Å. In the latter case the Mo–Cl–Mo angles average 89°, compared with the average of 84.8(1)° in our case, thus showing, in addition to the long metal–metal distance, that no important metal–metal interactions occur in these cases. The longer Mo ··· Mo distance found in our case with respect to the chloride-bridged dimers[33] is no doubt due to the larger size of the bridging iodide. Similar structural parameters (M ··· M distance in Å, M–X–M angles in °) were found for $[W_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$ [3.539(3); 87.9(2), 88.7(2), 86.9(2)][34] and for $[Nb_2Cl_3(CO)_8]^-$ [3.631(1); 88.2(1), 87.8(1), 88.8(1)].[35]

It is interesting that the co-ordination around molybdenum in $[Mo_2I_5(CO)_6]^-$ can be regarded as being very similar to that in the arene-containing cation, *i.e.* molybdenum is seven-co-ordinated, three positions being occupied by the bridging iodides and the other four by the three carbonyl groups and by the terminal iodide.

In the dimeric anion the terminal Mo–I distances [average 2.840(8) Å] are significantly shorter than those of the bridging iodides [average 2.896(20) Å]. The molecular symmetry of $[Mo_2I_5(CO)_6]^-$ is approximately C_{2v} with two orthogonal planes, one containing I(2), I(3), and I(4) and the other containing I(5), I(6), Mo(2), Mo(3), I(3), C(5), and C(8), the binary axis lying along the intersection of these two planes. This point will be discussed further in connection with the i.r. spectra of these compounds.

As indicated in the Experimental section, the 1:1 interaction of I_2 with the molybdenum(0)–arene complexes leads to the ionic complexes containing the dimeric anion. These results are at variance with respect to earlier ones,[13] in that no complexes of the known[13] $[MoI(CO)_3(\eta^6\text{-arene})]^+$ cation with a counter anion different from I^- or I_3^- were expected to be stable. Moreover, our results show that the ionic products are formed rapidly. The isolation of compounds (**1**)—(**4**) is presumably attributable to their low solubility in the reaction medium. In

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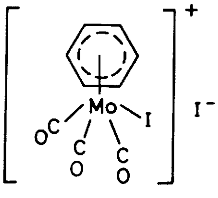
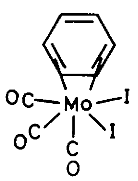
* Value calculated from the co-ordinates reported in this paper.

† The similarity of the Mo ··· Mo distances for $[Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$ and $[Mo_2Cl_3(CO)_4\{P(OMe)_3\}_4]^{n+}$ suggests that in the latter the metal has a +II oxidation state and the complex therefore a +1 charge.

the case of the hexamethylbenzene derivative, however, the reaction is more complicated, see below, and compound (**4**) can be isolated in low yields provided particular reaction conditions are employed, see Experimental section. It is perhaps surprising that this reaction, which requires a considerable degree of rearrangement from the mononuclear molybdenum(0) complex to products (**1**)—(**4**), takes place with such a high degree of selectivity. It is tempting to suggest that the attack on the molybdenum(0) complex may occur *via* the formation of the molybdenum(II) ionic compound shown in (**I**), which may rapidly induce the $\eta^6 \longrightarrow \eta^4$ rearrangement of the arene group, thus admitting I^- into the co-ordination sphere of the metal to give (**II**). The anionic dimer formation is presumably also induced by the requirement of the central metal atom to reach the inert-gas-rule configuration in a system not containing free carbon monoxide: this leads to the formation of iodide bridges in the absence of additional strong ligands for molybdenum(II), except iodide. The existence in solution of a species such as (**II**) is substantiated by the isolation of several η^4 derivatives of transition-metal arene complexes.[37,38a,b] Moreover, complexes in which the electron system of the six-membered ligand is not fully utilized for bonding have been suggested as reaction intermediates, *e.g.* in the reaction of $[V(CO)_6]$ with aromatic hydrocarbons.[38c] If (**I**) and (**II**) are easily interconverted, this would correspond, in the direction (**II**) $\longrightarrow$ (**I**), to a halide abstraction followed by η^6 co-ordination of the type already described in the literature.[38b,d] It is to be noted that we have no evidence that a compound such as (**I**) has any definite existence in our system: this point will be discussed again in a subsequent section. However, it suffices to say that the failure to isolate an ionic species such as (**I**) in our system is understandable in view of the fact that I^- would promptly interact with the numerous Lewis acids present.

