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# OXIDATION OF $\eta^6$ -ARENE COMPLEXES OF GROUP VI METALS. IV (\*). MOLYBDENUM(II) ARENE-CARBONYL COMPOUNDS CONTAINING POLYIODIDES (\*\*)

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*Summary* – The reaction of  $\text{Mo}_2\text{I}_4(\text{CO})_8$  with  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]\text{I}_3$  affords  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{MoI}_2(\text{I}_3)(\text{CO})_4]$ , **1**, containing a coordinated tri-iodide ligand, as the major product. The reaction also affords small amounts of the complex  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]\text{I}_5$ , **2**. Compound **2** has also been synthesized by reacting  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]\text{I}_3$  with  $\text{I}_2$  in equimolar amounts or by interaction of  $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)$  with  $\text{I}_2$  in 1:3 molar ratio. The penta-iodide anions in compound **2** are arranged in an infinite chain of alternating  $\text{I}_3^-$  and  $\text{I}_2$  groups with  $\text{I}\cdots\text{I}$  contacts of 3.468(1) Å. *Crystal data*; compound **1**: orthorhombic; space group  $Pna2_1$ ;  $a = 24.750(3)$ ,  $b = 11.521(3)$ ,  $c = 11.348(3)$  Å,  $V = 3236(1)$  Å<sup>3</sup>;  $Z = 4$ ;  $d_c = 2.691$  g cm<sup>-3</sup>;  $\mu$  (Mo- $K_\alpha$ ) = 61.35 cm<sup>-1</sup>;  $R = 0.046$  ( $R_w = 0.049$ ) for 1827 reflections having  $F_0^2 > 3\sigma(F_0^2)$ ; compound **2**: monoclinic; space group  $P2_1/m$ ;  $a = 15.006(3)$ ,  $b = 9.647(3)$ ,  $c = 8.986(3)$  Å,  $\beta = 95.76(2)^\circ$ ;  $V = 1294.3(6)$  Å<sup>3</sup>;  $Z = 2$ ;  $d_c = 2.830$  g cm<sup>-3</sup>;  $\mu$  (Mo- $K_\alpha$ ) = 71.97 cm<sup>-1</sup>;  $R = 0.042$  ( $R_w = 0.051$ ) for 1509 reflections having  $F_0^2 > 3\sigma(F_0^2)$ .

(\*) For Part III, see preceding paper

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In earlier papers of this series<sup>1-3</sup> we described the oxidation of molybdenum(0) tricarbonyl-arene complexes with I<sub>2</sub> and isolated and structurally characterised compounds containing the [MoI(CO)<sub>3</sub>(η<sup>6</sup>-arene)]<sup>+</sup> cation and the [Mo<sub>2</sub>I<sub>5</sub>(CO)<sub>6</sub>]<sup>-</sup> anion. The reaction between Mo(CO)<sub>3</sub>(η<sup>6</sup>-arene) and I<sub>2</sub> in 1:1 molar ratio affords [MoI(CO)<sub>3</sub>(η<sup>6</sup>-arene)][Mo<sub>2</sub>I<sub>5</sub>(CO)<sub>6</sub>] as the kinetically-controlled product.<sup>1</sup> The anion is thermally unstable and the stability of the cation increases with the methyl substitution on the arene. With C<sub>6</sub>Me<sub>6</sub> as the carbocyclic ligand, the cation is indefinitely stable; in this case, thermal decomposition affords [MoI(CO)<sub>3</sub>(η<sup>6</sup>-arene)][MoI<sub>3</sub>(CO)<sub>4</sub>].<sup>1</sup> When the oxidation is performed with two moles of iodine per molybdenum(0) complex, the [MoI(CO)<sub>3</sub>(η<sup>6</sup>-arene)]I<sub>3</sub> complexes are formed, from which the BPh<sub>4</sub> salts can be prepared by ion metathesis. When the [MoI(CO)<sub>3</sub>(η<sup>6</sup>-arene)][Mo<sub>2</sub>I<sub>5</sub>(CO)<sub>6</sub>] salts are reacted with CO at atmospheric pressure and room temperature, the already known<sup>4</sup> Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub> can be prepared in high yields. Mo<sub>3</sub>I<sub>4</sub>(CO)<sub>8</sub> was found<sup>2</sup> to easily transfer a molecule of I<sub>2</sub> to a number of substrates, being in turn reduced to the known<sup>5</sup> Mo<sub>2</sub>I<sub>2</sub>(CO)<sub>8</sub>. The following compounds were all found to catalyse the carbonylation of [Mo(CO)<sub>3</sub>(η<sup>6</sup>-arene) to Mo(CO)<sub>6</sub> in the parent arene as solvent:<sup>3</sup> I<sub>2</sub>, [MoI(CO)<sub>3</sub>(η<sup>6</sup>-arene)][Mo<sub>2</sub>I<sub>5</sub>(CO)<sub>6</sub>], Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub>. The mechanism of the catalysed reaction is believed to be related to a two-electron inner-sphere electron transfer taking place between Mo(CO)<sub>3</sub>(η<sup>6</sup>-arene) and salts of the [MoI(CO)<sub>3</sub>(η<sup>6</sup>-arene)]<sup>+</sup> cations (arene' ≠ arene).<sup>3</sup>

In the course of these studies, additional derivatives of the [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]<sup>+</sup> cation were obtained, whose anions exhibit interesting free and coordinated polyiodide functionalities. The synthesis and structural characterisation of these derivatives are the subject of this paper.

