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# Synthesis of $Mo_2X_4(PMe_3)_4$ ($Mo\overset{4}{-}Mo$) (X = Cl, Br, I) Compounds by Decarbonylation of $Mo_2X_4(CO)_8$ and by Comproportionation of $Mo(CO)_6$ and $MoX_3(PMe_3)_3$. X-ray Crystal Structure of $Mo_2I_4(PMe_3)_4\cdot 2THF$

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Since the discovery of multiple metal-metal bonds,[1] many compounds have been synthesized and their physicochemical properties studied. Most of the chemical reactivity studies have, however, been restricted to simple ligand substitution reactions.[2] This is especially true in the quadruply bonded dimolybdenum(II) chemistry, which is the richest in the metal-metal multiple bond field;[2] in fact, with only a few exceptions, all such compounds are synthesized *via* the molybdenum(II) acetate, $Mo_2(OAc)_4$. The reaction of $Mo(CO)_6$ with acetic acid to afford $Mo_2(OAc)_4$[3] is therefore by far the most important route to assemble the quadruple bond between molybdenum(II) centers. The exceptions alluded to above are the reaction of $MoX_3$ (X = Cl, Br) with amines and phosphines,[4] the reduction of $MoCl_4$ with sodium amalgam in the presence of phosphines,[5] the reaction of $MoH_4(PMePh_2)_4$ with hydrochloric acid,[6] and the reduction of $Mo_2X_9^{3-}$ by the Jones reductor.[7]

Recently we discovered a novel route to the $Mo_2^{4+}$ core, i.e., the decarbonylation of the molybdenum(II) carbonyl derivative $Mo_2I_4(CO)_8$[8] in the presence of the appropriate ligand, and this one reaction has been the subject of a preliminary communication.[9] We describe here in more detail that reaction and a considerable range of related chemistry. Further studies carried out by us on this system revealed that, depending on the nature of the ligand and/or the solvent, two different pathways can be followed, i.e., formation of quadruply bonded dimers or disproportionation to Mo(0) and Mo(III) compounds. For example, $Mo_2I_4(CO)_8$ and $PR_2Ph$ (R = Me, Et) reacted in refluxing toluene to afford $Mo_2I_4(PR_2Ph)_4$ as the main product, while *cis*-$Mo(CO)_4(PR_2Ph)_2$ and *fac*-$Mo(CO)_3(PR_2Ph)_3$ were detected in solution by IR spectroscopy and *mer*-$MoI_3(PMe_2Ph)_2(POMe_2Ph)$ was also isolated in small amounts and characterized by X-ray crystallography.[10] On the other hand, when the reaction of $Mo_2I_4(CO)_8$ and $PEt_2Ph$ was performed in refluxing tetrahydrofuran, the quadruply bonded dimer was not produced and the products were instead Mo(0) carbonyl derivatives and $[PHEt_2Ph][MoI_4(PEt_2Ph)_2]$.[10] This led us to consider the intermediacy of a dicarbonyl mononuclear adduct that could, depending on the conditions, lead on the one hand to disproportionation or on the other hand to processes of dimerization and decarbonylation that afford $Mo_2I_4L_4$. This hypothesis was based on the existence in the literature of $MoX_2(CO)_2L_2$ (X = Cl, Br, I) derivatives, L being a soft donor ligand, obtained by subjecting $MoX_2(CO)_3L_2$ to "slightly" forcing conditions (generally reflux in a solvent such as $CH_2Cl_2$ or $CHCl_3$).[11] The room-temperature interaction of $Mo_2X_4(CO)_8$ with several ligands L is known to afford mononuclear $MoX_2(CO)_3L_2$ compounds.[12] Also, $MoX_2(CO)_3L_2$ compounds with hard donor ligands such as THF, pyridine, nitriles and others, have been shown to be unstable at room temperature or above with respect to disproportionation to Mo(0) and Mo(III) derivatives.[13,14]

**Table I.** Analytical and Spectroscopic Properties of $Mo_2X_4(PMe_3)_4$ (X = I, Br, Cl)

| | X | $^1H$ NMR,[a] $\delta$ | $^{31}P$ NMR,[a,b] $\delta$ | anal.[c] % C | anal.[c] % H |
|---|---|---|---|---|---|
| 1 | I | 1.76 s, br | −14.98 s | 14.5 (14.4) | 3.8 (3.6) |
| 2 | Br | 1.57 s, br | −11.45 s | 17.6 (17.7) | 4.4 (4.4) |
| 3 | Cl | 1.47 s, br | −9.27 s | | |

[a] Solvent = $C_6D_6$. [b] Reference = external 85% $H_3PO_4$. [c] Calculated values in parentheses.

