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OXIDATION OF η^6 -ARENE COMPLEXES OF GROUP VI METALS. II*. A CONVENIENT PREPARATION OF $\text{Mo}_2\text{I}_4(\text{CO})_8$, ITS REACTIVITY AND ITS CRYSTAL AND MOLECULAR STRUCTURE ()**

FAUSTO CALDERAZZO (°) and RINALDO POLI (*)**

Dipartimento di Chimica e Chimica Industriale, Sezione di Chimica Inorganica, Università di Pisa, via Risorgimento 35, I-56100 Pisa, Italy

PIER FRANCESCO ZANAZZI

Dipartimento di Scienze delle Terra, Sezione Cristallografia, Università di Perugia, p.za Università, I-06100 Perugia, Italy

Summary – The ionic $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene})][\text{Mo}_2\text{I}_5(\text{CO})_6]$ compounds (arene = $\text{C}_6\text{H}_5\text{Me}$, **2**; 1,4- $\text{C}_6\text{H}_4\text{Me}_2$, **3**; 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, **4**) react with CO at atmospheric pressure and room temperature in toluene to give $\text{Mo}_2\text{I}_4(\text{CO})_8$, **1**, in yields as high as 88%. Compound **1** has been studied by X-ray diffraction methods. Crystal data: triclinic, space group $P-1$, $a = 10.242(3)$, $b = 7.331(3)$, $c = 6.937(3)$ Å. $\alpha = 112.88(2)$, $\beta = 102.93(2)$, $\gamma = 81.00(2)^\circ$, $Z = 1$, $R = 0.041$ for 495 observed reflections. Disproportionation of **1** into MoI_3 and $\text{Mo}_2\text{I}_2(\text{CO})_8$ has been observed by interaction with water or by thermal treatment in toluene. Compound **1** reacts with Lewis bases to afford $\text{MoI}_2(\text{CO})_3\text{L}_2$ and with $[\text{NBu}_4]\text{I}$ to yield the $[\text{MoI}_3(\text{CO})_4]^-$ anion. Reduction of **1** to $\text{Mo}_2\text{I}_2(\text{CO})_8$ can be accomplished with a number of reducing agents.

(*) For Part I, see ref. 5.

(**) Work supported by the Consiglio Nazionale delle Ricerche (CNR, Roma) and by the Ministero della Pubblica Istruzione (MPI).

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

(***) Present address: University of Maryland, Department of Chemistry and Biochemistry, College Park, Maryland 20742, U.S.A.

(°) To whom correspondence should be addressed.

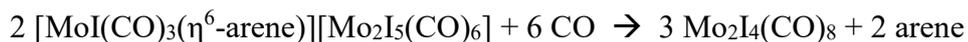
Although the oxidation of $\text{Cr}(\text{CO})_6$ by di-halogens affords chromium(III) halides,¹ the halocarbonyl complexes of molybdenum and tungsten, $\text{M}_2\text{X}_4(\text{CO})_8$, ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{Cl}, \text{Br}$) can be isolated by oxidizing $\text{M}(\text{CO})_6$, $\text{M} = \text{Mo}, \text{W}$, under mild conditions.² The corresponding iodides have been reported to be formed by reacting $\text{M}(\text{CO})_6$, $\text{M} = \text{Mo}, \text{W}$ with I_2 under photolytic conditions.³ However, only the tungsten derivative, $\text{W}_2\text{I}_4(\text{CO})_8$, was isolated in good yields. The reaction of $\text{Mo}(\text{CO})_6$, with I_2 was reported to give a mixture of products, among which $\text{Mo}_2\text{I}_4(\text{CO})_8$, **1**, was isolated in small amounts. No subsequent paper concerning compound **1** has been published ever since.

While we investigated the catalytic activity of I_2 in the carbonylation of $\text{Mo}(\eta^6\text{-arene})(\text{CO})_3$ to $\text{Mo}(\text{CO})_6$,⁴ we discovered that the ionic⁵ $[\text{MoI}(\eta^6\text{-arene})(\text{CO})_3][\text{Mo}_2\text{I}_5(\text{CO})_6]$ (arene = $\text{C}_6\text{H}_5\text{Me}$, **2**; 1,4- $\text{C}_6\text{H}_4\text{Me}_2$, **3**; 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, **4**) complexes readily take carbon monoxide up to yield **1** in good yields. The possibility of isolating compound **1** in gram quantities by this synthetic route allowed us to study its reactivity in some detail for the first time, which we report in this paper together with its crystal and molecular structure^a.