## EXPERIMENTAL

All operations were carried out under an atmosphere of prepurified nitrogen with standard Schlenk tube techniques. Solvents were purified by conventional methods and distilled prior to use. The IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer, Solution spectra were measured on an expanded abscissa scale and calibrated with both CO and H<sub>2</sub>O<sub>(g)</sub>. Elemental analyses were carried out at the Istituto di Chimica Farmaceutica, Università di Pisa. The following compounds

were prepared according to published procedures:<sup>1,2</sup> Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub>, Mo(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>), [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>3</sub>.

REACTION OF Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub> WITH [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>3</sub>. PREPARATION OF [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>5</sub>, **1**.

Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub> (0.24 g, 0.26 mmol) and [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>3</sub> (0.45 g, 0.53 mmol) were mixed in dichloromethane (25 cm<sup>3</sup>). The resulting solution was immediately filtered and cooled to about -30 °C. Black crystals formed within several days. They were decanted and dried *in vacuo*. Yield: 0.37 g (54%). *Elem. anal.*, found % (calcd. for C<sub>19</sub>H<sub>18</sub>I<sub>6</sub>Mo<sub>2</sub>O<sub>7</sub>): C, 17.2 (17.4); H, 1.3 (1.4). IR (Nujol mull): 2065 s, 2000 vs, 1975 s, 1280 w, 1065 w, 1015 w, 995 w, 560 m, 530 m, 510 m-s, 480 m, 460 m, 430 w, 425 sh, 400 w cm<sup>-1</sup>. IR (CH<sub>2</sub>Cl<sub>2</sub>): 2066 s, 2010 vs, 1948 w cm<sup>-1</sup>. A single crystal was used for the subsequent X-ray diffractometric experiment.

Among the pseudo-octahedrally-shaped crystals of **1**, a few black parallelepipedal crystals were noted. One of these was used in the X-ray study and found to correspond to compound **2** (see below).

PREPARATION OF [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>5</sub>, **2**

From [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>3</sub> and I<sub>2</sub> - Iodine (0.07 g, 0.27 mmol) was dissolved in dichloromethane (20 cm<sup>3</sup>) and 0.21 g (0.25 mmol) of [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>3</sub> was added. After brief stirring at room temperature, the reaction mixture was filtered and the solution cooled to about -30 °C. Dark needles precipitated out, which were decanted, washed with *n*-pentane and dried *in vacuo* (38% yield). *Elem. anal.*, found % (calcd for C<sub>15</sub>H<sub>18</sub>I<sub>6</sub>MoO<sub>3</sub>): C, 15.9 (16.3); H, 1.5 (1.6). The compound showed IR bands (Nujol) at: 2067 s, 2003 s, 1270 w, 1060 w, 1010 w, 990 w, 575 w, 555 m, 510 m, 455 m, 430 w and 400 vw cm<sup>-1</sup>; IR (CH<sub>2</sub>Cl<sub>2</sub>): 2067 s and 2011 s cm<sup>-1</sup>.

A single crystal was selected and found to have the primitive cell as that of the crystallographically characterised penta-iodide obtained as described above.

From Mo(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>) and I<sub>2</sub> in 1:3 molar ratio - Mo(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>) (0.36 g, 1.05 mmol) was dissolved in toluene (50 cm<sup>3</sup>). This solution was added dropwise at room temperature to a solution of I<sub>2</sub> (0.80 g, 3.15 mmol) in 30 cm<sup>3</sup> of the same solvent. The resulting black microcrystalline

precipitate was filtered off, washed with toluene (3 x 5 cm<sup>3</sup>) and dried *in vacuo*. Yield: 0.81 g (70%). The identity of this material with the penta-iodide was confirmed by IR (Nujol mull).

## X-RAY CRYSTALLOGRAPHY

*Compound 1<sup>a</sup>* — A crystal with approximate dimensions (mm) 0.15 x 0.10 x 0.09 was mounted on a computer-controlled Philips PW 1100 single-crystal automatic diffractometer, equipped with graphite monochromatized Mo-K $\alpha$ , radiation ( $\lambda = 0.71069$  Å). The crystals are orthorhombic. The cell dimensions, determined by a least-squares calculation based on the setting angles of 25 reflections with  $2\theta$  angles ranging between 17 and 20°, are:  $a = 24.750(3)$ ,  $b = 11.521(3)$ ,  $c = 11.348(3)$  Å. The space group is  $Pna2_1$  (from systematic extinctions and intensity statistics). The calculated density for four molecules of  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{MoI}_2(\text{I}_3)(\text{CO})_4]$ , MW = 1311.3, in the unit cell is  $d_c = 2.691$  g x cm<sup>-3</sup>. The absorption coefficient for Mo-K $\alpha$ , is  $\mu = 61.35$  cm<sup>-1</sup>.