In an effort to clarify the potentially complex relationships between all these different compounds we studied the $Mo_2I_4(CO)_8$–$PMe_3$ system in more detail. We report here the results of these studies, which have led to the discovery of yet another route to $Mo_2X_4(PR_3)_4$ complexes, i.e. comproportionation of Mo(0) and Mo(III) complexes.

## Experimental Section

All operations were carried out under an atmosphere of prepurified argon with standard Schlenk tube techniques. Solvents were dried by conventional methods and distilled under dinitrogen prior to use. Instruments used were as follows: IR, Perkin-Elmer 783; $^1H$-NMR, Varian EM390; $^{31}P$-NMR, Varian XL200; UV/visible, Cary 17. Solution IR spectra were recorded on an expanded abscissa and calibrated with both CO(g) and $H_2O$(g); band positions are believed to be accurate to ±1 $cm^{-1}$. Elemental analyses were by Galbraith Laboratories Inc., Knoxville, TN. The following materials were prepared according to known procedures: $Mo_2I_4(CO)_8$,[8b,c] $MoI_3(PMe_3)_3$.[15]

**Reaction of $Mo_2I_4(CO)_8$ with $PMe_3$. Preparation of $Mo_2I_4(PMe_3)_4$ (1). A. In Toluene.** A 0.17-g sample of $Mo_2I_4(CO)_8$ (0.18 mmol) was treated with 70 $\mu$L of $PMe_3$ (0.70 mmol) in 10 mL of toluene. Evident gas evolution occurred, resulting in the production of a yellow solution and some flocculent yellow solid. The solution had IR bands at 2022 s, 1982 s, 1952 s, 1912 s, 1898 s, and 1885 sh $cm^{-1}$. After 3 h of stirring at room temperature, the IR spectrum had not changed. The mixture was then refluxed for ca. $^1/_2$ h, during which time the color turned emerald green. At this point the solution had the following IR bands: 2071 vw, 2022 s, 1982 m, 1952 s, ca. 1940 sh, and 1912 s $cm^{-1}$. Reflux was continued for 4 h more. The final solution was blue and showed no significant IR absorption due to carbonyl groups. After filtration, the solution was evaporated to dryness and the blue residue recrystallized from hot *n*-hexane (10 mL). After the mixture was cooled to −20 °C, the solution was decanted from the blue crystals, which were then dried in vacuo. Yield: 0.08 g (44%). IR (Nujol mull/$cm^{-1}$): 1420 m, 1415 sh, 1295 m, 1280 m, 1165 w, 900 s, 850 w, 730 m, 670 w, 345 w, 335 w. Elemental analyses and UV/visible, $^1H$ NMR, and $^{31}P$ NMR spectroscopic properties are reported in Table I.

An independent experiment was carried out under the same conditions, except that the solution was refluxed only for a short period to give an IR spectrum similar to that obtained after $^1/_2$ h in the above-described experiment. This mixture was evaporated to dryness, and the residue was dissolved again in toluene. The resulting solution had the same IR spectroscopic properties, with the exception of the band at 1982 $cm^{-1}$, associated with $Mo(CO)_6$, which was no longer present. This solution was chromatographed on $SiO_2$, eluting with *n*-hexane. A blue band traveled with the same speed of the solvent. Such a solution showed a visible spectrum identical with that of compound **1**, and an IR spectrum with bands at 2073 w, 1953 m and 1945 s $cm^{-1}$, assigned to the compound $Mo(CO)_5(PMe_3)$ on the basis of a comparison with the spectrum of a pure sample.[16]

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(16) We are grateful to Prof. D. J. Darensbourg for providing a sample of pure $Mo(CO)_5(PMe_3)$.