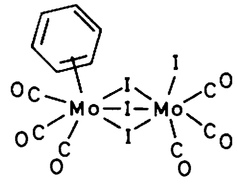


(**I**)

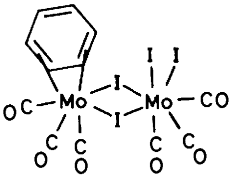


(**II**)

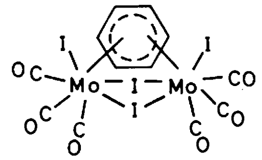
On the basis of the results obtained with the hexamethylbenzene derivative, see Experimental section, it is reasonable to assume that at least another compound may have a transient existence in solution. When the molybdenum(0) complex $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$ was treated with I_2 in toluene as solvent, a product of analytical composition $[\{[MoI_2(CO)_3]_2C_6Me_6\}_n]$, presumably dimeric ($n = 1$), could be isolated for which structures (**III**)—(**VI**) can be tentatively suggested. Unfortunately, we have not yet been able to grow single crystals of this compound. This product has an i.r. spectrum (Nujol mull) distinctly different from those of compounds (**4**) and (**5**). The identity of this product with (**5**) can also be excluded on the grounds that the latter, which contains the $[MoI_3(CO)_4]^-$ anion, is formed only over longer reaction times, in agreement with the high degree of molecular rearrangement required (see below). On the other hand, upon contact with dichloromethane the product shows an i.r. spectrum typical of compound (**4**), thus supporting the view that a fast ligand transfer occurs between (**I**) or (**II**) and one of the species (**III**)—(**VI**) to give the trinuclear complex. Although complexes with an arene–metal structure of the type (**V**) have been reported, *e.g.* $[Pd_2(C_6H_6)_2(AlCl_4)_2]$[38e] and $[VH(\eta^5\text{-}C_5H_5)_2(C_6H_6)]$,[23b] the metal–metal distance in both cases is rather short, 2.57 and 2.425(1) Å, respectively, whereas in our case the molybdenum–molybdenum distance would be much longer for an iodide-bridged species such as (**V**), as judged from the results of the present *X*-ray investigation on compound (**3**) [3.909(4) Å]. We therefore prefer to suggest that the precursor to (**4**) probably has a structure similar to (**III**), (**IV**), or (**VI**). Examples of η^2- and η^4-arenes have been reported.[38f]



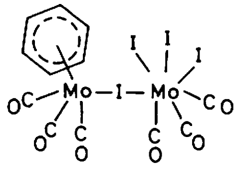
(**III**)



(**IV**)



(**V**)



(**VI**)

$[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4]$, (**5**). While prolonged standing of compounds (**1**)—(**3**) in dichloromethane solution at room temperature results in decomposition to intractable materials, analogous decomposition of compound (**4**) selectively affords the binuclear derivative (**5**). This reaction is always accompanied by the formation of small amounts of a brown, insoluble, non-carbonyl compound, which is assumed to be MoI_2.[39,40] Since the reaction occurs under a dinitrogen atmosphere, the formation of $[MoI_3(CO)_4]^-$, containing *four* carbonyl groups, can be rationalized only by assuming a transfer of a CO between the two molybdenum centres of the $[Mo_2I_5(CO)_6]^-$ anion of (**4**). The stoicheiometry is therefore suggested to be as in equation (3). This observation suggests

$$[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][Mo_2I_5(CO)_6] \longrightarrow MoI_2 + 2CO + [MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4] \quad (3)$$

that, while $[Mo_2I_5(CO)_6]^-$ is unstable in solution, decomposing to $[MoI_3(CO)_4]^-$, the $[MoI(CO)_3(\eta^6\text{-arene})]^+$ cations also have limited stability and a considerable lifetime is achieved only with C_6Me_6. In effect, while compounds (**1**)—(**4**) as solids show signs of decomposition on standing at room temperature under dinitrogen for long periods of time, being more evident for the less methyl-substituted arene derivatives, solid samples of (**5**) are stable indefinitely under the same conditions.