The intensities were collected up to  $2\theta = 50^\circ$ ; the  $\omega$ - $2\theta$  scan technique was employed, the scan range being 1.2° and the speed 0.05° s<sup>-1</sup>. A total of 3055 reflections was measured, of which 1228, having  $I < 3\sigma(I)$ , were considered as “unobserved” and excluded from the refinement. Three standard reflections which were measured periodically showed no apparent variation in intensity during data collection. The data were corrected for Lorentz and polarization factors. A semiempirical absorption correction according to the method of North *et al.*,<sup>6</sup> based on the intensity change during the azimuthal scans, was applied. A further correction was applied during the refinement according to the empirical method of Walker and Stuart.<sup>7</sup> Transmission factors were in the range 0.93 - 0.49.

The structure was solved by direct methods with MULTAN-76<sup>8</sup> and refined by the full-matrix least-squares method with the SHELX-76<sup>9</sup> package of programmes. The benzene ring was constrained to a perfect hexagon (C-C = 1.395 Å) and refined as a rigid group. Anisotropic thermal parameters were refined for Mo, I and O atoms only. Concerning the C-O distances of the carbonyl groups linked in the cationic moiety, they are quite unrealistic, with values shorter than normally found. This can be due either to thermal motion, to positional disorder, or can simply be the result of errors in the measured intensities owing to a not completely adequate absorption correction. The

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<sup>a</sup> Atomic coordinates for this structure have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on request from: The Director, Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

refinement converged to  $R$  (unweighted) = 0.046 and  $R_w$  (weighted) = 0.049 [ $w = (\sigma^2(F_o) + 0.0001 F_o^2)^{-1}$ ] for 200 parameters and 1827 observed reflections.

The atomic scattering factors were taken from ref. 9 for O and C and from ref. 10 for Mo and I; the correction for anomalous dispersion was included. The atomic coordinates are listed in table 1 and selected bond distances and angles are in table 2 (cation) and table 3 (anion).

TABLE 1. FRACTIONAL ATOMIC COORDINATES FOR  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{MoI}_2(\text{I}_3)(\text{CO})_4]$  (I) WITH E.S.D.'s REFERRED TO THE LEAST SIGNIFICANT FIGURE.

Atom	$X/a$	$Y/b$	$Z/c$
Mo(1)	0.4016(1)	0.4137(2)	0.3760
Mo(2)	0.5794(1)	1.0197(2)	0.3614(3)
I(1)	0.4252(1)	0.3976(3)	0.6174(3)
I(2)	0.6364(1)	0.9895(2)	0.5779(3)
I(3)	0.6139(1)	1.2564(2)	0.3427(3)
I(4)	0.6736(1)	0.9544(2)	0.2276(3)
I(5)	0.7285(1)	0.7268(2)	0.3206(3)
I(6)	0.7802(1)	0.5270(2)	0.3913(3)
O(1)	0.3926(8)	0.1619(19)	0.4213(26)
O(2)	0.4672(10)	0.3113(29)	0.1810(25)
O(3)	0.5051(11)	0.5274(18)	0.4155(22)
O(4)	0.4627(9)	0.9314(23)	0.3264(18)
O(5)	0.5465(11)	1.0931(21)	0.1025(16)
O(6)	0.5105(9)	1.1492(21)	0.5567(20)
O(7)	0.5848(10)	0.7507(19)	0.4075(25)
C(1)	0.4003(15)	0.2472(11)	0.4110(33)
C(2)	0.4470(13)	0.3490(32)	0.2518(25)
C(3)	0.4740(8)	0.4794(36)	0.3945(44)
C(4)	0.5053(13)	0.9648(24)	0.3364(29)
C(5)	0.5576(11)	1.0687(23)	0.1954(25)
C(6)	0.5373(12)	1.1028(23)	0.4869(25)
C(7)	0.5842(12)	0.8452(25)	0.3873(28)
C(8)	0.3506(8)	0.4894(15)	0.2189(12)
C(9)	0.3171(8)	0.4105(15)	0.2768(12)
C(10)	0.3044(8)	0.4271(15)	0.3854(12)
C(11)	0.3252(8)	0.5225(15)	0.4560(12)
C(12)	0.3587(8)	0.6014(15)	0.3980(12)
C(13)	0.3714(8)	0.5848(15)	0.2794(12)
C(14)	0.3605(15)	0.4779(32)	0.0873(40)
C(15)	0.2920(14)	0.3031(29)	0.2087(31)
C(16)	0.2669(15)	0.3329(33)	0.4605(34)
C(17)	0.3029(14)	0.5513(29)	0.5791(33)
C(18)	0.3807(19)	0.7092(38)	0.4711(42)

C(19)	0.4063(16)	0.6814(33)	0.2128(38)
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TABLE 2 - SELECTED BOND DISTANCES (Å) AND ANGLES (deg) FOR THE [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]<sup>+</sup> CATION IN COMPOUNDS **1** AND **2**, WITH E.S.D.'S IN PARENTHESES REFERRED TO THE LEAST SIGNIFICANT FIGURE