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**Table II.** Crystal Data for $Mo_2I_4(PMe_3)_4 \cdot 2THF$

| | |
|---|---|
| formula | $C_{20}H_{52}I_4Mo_2O_2P_4$ |
| fw | 1148.03 |
| space group | *Cmcm* |
| syst abs | $hkl$, $h+k \neq 2n$; $h0l$, $l \neq 2n$ |
| $a$, Å | 19.412 (5) |
| $b$, Å | 9.789 (6) |
| $c$, Å | 20.165 (8) |
| $\alpha$, deg | 90 |
| $\beta$, deg | 90 |
| $\gamma$, deg | 90 |
| $V$, Å$^3$ | 3832 (5) |
| $Z$ | 4 |
| $d_{calcd}$, g/cm$^3$ | 3.980 |
| cryst size, mm | 0.4 × 0.4 × 0.6 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 80.203 |
| data collcn instrum | CAD-4 |
| radiation (monochromated in incident beam) | Mo K$\alpha$ ($\lambda_{\bar{\alpha}}$ = 0.71073 Å) |
| orientation reflcns: no.; range ($2\theta$), deg | 25; 26–36 |
| temp, °C | 25 |
| scan method | $\omega$–$2\theta$ |
| data calcn range ($2\theta$), deg | 4–50 |
| no. of unique data; total with $F_o^2 > 3\sigma(F_o^2)$ | 1936; 1487 |
| no. of params refined | 64 |
| transmissn factors: max; min | 0.995; 0.683 |
| $R^a$ | 0.033 |
| $R_w^b$ | 0.058 |
| quality-of-fit indicator$^c$ | 1.809 |
| largest shift/esd, final cycle | 0.00 |
| largest peak, e/Å$^3$ | 0.45 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_{observn} - N_{paras})]^{1/2}$.

**Table III.** Positional Parameters and Their Estimated Standard Deviations for $Mo_2I_4(PMe_3)_4 \cdot 2THF$

| atom | $x$ | $y$ | $z$ | $B$,$^a$ Å$^2$ |
|---|---|---|---|---|
| Mo(1) | 0.500 | 0.12338 (9) | 0.250 | 3.05 (2) |
| Mo(2) | 0.500 | −0.09407 (9) | 0.250 | 2.99 (2) |
| I(1) | 0.500 | 0.23647 (6) | 0.12452 (3) | 4.86 (1) |
| I(2) | 0.37011 (3) | −0.20780 (7) | 0.250 | 5.10 (1) |
| P(1) | 0.3720 (1) | 0.1885 (2) | 0.250 | 4.30 (5) |
| P(2) | 0.500 | −0.1603 (2) | 0.3726 (1) | 4.25 (5) |
| C(1) | 0.3187 (4) | 0.1430 (8) | 0.1779 (4) | 5.8 (2) |
| C(2) | 0.3683 (6) | 0.3807 (9) | 0.250 | 7.1 (3) |
| C(3) | 0.5748 (4) | −0.1175 (7) | 0.4242 (4) | 5.6 (2) |
| C(4) | 0.500 | −0.3537 (9) | 0.3784 (6) | 6.7 (3) |
| O(1) | 0.134 | 0.000 | 0.500 | 18.5* |
| C(11) | 0.182 | −0.028 | 0.558 | 8.5* |
| C(12) | 0.240 | 0.095 | 0.484 | 16.2* |
| O(2) | 0.263 | 0.000 | 0.500 | 20.2* |
| C(21) | 0.221 | 0.057 | 0.553 | 9.7* |
| C(22) | 0.157 | 0.100 | 0.511 | 14.6* |

[a] Values marked with an asterisk denote isotropically refined atoms. Values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}$.