RESULTS AND DISCUSSION

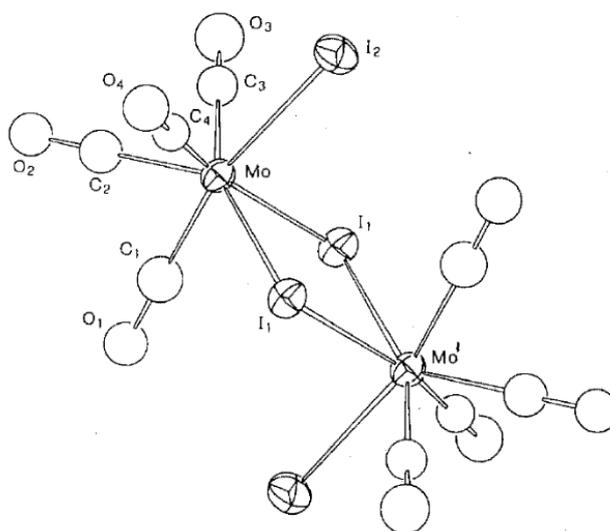
The $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene})][\text{Mo}_2\text{I}_5(\text{CO})_6]$ complexes⁵ (arene = $\text{C}_6\text{H}_5\text{Me}$, **2**; 1,4- $\text{C}_6\text{H}_4\text{Me}_2$, **3**; 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, **4**) absorb CO in toluene at room temperature to afford $\text{Mo}_2\text{I}_4(\text{CO})_8$, **1**, in good yields. Since the complexes **2-4** are readily prepared by di-iodine oxidation of the corresponding molybdenum(0) tricarbonyl-arene derivatives, compound **1** can be conveniently synthesized from the latter in a two-step single-flask reaction. The first oxidation step must be carried out under an inert atmosphere and carbon monoxide was introduced into the system after the oxidation was over. By operating under these conditions, no carbonyl compound other than **1** was detected spectroscopically; since compound **1** was isolated in yields as high as 88% from $\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{Me})(\text{CO})_3$, both the cation and the anion of complexes **2-4** must be involved in the formation of **1**. This suggests that the stoichiometry is that shown in equation 1.

^a Papers dealing with the reactivity of $\text{Mo}_2\text{I}_4(\text{CO})_8$ with nitrogen and phosphorus donor atoms have recently appeared: 1) F.A. COTTON, R. POLI, *Inorg. Chem.*, 25, 3703 (1986); 2) *ibid.*, 25, 3624 (1986). We are grateful to the Authors for sending copies of these papers prior to publication.



1

A number of papers suggested^{3,6,7} a dinuclear, halide-bridged structure for $\text{Mo}_2\text{X}_4(\text{CO})_8$ ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{halide}$), but no X-ray crystallographic studies had appeared in the literature at the beginning of this work. We therefore undertook an X-ray analysis on a single crystal of compound **1**. While this work was in progress, a paper by Cotton and coworkers appeared reporting⁸ the crystal and molecular structure of $\text{W}_2\text{Br}_4(\text{CO})_8$. Thus, our results complement those referring to the tungsten(II) derivative. The molecular structure of **1**, as shown in the figure, is in agreement with earlier suggestions: the molybdenum centre is hepta-coordinated, the C2 carbonyl group being the capping ligand of the basic capped octahedral structure. The two capped octahedra share the I1-I1' edge. However, contrary to an earlier suggestion,³ the two terminal iodides are in a relative trans configuration, the molecule thus exhibiting an approximate C_{2h} symmetry. In agreement with the capped octahedral geometry, the I2-Mo-(μ -I) bond angles are close to 90° , while the I1-Mo-I1' angle is smaller (84.2°), certainly due to steric requirements in the bridge. The average angle at molybdenum between the capping C2 and the other carbonyl groups is $73.3(12)^\circ$, to be compared with $75.7(6)^\circ$ in the $[\text{MoI}_3(\text{CO})_4]^-$ anion. The Mo-I bond length is, as expected, shorter in the terminal iodide bond [$2.885(2) \text{ \AA}$] than in the bridging ones [average, $2.895(3) \text{ \AA}$]. The Mo \cdots Mo separation of $4.298(5) \text{ \AA}$ is in agreement with the absence of any metal-metal interaction, see table 1.