In spite of the fact that compound (**5**) contains more carbon monoxide per molybdenum than the starting compound (**4**), it was not possible to prepare it by a route other than that outlined in equation (3). Treatment of any of compounds (**1**)—(**4**) with carbon monoxide led to a completely different behaviour,[41] dimeric $[Mo_2I_4(CO)_8]$[42] being the main product of the reaction.

The anionic derivatives $[MoX_3(CO)_4]^-$ (X = Cl,[43,44] Br,[43,44] or I[45]) have been reported, the iodo derivative being prepared by I_2 oxidation of $[MoI(CO)_5]^-$. The geometry of $[MoI_3(CO)_4]^-$ may best be described as a capped octahedron, the distorted octahedron being defined by three carbonyl groups [C(1), C(3), and C(4) in Figure 2(*b*); average interligand angle at molybdenum 114.1(6)°] and by the three iodide ligands; the capping ligand is the C(2) carbonyl group and the average of the angles at molybdenum between C(2) and the other carbonyl groups is 75.7(6)°. These values compare quite well with those of $[WBr_3(CO)_4]^-$ (112.8 and 74.1°, respectively).[46]

Table 8. Infrared data (cm^{-1}) in the carbonyl stretching region for molybdenum(II) carbonyl complexes[a]

Compound				
(**1**)	2 083m	2 031s	1 967m—s	*ca.* 1 940 (sh)
(**2**)	2 080m	2 030s	1 966m—s	*ca.* 1 940 (sh)
(**3**)[b]	2 075m	2 025s	1 964m—s	*ca.* 1 940 (sh)
(**4**)	2 069m	2 026s	1 961m	*ca.* 1 940 (sh)
	2 015s			
(**5**)	2 069m	2 014s		1 949w
(**6**)[c]	2 067s	2 011s		
(**7**)	2 069s	2 013s		
$[NBu_4][MoI_3(CO)_4]$	2 072s	2 010s		1 945m

[a] Dichloromethane solution. [b] The tungsten analogue has carbonyl bands (CH_2Cl_2) at 2 073m, 2 019s (asymmetric), 1 947m—s, and 1 925 (sh) cm^{-1}. [c] CaF_2 cells.

Treatment of complex (**5**) with donor solvents, as in the case of the trinuclear complexes (**1**)—(**4**), leads to arene substitution with production of the neutral $[MoI_2(CO)_3L_2]$ complexes, see equation (4). The derivatives of L = thf or Et_2O were identified

$$[MoI(CO)_3(\eta^6\text{-}C_6Me_6)][MoI_3(CO)_4] + 4L \longrightarrow 2[MoI_2(CO)_3L_2] + C_6Me_6 + CO \quad (4)$$

spectroscopically in solution: carbonyl bands at 2 018s, 1 937s, and 1 928 (sh) (thf) and 2 022s and 1 941s (asymmetric) cm^{-1}(Et_2O).

$[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]X$ (X = I_3 *or* BPh_4). While the 1:1 reaction between the molybdenum(0) complexes and I_2 leads to compounds (**1**)—(**4**) or (**5**), depending on the reaction conditions, treatment of the molybdenum(0) complexes with I_2 in 1:2 ratio leads, in the hexamethylbenzene case, to exclusive formation of the tri-iodide derivative $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3$, (**6**). Its formulation is supported by elemental analysis and by the spectroscopic data for the carbonyl stretching region. Moreover, the tetraphenylborate salt, (**7**), could be obtained only by the metathetical reaction (6) in dichloromethane as solvent.

$$[Mo(CO)_3(\eta^6\text{-}C_6Me_6)] + 2I_2 \longrightarrow \underset{(\mathbf{6})}{[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3} \quad (5)$$

$$[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3 + BPh_4^- \longrightarrow \underset{(\mathbf{7})}{[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]BPh_4} + I_3^- \quad (6)$$