Compound <b>1</b>		Compound <b>2</b>	
Mo1-I1	2.807(3)	Mo-I1	2.822(2)
Mo1-C1	1.96(2)	Mo-C1	1.99(2)
Mo1-C2	1.95(3)	Mo-C2	2.02(2)
Mo1-C3	1.96(3)	Mo-C3	2.43(1)
Mo1-C8	2.35(2)	Mo-C4	2.46(2)
Mo1-C9	2.37(2)	Mo-C5	2.37(1)
Mo1-C10	2.42(2)	C1-O1	1.10(2)
Mo1-C11	2.44(2)	C2-O2	1.10(3)
Mo1-C12	2.42(2)	C3-C6	1.53(2)
Mo1-C13	2.38(2)	C4-C7	1.48(2)
C1-O1	1.01(3)	C5-C8	1.52(2)
C2-O2	1.04(4)	C3-C4	1.43(2)
C3-O3	1.00(4)	C4-C5	1.42(2)
C8-C14	1.52(5)	C3-C3'	1.48(3)
C9-C15	1.59(4)	C5-C5'	1.45(3)
C10-C16	1.61(4)	C1-Mo-I1	72.9(4)
C11-C17	1.54(4)	C1-Mo-I2	126.0(7)
C12-C18	1.59(5)	C1-Mo-C2	76.7(8)
C13-C19	1.60(4)	Mo-C1-O1	173(1)
C1-Mo1-I1	75(1)	Mo-C2-O2	178(2)
C2-Mo1-I1	124(1)		
C3-Mo1-I1	74.4(6)		
C1-Mo1-C2	77(1)		
C1-Mo1-C3	112(1)		
C2-Mo1-C3	72(1)		
Mo1-C1-O1	169(3)		
Mo1-C2-O2	173(3)		
Mo1-C3-O3	165(2)		

TABLE 3 - SELECTED BOND DISTANCES (Å) AND ANGLES (deg) FOR THE [MoI<sub>2</sub>(I<sub>3</sub>)(CO)<sub>4</sub>]<sup>-</sup> ANION IN COMPOUND **1**, WITH E.S.D.'S IN PARENTHESES REFERRED TO THE LEAST SIGNIFICANT DIGIT

Mo2-I2	2.854(5)	I2-Mo2-I3	91.9(1)
Mo2-I3	2.854(3)	I2-Mo2-I4	91.3(1)
Mo2-I4	2.882(4)	C4-Mo2-I2	123.2(9)
Mo2-C4	1.96(3)	C5-Mo2-I2	163.7(8)
Mo2-C5	2.04(3)	C6-Mo2-I2	72.8(9)
Mo2-C6	2.01(3)	C7-Mo2-I2	74.1(8)

Mo2-C7	2.03(3)	I3-Mo2-I4	88.2(1)
I4-I5	3.136(4)	C4-Mo2-I3	125.1(9)
I5-I6	2.753(3)	C5-Mo2-I3	75.3(8)
C4-O4	1.13(4)	C6-Mo2-I3	75.7(9)
C5-O5	1.12(3)	C7-Mo2-I3	159.0(8)
C6-O6	1.16(4)	C4-Mo2-I4	126.6(9)
C7-O7	1.11(4)	C5-Mo2-I4	78.4(8)
		C6-Mo2-I4	156.6(9)
		C7-Mo2-I4	76.8(8)
		C4-Mo2-C5	73(1)
		C4-Mo2-C6	77(1)
		C4-Mo2-C7	76(1)
		C5-Mo2-C6	123(1)
		C5-Mo2-C7	115(1)
		C6-Mo2-C7	113(1)
		Mo2-I4-I5	113.0(1)
		I4-I5-I6	176.8(1)
		Mo2-C4-O4	177(3)
		Mo2-C5-O5	178(3)
		Mo2-C6-O6	176(3)
		Mo2-C7-O7	176(3)

*Compound 2<sup>a</sup>*- A crystal of approximate dimensions (mm) 0.25 x 0.10 x 0.05 protected in a glass capillary was mounted on the above-mentioned diffractometer. The crystals are monoclinic. The cell dimensions, determined as for compound **1**, are:  $a = 15.006(3)$ ,  $b = 9.647(3)$ ,  $c = 8.986(3)$  Å,  $\beta = 95.76(2)^\circ$ ,  $V = 1294.3(6)$  Å<sup>3</sup>. The space group is  $P2_1/m$  (from systematic extinctions and intensity statistics). The calculated density is 2.830 g cm<sup>-3</sup> for two molecules of [MoI(CO)<sub>3</sub>( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)]I<sub>5</sub> in the unit cell. The absorption coefficient for Mo- $K\alpha$ , is  $\mu = 71.97$  cm<sup>-1</sup>. The intensities were collected up to  $2\theta = 50^\circ$ ; the  $\omega$ - $2\theta$  scan technique was employed, the scan range being  $1.6^\circ$  and the speed  $0.06^\circ$  s<sup>-1</sup>. A total of 2304 reflections was measured, 795 of which, having  $I < 3\sigma(I)$ , were considered as “unobserved” and excluded from the refinement. The data were treated as described previously for compound **1**. Transmission factors were in the range 0.99 - 0.49.

The structure was solved by Patterson and direct methods and refined by the full-matrix least-squares method as for compound **1** (see above). Several cycles of refinement with anisotropic thermal parameters assigned to Mo and I atoms converged to an  $R$  value of 0.042 for 1509 observations and 125 parameters. The  $R_w$  was 0.051 [ $w = (\sigma^2(F_o))^{-1}$ ]. The atomic coordinates are in table 4 and relevant bond distances and angles are in tables 2 (cation) and 5 (anion).