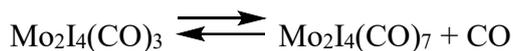
A view of the $\text{Mo}_2\text{I}_4(\text{CO})_8$ molecule with the numbering scheme used.

TABLE 1 - RELEVANT BOND DISTANCES (Å) AND ANGLES (deg) FOR Mo₂I₄(CO)₈ WITH E.S.D.'S IN PARENTHESES

Mo-I(1)	2.896(3)	I(2)-Mo-C(1)	155.5(9)
Mo-I(1)'	2.894(2)	I(2)-Mo-C(2)	123.3(9)
Mo-I(2)	2.855(2)	I(2)-Mo-C(3)	74.3(8)
Mo-C(1)	1.960(28)	I(2)-Mo-C(4)	74.9(7)
Mo-C(2)	1.927(25)	I(2)-Mo-I(1)'	91.6(1)
Mo-C(3)	2.025(29)	C(1)-Mo-C(2)	71.2(13)
Mo-C(4)	2.022(27)	C(1)-Mo-C(3)	113.5(12)
O(1)-C(1)	1.215(32)	C(1)-Mo-C(4)	111.3(12)
O(2)-C(2)	1.171(30)	C(1)-Mo-I(1)'	78.4(9)
O(3)-C(3)	1.115(35)	C(2)-Mo-C(3)	74.1(12)
O(4)-C(4)	1.127(33)	C(2)-Mo-C(4)	74.5(11)
		C(2)-Mo-I(1)'	126.8(9)
I(1)-Mo-I(2)	90.5(1)	C(3)-Mo-C(4)	111.6(11)
I(1)-Mo-C(1)	78.2(9)	C(3)-Mo-I(1)'	79.6(8)
I(1)-Mo-C(2)	128.5(9)	C(4)-Mo-I(1)'	158.6(7)
I(1)-Mo-C(3)	157.3(8)	Mo-I(1)-Mo'	95.8(1)
I(1)-Mo-C(4)	79.5(7)	Mo-C(1)-O(1)	177.8(25)
I(1)-Mo-I(1)'	84.2(1)	Mo-C(2)-O(2)	178.7(25)
		Mo-C(3)-O(3)	177.8(26)
		Mo-C(4)-O(4)	178.4(23)

The primed atoms are related to the unprimed ones by the symmetry operation 1-x, 2-y, 1-z.

The formation of compound **1** from **2-4** has been carried out in a gasvolumetric apparatus and final molar ratios (absorbed CO/Mo) of about 0.6 were repeatedly obtained for *dilute solutions*, instead of the expected value of 1, if the reaction of equation 1 was exclusively operating under these conditions. Moreover, when an analytically pure sample of Mo₂I₄(CO)₈ was dissolved in toluene under an atmosphere of carbon monoxide, a small but significant amount of CO was evolved. Such loss of CO had been observed earlier with Mo₂X₄(CO)₈⁷ and it had been attributed to traces of oxygen or moisture in the solvent. In our hands, however, Mo₂I₄(CO)₈ underwent loss of CO even in a carefully dried solvent and under a carbon monoxide atmosphere. We therefore prefer to postulate an equilibrium between Mo₂I₄(CO)₈ and a species with a lower CO content, probably Mo₂I₄(CO)₇, **5**, whose structure should contain three bridging iodides instead of two, in order to attain the 18-electron configuration for each molybdenum. This hypothesis is supported by the recent isolation⁸ of W₂Br₄(CO)₇. The intervention of the solvent (an aromatic hydrocarbon) in equilibrium 2 should be excluded by the IR observations, *vide infra*.