The formation of the tri-iodide derivative by reaction (5) may be explained by considering that it results from the addition of I_2 to an intermediate such as (**I**) or (**II**). It is important to note that conditions were established in this work which lead to the exclusive formation of the tri-iodide derivative. The results obtained can therefore be used to explain the formation of the corresponding tungsten complex $[WI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3$ reported earlier.[13] It is quite possible that the oxidation of molybdenum(0) and tungsten(0) arene derivatives proceeds *via* similar reaction paths and our isolation and characterization of $[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$, (**8**), see below, isostructural with the molybdenum compound (**3**), supports this idea. It is also interesting that the analytical results reported by Snow *et al.*[13] are consistent with the $[WI(CO)_3(\eta^6\text{-}C_6Me_6)]I$ formulation, while the crystals, presumably obtained at a locally higher concentration of I_2, were those of the tri-iodide. On the other hand, the analytical results (C, 15.5; H, 1.25; I, 51.5; Mo, 20.4%) reported[13] for the molybdenum–mesitylene complex, believed to be $[MoI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]^+I^-$, show too much impurity for molybdenum iodides, and are in fact rather close to those calculated for compound (**3**) in Table 1 (C, 15.2; H, 0.8; I, 53.6; Mo, 20.2%).

The derivatives of type (**I**) or (**II**) containing a Mo:I ratio of 1:1 could not be observed under our experimental conditions. Attempts to prepare them by treating $[Mo(CO)_3(\eta^6\text{-}C_6Me_6)]$ with $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3$ in dichloromethane did not give the expected $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I$, but rather (**4**) initially, and then (**5**), see equation (3). It is possible that the failure to observe the iodide in our reaction mixtures may be attributed to the weakness of the molybdenum–arene bond, expulsion of the arene ligand from the co-ordination sphere of molybdenum and consequent formation of more complex anions being the preferred reaction pathway.

The tri-iodide complex (**6**), like (**1**)—(**5**), reacts with donor solvents, see equation (7). The tetraphenylborate salt (**7**) is, on

$$[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]I_3 + 2L \longrightarrow [MoI_2(CO)_3L_2] + C_6Me_6 + I_2 \quad (7)$$

the other hand, unreactive and its MeCN solutions show little change in i.r. spectrum over a few hours. This shows that the $[MoI(CO)_3(\eta^6\text{-}C_6Me_6)]^+$ cation is intrinsically stable in donor solvents and its reaction must be ascribed to an initial attack of an iodide ion derived from either $[Mo_2I_5(CO)_6]^-$, $[MoI_3(CO)_4]^-$, or I_3^-, followed by arene replacement with two solvent molecules. Accordingly, when a MeCN solution of complex (**7**) was treated with some NEt_4I, rapid formation of $[MoI_2(CO)_3(MeCN)_2]$ occurred.

$[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$, (**8**). In order to acquire further information on the iodine oxidation pathway of tricarbonylarene complexes, we decided to investigate a tungsten system, $[W(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$. Interaction of this with an equimolar amount of I_2 [equation (8)] resulted in

$$3[W(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)] + 3I_2 \longrightarrow 2(C_6H_3Me_3\text{-}1,3,5) + [WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6] \quad (8)$$

the formation of a crystalline solid whose analytical properties and crystal structure show it to be $[WI(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)][W_2I_5(CO)_6]$, (**8**), namely the analogue of the product of oxidation of $[Mo(CO)_3(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$, by iodine (**3**). A transient species was observed during this preparation (see Experimental section), which could be the tungsten analogue of structure (**III**), (**IV**), or (**VI**) discussed above.

Although the crystal structure of compound (**8**) is rather imprecise (see the standard deviations of the structural parameters in Tables 5 and 6), it allowed us (*a*) to determine unequivocally the stoicheiometry of the compound, (*b*) to acquire further data on the problem of arene orientation in the class of $[M(\eta^6\text{-arene})L_4]^+$ cations (see below for a more detailed discussion), and (*c*) to characterize the yet unknown $[W_2I_5(CO)_6]^-$ anion. The latter is isostructural with its molybdenum analogue discussed above, having an approximate C_{2v} symmetry. All the W-I, W–C(carbonyl), and W–C(ring) bond distances, both in the cation and the anion, are not significantly different from the corresponding Mo–I, Mo–C(carbonyl), and Mo–C(ring) in compound (**3**) (see Tables 5 and 6); nevertheless, the unit-cell dimensions are somewhat greater for the molybdenum compound. This can be tentatively ascribed to stronger intermolecular interactions in the tungsten compound.

Carbonyl Stretching Vibrations.—The i.r. spectra of the complexes reported in this paper are collected in Table 8. For most of the ionic compounds, due to their rather low solubility in the common organic solvents and their reactivity towards those having Lewis-donor properties [see equations (1), (4), and (7)], the spectra had to be measured in dichloromethane and therefore a low degree of resolution could only be obtained. However, a number of conclusions could be made.