TABLE 4. FRACTIONAL ATOMIC COORDINATES FOR  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]\text{I}_5$  (**2**) WITH E.S.D.'s REFERRED TO THE LEAST SIGNIFICANT FIGURE.

Atom	<i>X/a</i>	<i>Y/b</i>	<i>Z/c</i>
Mo(1)	0.8748(1)	0.2500	0.2118(2)
I(1)	1.0141(1)	0.2500	0.0229(2)
I(2)	0.4642(1)	0.2500	0.1901(3)
I(3)	0.3042(1)	0.2500	0.3569(2)
I(4)	0.1459(1)	0.2500	0.5065(2)
I(5)	0.3266(1)	0.3927(2)	0.7677(2)
O(1)	0.9882(10)	0.5154(15)	0.2994(14)
O(2)	0.8958(14)	0.2500	0.5603(19)
C(1)	0.9486(10)	0.4187(19)	0.2615(16)
C(2)	0.8901(17)	0.2500	0.4374(30)
C(3)	0.7783(9)	0.3264(16)	0.3945(44)
C(4)	0.7495(11)	0.4002(16)	-0.0068(15)
C(5)	0.7273(10)	0.3251(17)	0.1175(16)
C(6)	0.8043(12)	0.4041(22)	0.2444(18)
C(7)	0.7390(14)	0.5530(18)	-0.1439(20)
C(8)	0.6959(13)	0.4074(22)	0.3742(18)

TABLE 5 - BOND DISTANCES (Å) AND ANGLES (deg) FOR THE  $[\text{I}_3\cdot\text{I}_2]^-$  ANION IN COMPOUND **2**

I2-I3	2.955(5)	I2-I3-I4	177.7(1)
I3-I4	2.844(2)		
I5-I5'	2.753(3)		
I2...I5 <sup>i</sup>	3.468(1)		

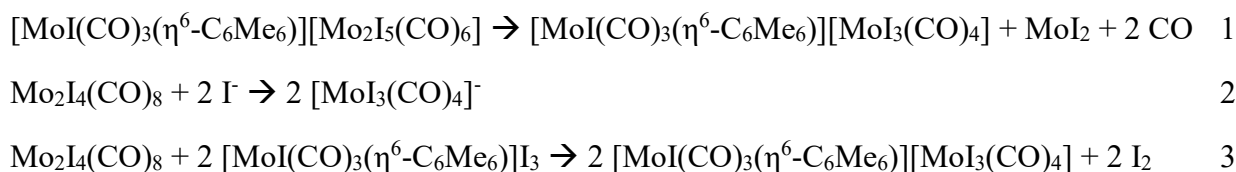
*i* = 1-x,1-y,1-z

Tables of thermal parameters and  $F_o$ - $F_c$  have been deposited as Supplementary Material for both compounds **1** and **2** and can be obtained from Società Chimica Italiana, Viale Liegi 48, I-00198 Roma, Italy, upon full citation of the present article.

## RESULTS AND DISCUSSION

As stated above, we found that  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{Mo}_2\text{I}_5(\text{CO})_6]$ , **3**, thermally decomposes to  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{MoI}_3(\text{CO})_4]$ , **4**. The crystals of the product were recovered together with a powder, believed to be  $\text{MoI}_2$ , see eq. 1. Compounds of the  $[\text{Mo}_2\text{I}_5(\text{CO})_6]^-$  anion with less methyl-

substituted arene groups failed to afford clean products, presumably because of the low stability of the cation. We were able to crystallographically characterise compound **4**, but we could not prepare it in a pure state because of difficulties in its separation from the insoluble MoI<sub>2</sub>. In an attempt to find an alternative synthesis for compound **4**, we considered that the [MoI<sub>3</sub>(CO)<sub>4</sub>]<sup>-</sup> anion could be prepared by reacting Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub> with I<sup>-</sup>, according to eq. 2. We therefore treated Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub> with [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>3</sub> with the hope that a di-iodine molecule would be released from the I<sub>3</sub><sup>-</sup> counter-anion to afford the stoichiometry of eq. 3. Our expectation was not fulfilled, and a compound analysing correctly for the derivative of the new [MoI<sub>5</sub>(CO)<sub>4</sub>]<sup>-</sup> anion was obtained instead. The IR spectroscopic properties (see *Experimental*) were similar to those of the expected compound **4**, thus suggesting that the carbonyl groups have similar arrangements in [MoI<sub>3</sub>(CO)<sub>4</sub>]<sup>-</sup> and in the new anion. An X-ray diffractometric study (*vide infra*) revealed that the latter contains a coordinated I<sub>3</sub> group. The [MoI<sub>3</sub>(CO)<sub>4</sub>]<sup>-</sup> and [MoI<sub>5</sub>(CO)<sub>4</sub>]<sup>-</sup> anions thus differ merely for one of the ligands being I<sup>-</sup> in the former and I<sub>3</sub><sup>-</sup> in the latter. We can therefore better formulate our compound **1** as [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)] [MoI<sub>2</sub>(I<sub>3</sub>)(CO)<sub>4</sub>]<sup>-</sup>.



The formation of the tri-iodide-containing anion can therefore be described as indicated in eq. 4. This shows that the Lewis base power of the I<sup>-</sup> ion, although reduced upon interaction with the Lewis acidity of I<sub>2</sub> in the formation of the I<sub>3</sub><sup>-</sup> ion, is still sufficient to cause the bridge splitting of Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub> required by reaction 4.