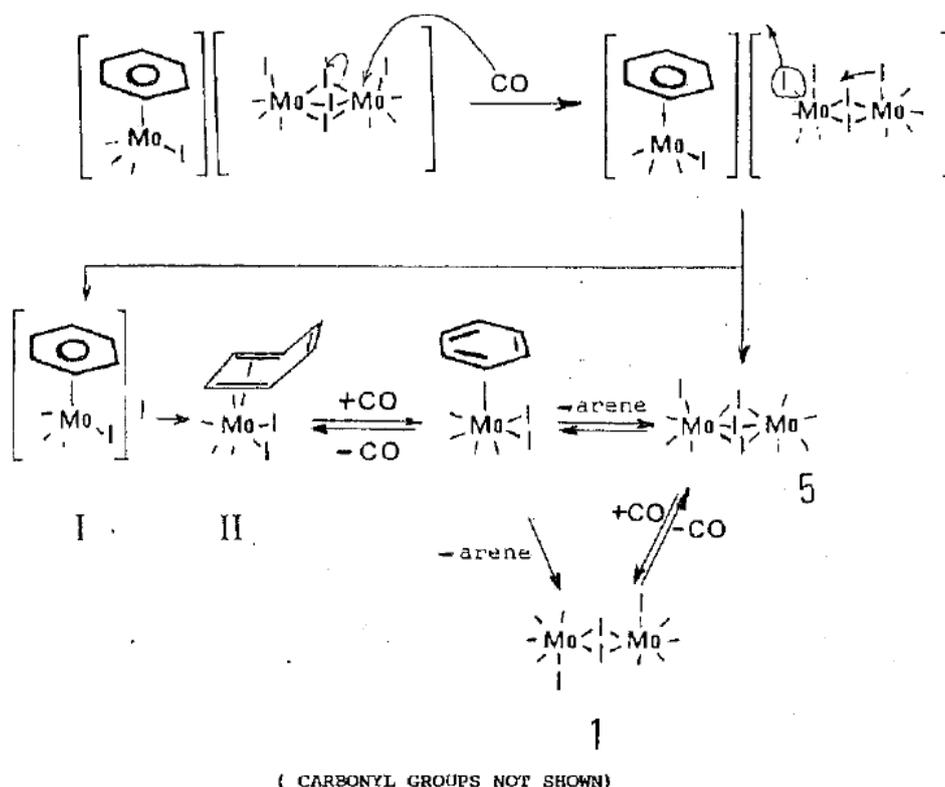


2

From the gasvolumetric results, a maximum yield of 60% of compound **1** should be expected when operating in dilute solution. A higher yield was nevertheless obtained, although a small amount of the heptacarbonyl in admixture with **1** cannot be excluded. On the other hand, higher yields of **1** can be attributed to its precipitation from the highly concentrated solutions initially employed, thus shifting equilibrium 2 to its left.

Reaction 1 is remarkable in that an ionic product undergoes a fast CO absorption affording a neutral molecule. Since both the cation and the anion must contribute to the formation of the observed product, we suggest a reaction pathway similar to that shown in the scheme. In view of its presumably easy bridging-to-terminal iodide interconversion, the $[\text{Mo}_2\text{I}_5(\text{CO})_6]^-$ anion is likely to be highly reactive towards CO. The resulting species would then transfer an iodide to the $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene})]^+$ cation to form **5** and the iodides **I** or **II**. The uncharged iodide **II** was suggested⁵ to be the initial product of the $\text{I}_2\text{-Mo}(\text{CO})_3(\eta^6\text{-arene})$ interaction eventually leading to the ionic compounds **2-4**. Addition of CO to either **5** or **II** could then lead to **1** by the routes indicated in the scheme.

SCHEME



According to the approximate C_{2h} symmetry observed in the solid state, four IR-active CO stretching vibrations ($A_u + 3 B_u$) are expected for **1**. However, five bands were observed in toluene solution. We believe this to be due to equilibrium 2; a possible intervention of the solvent is excluded since the same spectrum was observed in non-coordinating solvents such as *n*-pentane and dichloromethane. The spectra had to be measured in CaF_2 cells; KBr cells originated new bands closely resembling the pattern reported³ for $Mo_2I_4(CO)_8$, presumably due to bromide-containing species.

In order to exclude the intervention of moisture in the observed loss of CO from solutions of **1**, a toluene solution of **1** was reacted with a small amount of water. Gas evolution was observed, the reaction giving rise, however, to a dark brown precipitate and to a yellow solution containing the known⁹ molybdenum(I) dimer $Mo_2I_2(CO)_8$ as the only carbonyl species detectable by IR. The brown solid is most probably MoI_3 , see equation 3, the driving force for the disproportionation being the hydration of MoI_3 . Disproportionation 3 was observed even in the absence of water, in refluxing toluene, both MoI_3 and $Mo_2I_2(CO)_8$ being isolated from the thermal reaction.