For the sake of simplicity, we discuss the spectroscopic properties of compound (**5**) first. Since both the cation, $[\mathrm{MoI(CO)_3(\eta^6\text{-}C_6Me_6)}]^+$, and the anion,[41] $[\mathrm{MoI_3(CO)_4}]^-$, have been separately obtained with non-carbonyl-containing counter ions, in compounds (**6**) and (**7**) and in $[\mathrm{NBu_4}][\mathrm{MoI_3(CO)_4}]$, respectively, the i.r. spectra of these can be combined to obtain that of compound (**5**); therefore, the weak band at 1 949 $\mathrm{cm^{-1}}$ is assigned to the anion, while each of the other bands at 2 069 and 2 014 $\mathrm{cm^{-1}}$ is the result of the overlap of a band of the cation with a band of the anion. An accidental coincidence of two vibrational frequencies probably occurs for the cation, whose C_s symmetry allows the prediction of three bands ($2A' + A''$), while the three-band spectrum of the anion is in agreement with its C_{3v} symmetry ($2A_1 + E$) [see Figure 2(*b*)]. These considerations apply, of course, if the solid-state geometries remain unaltered in solution.

The bands of $[\mathrm{MoI(CO)_3(\eta^6\text{-}C_6Me_6)}]^+$ are also evident in the i.r. spectrum of compound (**4**) at 2 069 and 2 015 $\mathrm{cm^{-1}}$; the remaining bands, namely those at 2 026s, 1 961m, and *ca.* 1 940 (sh) $\mathrm{cm^{-1}}$, are therefore to be assigned to the CO stretching vibrations of the new $[\mathrm{Mo_2I_5(CO)_6}]^-$ anion. We cannot, however, rule out the possibility that other bands of the anion remain hidden under the strong bands of the cation, since five bands ($2A_1 + 2B_1 + B_2$) are expected for the C_{2v} symmetry of $[\mathrm{Mo_2I_5(CO)_6}]^-$ [see Figure 2(*a*)]. At this point, the spectra of compounds (**1**)—(**3**) can be fully interpreted as a combination of the $[\mathrm{Mo_2I_5(CO)_6}]^-$ bands, which to a first approximation do not depend on the counter cation, with those of the $[\mathrm{MoI(CO)_3(\eta^6\text{-}arene)}]^+$ cations, which show an expected shift to lower wavenumbers as the methyl substitution increases. In effect, the highest-wavenumber band of compound (**4**), which is at 2 069 $\mathrm{cm^{-1}}$, shifts to 2 075, 2 080, and 2 083 $\mathrm{cm^{-1}}$ for compounds (**3**), (**2**), and (**1**), respectively, and is still symmetric, thus suggesting that no band due to $[\mathrm{Mo_2I_5(CO)_6}]^-$ is probably present in this region; on the other hand, the second band of the cation in compound (**4**), namely at 2 015 $\mathrm{cm^{-1}}$, overlaps with the band of the anion at 2 026 $\mathrm{cm^{-1}}$ to give a single, more or less symmetric band in the poorly resolving $\mathrm{CH_2Cl_2}$, at 2 025, 2 030, and 2 031 $\mathrm{cm^{-1}}$ for compounds (**3**), (**2**), and (**1**), respectively.

The $[\mathrm{MoI_2(CO)_3L_2}]$ complexes can have C_s symmetry at most; therefore three bands are expected and these are actually observed. The bis(acetonitrile) complex also shows two C–N stretching vibrations at 2 311w and 2 288w $\mathrm{cm^{-1}}$ in toluene solution; the relative intensity of these suggests the two MeCN ligands occupy two co-ordination positions at an angle which is not far from 90°.[47]

Arene Ring Orientation in $[\mathrm{MI(CO)_3(\eta^6\text{-}arene)}]^+$ (M = Mo *or* W).—A large body of experimental data and theoretical interpretation[38f] is available on the arene ring orientation in d^6 half-sandwich complexes $[\mathrm{M(\eta^6\text{-}arene)L_3}]$. On the other hand, only a few examples are known of crystallographically characterized half-sandwich compounds of d^4 ions $[\mathrm{M(\eta^6\text{-}arene)L_4}]$, namely $[\mathrm{WI(CO)_3(\eta^6\text{-}C_6Me_6)}]^+\mathrm{I_3}^-$ of tungsten(II)[13] and $[\mathrm{V(CO)_4(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)}]^+[\mathrm{V(CO)_6}]^-$ of vanadium(I).[27] Although a tentative explanation in the vanadium cation has been proposed,[27] the relative lack of experimental data probably prevented a closer consideration of the problem. The cations reported here (see Figure 1) allow some more conclusions to be made.