We could not prepare compound **4** by using the simple iodide derivative [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I, since the latter is unknown and indications exist<sup>1</sup> suggesting its intrinsic instability.

Figure 1 shows a view of the cation and anion of compound **1**. The cation will be discussed in more detail in a following section, together with that of compound **2**. Will it suffice here to observe that its stoichiometry and arrangement of ligands in a four-legged piano-stool geometry is like those found earlier for other similar  $d^4$  ions.<sup>1,11</sup>

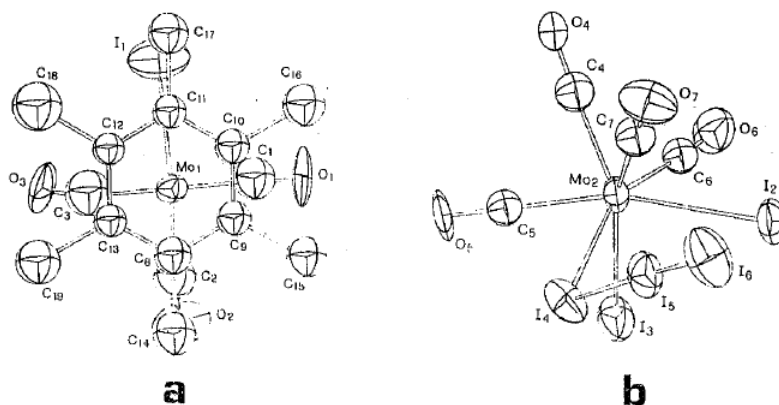
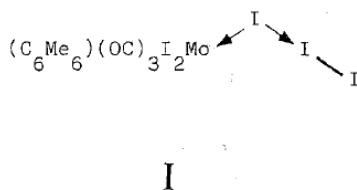


Fig. 1. ORTEP view of the cation (a) and the anion (b) of compound **1**,  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{MoI}_2(\text{I}_3)(\text{CO})_4]$ .

The anion (figure 1b) has substantially the same geometry found<sup>1</sup> for  $[\text{MoI}_3(\text{CO})_5]^-$ , *i.e.* the seven ligands are in a capped octahedral arrangement, the C4 carbonyl group capping the triangular face defined by the other three carbonyl groups. The I<sup>-</sup> and I<sub>3</sub><sup>-</sup> ligands define the opposite triangular face. The ideal  $C_{3v}$  symmetry of  $[\text{MoI}_3(\text{CO})_4]^-$  is reduced to  $C_1$  by the presence of the I<sub>3</sub> ligand. Bond distances and angles related to the coordination of the molybdenum centre agree well with those of the  $[\text{MoI}_3(\text{CO})_4]^-$  anion.<sup>1</sup> The only major difference is the length of the Mo-I<sub>3</sub> bond [2.882(4) Å], slightly but significantly longer than that of the Mo-I bonds [av. 2.860(5) Å]. This is expected on the grounds of a reduced Lewis basicity of the I<sub>3</sub><sup>-</sup> ion with respect to I<sup>-</sup>. The I<sub>3</sub> ligand is practically linear [I4-I5-I6, 176.8(1)°] and binds the molybdenum centre with an angle of 113.0(1)° to the donor atom. Although the existence of the tri-iodide ligand I<sub>3</sub> has been suggested earlier<sup>12a-c</sup> for some species, no transition metal-bonded I<sub>3</sub> ligands have been structurally characterised so far. It is interesting to note that in the nickel(II) compound<sup>12d</sup>  $\text{Ni}[o\text{-C}_6\text{H}_4(\text{PMe}_2)_2]_2(\text{I}_3) \cdot 2\text{I}_2$ , the I<sub>3</sub> group is at non-bonding distance from the central metal atom [ $\text{Ni} \cdots \text{I}_3$ , 3.491(1) Å] and it interacts with an I<sub>2</sub> unit. A somewhat related example is represented by  $\text{Pt}_2(\text{Me}_2\text{CHCS}_2)_4\text{I}_2 \cdot \text{I}_2$ , which shows axial iodide ligands weakly interacting [3.476(2) and 3.518(2) Å] with an I<sub>2</sub> molecule.<sup>12e</sup>