Compound **1** quickly reacts with donor solvents with CO evolution and formation of the tricarbonyl species $MoI_2(CO)_3L_2$, see equation 4. These compounds were characterized in solution by their IR spectra [ν_{CO} : 2032s, 1961s, 1940sh cm^{-1} (L = MeCN); 2018s, 1960s, 1947sh cm^{-1} (L = THF); 2022s, 1941s (asymmetric) cm^{-1} (L = Et_2O), in the corresponding L as solvent]. The spectrum for L = MeCN compares well with that of an authentic sample, obtained⁵ by oxidation of $Mo(CO)_3(MeCN)_3$ with di-iodine. The acetonitrile complex of molybdenum(II) has recently been reported¹⁰ independently. The reactivity found for $Mo_2I_4(CO)_8$ is similar to that observed¹¹ with other $Mo_2X_4(CO)_8$ complexes (M = Mo, W; X = halide).



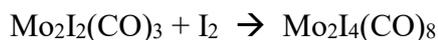
The reaction of **1** with NBu_4I is analogous to those already reported⁷ for $\text{M}_2\text{X}_4(\text{CO})_8$ ($\text{M} = \text{Mo}, \text{W}; \text{X} = \text{halide}$) reacting with X^- leading to the $[\text{MX}_3(\text{CO})_4]^-$ anion.⁷ As a matter of fact, a solution with carbonyl stretching vibrations at 2072s, 2010s and 1945m cm^{-1} (in dichloromethane as solvent) assigned to the $[\text{MoI}_3(\text{CO})_4]^-$ anion^{12,13} was obtained. In view of equilibrium 2, one would expect compound **1** to react with one equivalent of iodide to produce the $[\text{Mo}_2\text{I}_5(\text{CO})_6]^-$ anion present in compounds **2-4**.⁵ However, IR monitoring of the reaction showed that $[\text{MoI}_3(\text{CO})_4]^-$ and unreacted **1** are the only species present in solution. If we compare this result with the observed⁵ decomposition of $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{Mo}_2\text{I}_5(\text{CO})_6]$ to $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{MoI}_3(\text{CO})_4]$ and MoI_2 , we find evidence for the intrinsic low stability of the $[\text{Mo}_2\text{I}_5(\text{CO})_6]^-$ anion.



Treatment of compound **1** with selected reducing agents afforded the molybdenum(I) dimer⁹ $\text{Mo}_2\text{I}_2(\text{CO})_8$, see equation 6. A reducing agent with specific properties had to be chosen, namely: *a*) it had to be active in an inert solvent such as toluene or dichloromethane, in view of the reported reaction of compound **1** with donor solvents, see equation 4; *b*) it had to be void of donor properties. These requirements are met by $\text{RhCl}(\text{PPh}_3)_2(\text{CO})$ which is known^{14,15} to oxidatively add di-iodine to give rhodium(III) derivatives; by Bi_2Ph_4 which, unlike its Group congeners E_2Ph_4 ($\text{E} = \text{P}, \text{As}, \text{Sb}$), has practically no Lewis donor properties¹⁶ and reacts¹⁷ with I_2 to form BiPh_2I ; by elemental tellurium and by $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)$. In each case, the formation of $\text{Mo}_2\text{I}_2(\text{CO})_8$ was confirmed spectroscopically.



The nature of the oxidized species was not investigated with the exception of the product resulting from the reduction by $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)$, which was shown to be the known⁵ $[\text{MoI}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)][\text{MoI}_3(\text{CO})_4]$. This is also the ultimate product of the di-iodine oxidation of $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{Me}_6)$. The octacarbonyldimolybdenum(I) derivative, $\text{Mo}_2\text{I}_2(\text{CO})_8$, reacts with the stoichiometric amount of I_2 in dichloromethane to give **1** back, according to equation 7.