For $[\mathrm{M(\eta^6\text{-}arene)L_3}]$ complexes, see Figure 3(*a*), a 60° rotation of the arene ring around the C_3 symmetry axis affords an equivalent configuration; a rotation of 30° from the eclipsed configuration (*i*) gives rise to the staggered one (*ii*) with minimum steric strain. If strong electronic effects due to the arene substituents are present, these could outweigh the steric repulsion, forcing the structure to adopt an eclipsed configuration. A similar picture holds for d^4 $[\mathrm{M(\eta^6\text{-}arene)L_4}]$ molecules [see Figure 3(*b*)]. In such cases, a 30° rotation of the arene ring around the C_2 axis affords an equivalent structure. Therefore, starting from configuration (*iv*), which we could call 'eclipsed,' a rotation of the arene ring by only 15° gives rise to the configuration with minimum steric strain, (*v*), and which we will therefore call 'staggered'. In this configuration two hexagon vertices are at 45° with respect to the L ligands in the Newman projection shown in Figure 3, while the other four vertices are at 15° with respect to the nearest L. It has the C_{2v} point group, one of the two symmetry planes being that corresponding to the dashed line in the Newman projection of Figure 3, provided the four L ligands are equivalent and suitable ring substituents are present.

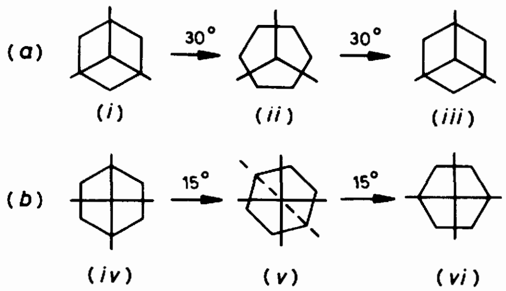


Figure 3. Limiting structures for $[\mathrm{M(\eta^6\text{-}arene)L_3}]$ (*a*) and $[\mathrm{M(\eta^6\text{-}arene)L_4}]$ (*b*) half-sandwich molecules

Simple geometric considerations lead us to anticipate that the difference in energy of configurations (*iv*) and (*v*), if only the steric strain is considered, will be less than that between (*i*) and (*ii*) for comparable metal–arene distances. Now, the structures known for tungsten(II),[13] $[\mathrm{WI(CO)_3(\eta^6\text{-}C_6Me_6)}]^+$, and for vanadium(I),[27] $[\mathrm{V(CO)_4(\eta^6\text{-}C_6H_2Me_4\text{-}1,2,4,5)}]^+$, are of the eclipsed type, therefore showing that an electronic effect is probably present; this is even more strongly suggested by the particular disposition of the $\mathrm{C_6H_2Me_4}$-1,2,4,5 group in the vanadium(I) compound.[27] Two of our molybdenum(II) cations, namely those of compounds (**3**) and (**5**), reported in Figure 1(*a*) and (*b*), and the tungsten(II) cation of compound (**8**) are the first examples of the 'staggered' configuration (*v*). The fact that the steric strain seems to prevail in these three cations suggests that the electronic effects induced by the ring substituents are relatively small for molybdenum(II) and tungsten(II). If the energy difference between the two possible configurations is not very large, as is suggested by the present results, it may well be that crystal-packing effects resulting from a change in counter anion may be sufficient to induce a configurational change.

Unfortunately, no theory is available for predicting the ring-substituent effect on the configurations in $[\mathrm{M(\eta^6\text{-}arene)L_4}]$ complexes and only the structure of the above mentioned vanadium(I) compound[27] suggests that the electron-donating methyl groups prefer to be in the eclipsed position in a structure of type (*iv*). Further experimental investigations, as well as theoretical work, would therefore be welcome in this field.

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