The Mo-I4-I5 angle of 113.0(1)° can be compared with the angle at the central atom of the I<sub>5</sub><sup>-</sup> anion (which is related to the tri-atomic anion of compound **1** if one considers I<sub>5</sub><sup>-</sup> to be the result of the donation of two electrons from I<sub>3</sub><sup>-</sup> to the Lewis acid I<sub>2</sub>), which is, for example, 95° in NMe<sub>4</sub>I<sub>5</sub>,<sup>13</sup> 840 in the KI<sub>3</sub>/KI<sub>5</sub> complex of valinomycin,<sup>14a</sup> 88.18(6)° in [Fe(S<sub>2</sub>CNEt<sub>3</sub>)<sub>3</sub>]I<sub>5</sub>,<sup>14b</sup> 110.1° in (ChinH)I<sub>3</sub>·I<sub>2</sub> (Chin = chinuclidine),<sup>15</sup> 84.8° in (phenacetin)<sub>2</sub>·HI<sub>5</sub>,<sup>16</sup> 90.7 and 96.5° in {[Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Se}<sub>3</sub>·I<sub>3</sub>·I<sub>2</sub>·½CH<sub>2</sub>Cl<sub>2</sub>,<sup>17</sup> 82.1 and 82.7° in [C<sub>6</sub>H<sub>4</sub>N<sub>2</sub>Se·C<sub>6</sub>H<sub>5</sub>N<sub>2</sub>Se]I<sub>3</sub>·I<sub>2</sub>,<sup>18</sup> and finally 86.1(1)° in [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>5</sub> (*vide infra*). The quite wide range of values for such an angle suggests that this parameter is probably highly dependent on packing forces. In the anion of compound **1**, the van der Waals interactions between the I<sub>3</sub><sup>-</sup> group and the I<sup>-</sup> ligands are most likely important too. These interactions might also be responsible for the orientation of the I<sub>3</sub> group, which is along a direction closest to I<sub>2</sub> rather than symmetrical with respect to the bridging iodides and to the C5 and C7 carbonyl groups (in the latter case, the anion would have attained C<sub>s</sub> symmetry).



The I-I bond lengths of the I<sub>3</sub> moiety are quite asymmetric [I4-I5, 3.136(4) Å; I5-I6, 2.753(3) Å], and suggest that the bonding description as an iodide ion simultaneously donating to the Mo(II) and I<sub>2</sub> Lewis acids, see **1**, is best suited to this species. A similar situation is found in the I<sub>5</sub><sup>-</sup> anion, the lengths of the bonds to the central atom being longer than those to the outer atoms {e.g. 3.14 vs. 2.81 Å in NMe<sub>4</sub>I<sub>5</sub>,<sup>13</sup> 3.09 vs. 2.76 Å in the KI<sub>3</sub>/KI<sub>5</sub> complex of valinomycin<sup>14a</sup> and 3.08 vs. 2.82 Å in [Fe(S<sub>2</sub>CNEt<sub>2</sub>)<sub>3</sub>]I<sub>5</sub>,<sup>14b</sup> average value reported}.

A closer examination of the crystalline material obtained in the reaction between Mo<sub>2</sub>I<sub>4</sub>(CO)<sub>8</sub> and [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>3</sub> revealed that a small amount of crystals having a different shape from those of compound **1** was also present. A preliminary crystallographic investigation showed different unit cell parameters from those of compound **1**. A crystallographic study was then undertaken and the compound resulted to have the formulation [MoI(CO)<sub>3</sub>(η<sup>6</sup>-C<sub>6</sub>Me<sub>6</sub>)]I<sub>5</sub>, **2**.

Figure 2 shows a view of the compound. The cation, which lies on a plane of symmetry (C2-O2-Mo1-I1, symmetry group  $C_s$ ), is identical to that of compound **1**. The anion consists of an infinite chain of alternating  $I_3^-$  and  $I_2$  groups and is therefore best described as  $\{[I_3 \cdot I_2]^- \}_\infty$ . The particular arrangement of the  $I_3^-$  and  $I_2$  units, *i.e.* that of a monodimensional polymer, appears to have a precedent only in the structure<sup>12c</sup> of  $Ni[\rho\text{-C}_6\text{H}_4(\text{PMe}_2)_2]_2(\text{I}_3)_2 \cdot 2\text{I}_2$ . The other known compounds containing  $I_5^-$  have the anion either as separate units<sup>13,14</sup> or as a two-dimensional (layered)<sup>15-18</sup> structure. The I-I bond lengths in the  $I_3^-$  moiety of compound **2** are asymmetric [2.955(2) vs. 2.844(2) Å] but not as much as in the discrete  $I_5^-$  anions<sup>13,14</sup> or as in the  $I_3$  ligand of the anion of compound **1** discussed above. The bonding interactions in the anion of compound **2** can be regarded as intermediate between those in the discrete  $I_5^-$  ions<sup>13,14</sup> and those in the two-dimensional polymers,<sup>15-18</sup> the latter always exhibiting a symmetrical  $I_3$  moiety. The contact distance between  $I_3^-$  and  $I_2$  groups [ $I_2 \cdots I_5$ , 3.468(1) Å] and the I-I distance in the  $I_2$  group [2.753(3) Å] are close to those typical of the layered structures (in the ranges 3.45 - 3.76 Å and 2.74 - 2.75 Å, respectively).