7

EXPERIMENTAL

Unless otherwise stated, all of the operations were carried out under an atmosphere of prepurified dinitrogen or argon. Solvents were carefully dried by conventional methods prior to use. The IR spectra were measured with a Perkin-Elmer 283 instrument equipped with grating; solution spectra in the carbonyl stretching region were measured on expanded abscissa scale and calibrated with both CO and water vapour; the wavenumber values are believed to be accurate to $\pm 1 \text{ cm}^{-1}$.

The gasvolumetric experiments were carried out in a gas-volumetric burette equipped with a thermostatic system, as described elsewhere.¹⁸ Elemental analyses were by the microanalytical laboratory of the Facoltà di Farmacia, Università di Pisa. The arene complexes of molybdenum(0), $\text{Mo}(\text{CO})_3(\eta^6\text{-arene})$, arene = $\text{C}_6\text{H}_5\text{Me}$;¹⁹ 1,4- $\text{C}_6\text{H}_4\text{Me}_2$;¹⁹ 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$ ²⁰ and $[\text{MoI}(\text{CO})_3(\eta^6\text{-arene})][\text{Mo}_2\text{I}_5(\text{CO})_6]$ ⁵ (arene as above) were prepared according to the literature.

REACTION OF COMPOUNDS $[\text{MoI}(\text{CO})_3(\eta^6\text{-ARENE})][\text{Mo}_2\text{I}_5(\text{CO})_6]$ (ARENE = $\text{C}_6\text{H}_5\text{Me}$, **2**; 1,4- $\text{C}_6\text{H}_4\text{Me}_2$, **3**; 1,3,5- $\text{C}_6\text{H}_3\text{Me}_3$, **4**) WITH CO. PREPARATION OF $\text{Mo}_2\text{I}_4(\text{CO})_8$, **1**

Preparative experiment - Compound **2** was prepared in situ from the toluene derivative $\text{Mo}(\text{CO})_3(\eta^6\text{-C}_6\text{H}_5\text{Me})$ (3.44 g; 12.64 mmol) and I_2 (3.22 g; 12.69 mmol) in toluene (100 ml) by dropwise addition of the oxidant in about 20 min at a temperature not higher than 20 °C. At the end of the I_2 addition, the volume was reduced to about 50 ml by evaporation under reduced pressure. The reaction mixture was then saturated with CO at atmospheric pressure. Within 30 min, gas absorption was noted while the brown solid disappeared to give rise to **1** as a red precipitate. Stirring was continued overnight. The product was collected by filtration, washed with *n*-pentane and dried in vacuo (5.16 g; 88% yield)^b. The product had an IR spectrum (ν_{CO} , toluene, measured under CO, CaF_2 cells: 2098m, 2040s, 1992sh, 1973m, 1951w cm^{-1}) identical to that of an analytically pure sample. The latter was obtained by dissolving the crude product in toluene under CO, and then adding

^b The compound is indefinitely stable at temperatures not higher than 0 °C.

pentane and cooling to about -30 °C. Satisfactory elemental analyses were obtained for this product. A single crystal from this crop was obtained for the X-ray diffractometric study.

Gasvolumetric experiment - Compound **2** (0.40 g) was suspended in 20 ml of toluene and, by operating under carbon monoxide in the gasvolumetric burette, CO was found to be absorbed at room temperature up to a CO/Mo molar ratio of 0.59. In another gasvolumetric experiment, compound **1** (0.24 g) was dissolved in toluene (25 ml) under CO. Gas evolution was observed, corresponding to a CO/Mo molar ratio of 0.2. In both experiments, the final solution had the same IR spectrum as that reported above for compound **1**. Similarly, compounds **3** and **4** absorbed CO in toluene at room temperature to final CO/Mo molar ratios of 0.63 and 0.61, respectively. The final solutions showed again the IR spectrum reported above for compound **1**.

THERMAL TREATMENT OF Mo₂I₄(CO)₈ IN TOLUENE

Compound **1** (1.22 g; 1.32 mmol) was shortly (for about 10 min) refluxed in toluene (30 ml) to give a suspension of a dark brown solid in an intensely coloured yellow solution. The latter had IR bands at 2051m, 1990s and 1980s cm⁻¹. Gas evolution was noted during this treatment. The solid was filtered off and the solution was evaporated to dryness to leave a black residue. This was recrystallised from hot *n*-heptane to afford 0.15 g of black crystals, identified as Mo₂I₂(CO)₈⁹ from the analytical and spectroscopic properties. The filtered solid still contained bonded CO, as evidenced by the CO stretching vibrations (Nujol) at 2050m, 2010s and about 1950s,br cm⁻¹. The solid was suspended in 25 ml of toluene and the thermal treatment was repeated for additional 2 h. The resulting black solid, recovered by filtration (0.6 g) analysed satisfactorily for MoI₃.