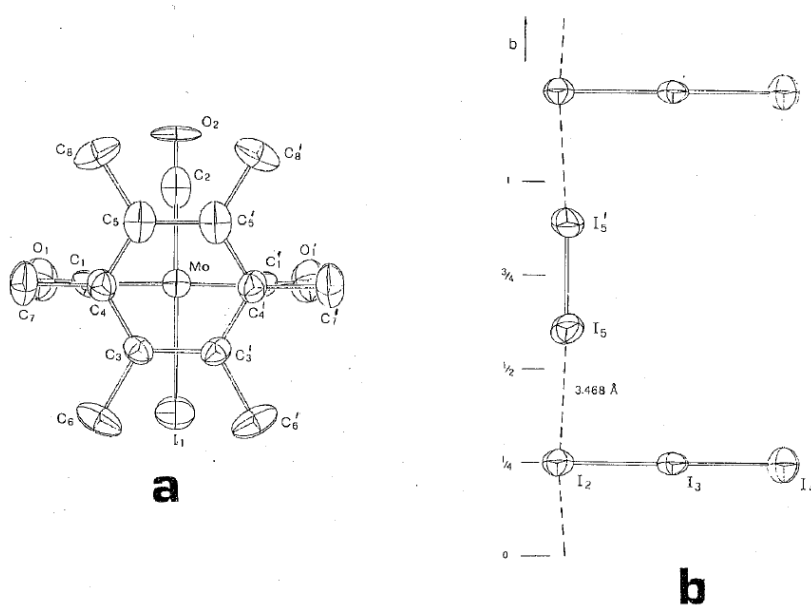
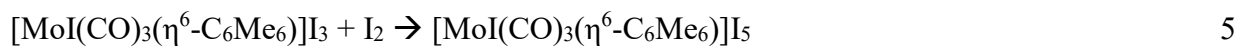


Fig. 2 - ORTEP view of the cation (a) and the anion (b) of compound **2**,  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]\text{I}_5$ .

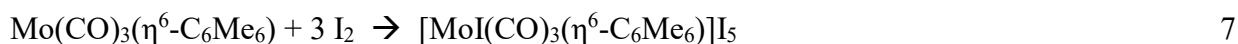
Once established the nature of the minor product of reaction 3, we tried to explain its formation. Compound **2** can be visualized as resulting from the interaction between  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]\text{I}_3$  and a molecule of  $\text{I}_2$ , see eq. 5. We know from previous work that  $\text{Mo}_2\text{I}_4(\text{CO})_8$  can act as a donor of  $\text{I}_2$ , according to eq. 6. Reaction 6 is known to proceed in the opposite direction, but it can be driven

to its right in the presence of a reducing or an I-subtracting agent. The tri-iodide derivative could then be sufficient for this purpose.



We cannot, however, prove this suggestion beyond any doubt since the amount of the hypothetical  $\text{Mo}_2\text{I}_2(\text{CO})_8$  formed according to eq. 6 was too low to allow its certain identification by spectroscopic methods. On the other hand, we were able to show that reaction 5 represents a good method for preparing **2** in gram quantities. The solution IR spectrum of **2** is, as expected, identical to that of the corresponding tri-iodide derivative in the carbonyl stretching region.<sup>1</sup> In addition to elemental analysis, the identity of the product of reaction 5 with the penta-iodide is proved by the determination of the unit cell parameters on a single crystal, which gave values identical, within experimental error, to those of the crystallographically characterised material.

Compound **2** was also obtained by a third method consisting of treating  $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)$  with  $\text{I}_2$  in a 1:3 molar ratio, see eq. 7.

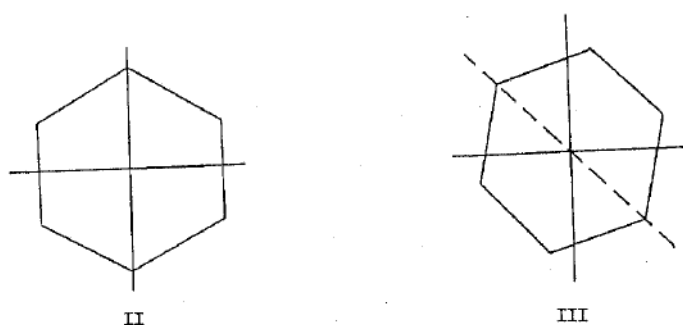


An interesting aspect of these results is the reluctance of molybdenum to be oxidised beyond the +II oxidation state. As a matter of fact, compound **2**, similar to all other compounds of the  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]^+$  cation isolated so far, is indefinitely stable at room temperature, even in air.

#### CATIONS OF COMPOUNDS **1** AND **2**: ORIENTATION OF THE ARENE RING

In Part I of this series of papers,<sup>1</sup> we presented a qualitative discussion about the orientation of the arene ring in half-sandwiched compounds of  $d^4$  cations. The complexes can be regarded as “eclipsed” when two hexagon vertices are along the directions of two of the M-L vectors in the projection along the M-arene axis, as in **II**, and “staggered” when the arene hexagon is rotated by

15°, as in **III**, with respect to the “eclipsed” situation. In ref. 1 we also presented the first structurally characterized “staggered” complexes, namely  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]^+$  (with  $[\text{Mo}_2\text{I}_5(\text{CO})_5]^-$  as counteranion) and  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]^+$  (with the counteranion  $[\text{MoI}_3(\text{CO})_4]^-$ , compound **4**). The conclusion was reached that steric effects win over the electronic ones for those cations, and that both these effects must indeed be very small. The suggestion was made<sup>1</sup> that packing forces may be sufficient to cause the rearrangement from one conformation to the other for the same cation. This hypothesis is now fully confirmed by the results presented in this paper: the cation  $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)]^+$ , which is common to compounds **1**, **2** and **4** is eclipsed (type **II**) in compounds **1** and **2** (see figures 1 and 2), while is staggered (type **III**) in compound **4**. The comparison between **1** and **4** is particularly striking, since the only difference there is  $\text{I}_3^-$  vs.  $\text{I}^-$  for one of the ligands in the anion. This is yet sufficient to determine a different orientation of the arene ligand in the solid state.



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