REACTION OF COMPOUND **1** WITH H₂O

Treatment of a toluene solution of **1** with a few drops of water resulted in a rapid gas evolution and precipitation of a dark solid, while the colour of the solution turned to yellow. The organic layer had an IR spectrum in the carbonyl stretching region consistent with the presence of Mo₂I₂(CO)₈ as the only carbonyl species present.

COLLECTION AND REDUCTION OF X-RAY DATA

A crystal of dimensions (mm) 0.20 x 0.15 x 0.10 was mounted on a computer-controlled Philips PW 1100 diffractometer equipped with graphite-monochromatized Mo- $K\alpha$ radiation. The crystals are triclinic. The cell dimensions, determined by least-squares calculation based on the setting angles of 25 reflections with 2θ angles ranging between 10 and 20° , are: $a = 10.242(3)$, $b = 7.331(3)$, $c = 6.937(3)$ Å, $\alpha = 112.88(2)$, $\beta = 102.93(2)$, $\gamma = 81.00(2)^\circ$. The space group is $P-1$ (from intensity distributions statistics). The calculated density for one dimeric $\text{Mo}_2\text{I}_4(\text{CO})_8$ molecule in the unit cell is 3.287 g cm^{-3} , the absorption coefficient for Mo- $K\alpha$ is $\mu = 78.76 \text{ cm}^{-1}$.

The intensities were collected up to $2\theta = 40^\circ$; the ω - 2θ scan technique was employed, the scan range being 1.4° and the speed $0.05^\circ \text{ s}^{-1}$. A total of 873 independent reflections were measured, of which 378, having $I \leq 3\sigma(I)$ 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 polarisation factors. A semiempirical absorption correction was applied on the basis of the variation in intensity during the azimuthal scans of some reflections according to the method of North and coworkers;²¹ the transmission factors were in the range 0.99-0.73.

The structure was solved by the Patterson method and refined by the full-matrix least-squares method with the SHELX-7622 package of programs. Anisotropic thermal parameters were refined for iodine and molybdenum atoms. The refinement converged to R (unweighted) = 0.041 and R (weighted) = 0.042 for 60 parameters and 495 observed reflections [$R_w = (\sum w(|F_o| - |F_c|)^2)^{1/2} / (\sum w F_o^2)^{1/2}$, $w = (\sigma^2(F_o) + 0.0032 F_o^2)^{-1}$]. The atomic scattering factors were taken from ref. 22 for oxygen and carbon and from ref. 23 for molybdenum and iodine; the correction for anomalous dispersion was included. Fractional atomic coordinates are in table 2 and relevant bond distances and angles are in table 1. Supplementary material (structure factors tables, 3 pages, and anisotropic and isotropic thermal parameters) has been deposited with the Editor and can be obtained from Società Chimica Italiana, Viale Liegi 48, I-00198 Roma, Italy, upon full citation of the present article.

TABLE 2. FRACTIONAL ATOMIC COORDINATES FOR $\text{Mo}_2\text{I}_4(\text{CO})_8$ WITH E.S.D.'s IN PARENTHESES.

Atom	X/a	Y/b	Z/c
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Mo	0.7085(2)	0.8936(3)	0.5257(3)
I(1)	0.4609(2)	0.7896(3)	0.2236(3)
I(2)	0.7520(2)	1.1384(3)	0.3218(3)
O(1)	0.5741(20)	0.6706(28)	0.7338(29)
O(2)	0.9283(20)	0.6205(29)	0.6902(29)
O(3)	0.9240(22)	1.1738(34)	0.8574(34)
O(4)	0.8205(21)	0.5993(31)	0.1177(33)
C(1)	0.6250(32)	0.7528(49)	0.6502(51)
C(2)	0.8447(31)	0.7218(45)	0.6259(51)
C(3)	0.8493(31)	1.0727(46)	0.7370(47)
C(4)	0.7818(27)	0.7032(42)	0.2655(45)

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