**Table IV.** Selected Bond Distances (Å) and Angles (deg) for $Mo_2I_4(PMe_3)_4 \cdot 2THF^a$

| | | | |
|---|---|---|---|
| Mo(1)–Mo(2) | 2.129 (1) | P(1)–C(1) | 1.839 (5) |
| Mo(1)–I(1) | 2.762 (1) | P(1)–C(2) | 1.883 (8) |
| Mo(1)–P(1) | 2.566 (2) | P(2)–C(3) | 1.835 (5) |
| Mo(2)–I(2) | 2.756 (1) | P(2)–C(4) | 1.896 (8) |
| Mo(2)–P(2) | 2.557 (2) | | |
| Mo(2)–Mo(1)–I(1) | 113.63 (2) | P(2)–Mo(2)–P(2) | 150.60 (9) |
| Mo(2)–Mo(1)–P(1) | 104.39 (5) | Mo(1)–P(1)–C(1) | 119.0 (2) |
| I(1)–Mo(1)–I(1) | 132.74 (3) | Mo(1)–P(1)–C(2) | 106.6 (3) |
| I(1)–Mo(1)–P(1) | 84.28 (2) | C(1)–P(1)–C(1) | 104.5 (4) |
| P(1)–Mo(1)–P(1) | 151.23 (9) | C(1)–P(1)–C(2) | 102.7 (3) |
| Mo(1)–Mo(2)–I(2) | 113.83 (2) | Mo(2)–P(2)–C(3) | 119.4 (2) |
| Mo(1)–Mo(2)–P(2) | 104.70 (4) | Mo(2)–P(2)–C(4) | 108.2 (3) |
| I(2)–Mo(2)–I(2) | 132.35 (3) | C(3)–P(2)–C(3) | 104.7 (4) |
| I(2)–Mo(2)–P(2) | 84.12 (2) | C(3)–P(2)–C(4) | 101.1 (3) |

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

**B. In Tetrahydrofuran.** A 0.33-g sample of $Mo_2I_4(CO)_8$ (0.35 mmol) was dissolved in 15 mL of THF. Gas evolution occurred, and the resulting red solution had IR bands at 2022 s, ca. 1945 sh, and 1928 s cm$^{-1}$. Treatment of this solution with $PMe_3$ (150 $\mu$L, 1.50 mmol) resulted in a color change from red to orange and an IR spectrum change to one having bands at 2023 s, 1953 s, and 1910 s cm$^{-1}$. The mixture was then refluxed overnight. The color changed to blue-green, and the final solution had IR bands at 2011 w, 1939 m, 1907 sh, 1897 m, 1880 sh, and 1841 w cm$^{-1}$. Blue crystals formed when the solution was cooled to room temperature; one of them was used in the subsequent X-ray crystallographic study. Yield: 0.16 g (40%). The IR spectrum (Nujol mull) had all the bands observed for compound **1** obtained in toluene and one more band at 1070 cm$^{-1}$. The $^1$H NMR spectrum had the same peak as the product obtained from toluene (see Table I), and in addition, it exhibited two broad triplets at $\delta$ 1.60 and 3.74 of relative intensity 1:1. Upon prolonged pumping, the crystals became opaque, a fact that was associated with the loss of interstitial THF and that prevented an accurate elemental analyses from being obtained for this product. The UV/visible absorption spectra of this compound and the one obtained from toluene were identical.

**Reaction of $Mo_2X_4(CO)_8$ (X = Br, Cl) with $PMe_3$. Preparation of $Mo_2X_4(PMe_3)_4$ (X = Br (2), Cl (3)).** These reactions were carried out as described above for the reaction of $Mo_2I_4(CO)_8$ and $PMe_3$ in toluene. $Mo_2Cl_4(CO)_8$[11a] and $Mo_2Br_4(CO)_8$[11b] were prepared in situ according to published procedures. After the addition of the halogen to $Mo(CO)_6$, the solvent ($Cl_2$ in one case,[11a] $CH_2Cl_2$ in the other[11b]) was evaporated at low temperature and the residue extracted with toluene and treated with $PMe_3$. After overnight reflux, compounds **2** and **3** were isolated in 80% and 67% yields, respectively, by adding *n*-hexane to the concentrated solutions and cooling to −20 °C. Analytical and spectroscopic properties of compounds **2** and **3** are reported in Table I.

**Reaction of $MoI_3(PMe_3)_3$ with $Mo(CO)_6$ in a 2:1 Ratio.** A 0.65-g sample of $MoI_3(PMe_3)_3$ (0.92 mmol) and 0.12 g of $Mo(CO)_6$ (0.46 mmol) were mixed in 20 mL of toluene. The resulting red solution was stirred overnight at room temperature. Apart from the formation of small amounts of a brown solid, no change was observed in either the color or the IR carbonyl stretching absorption of the solution. The mixture was then warmed to the reflux temperature. After ca. 2 h the color had changed to emerald green, and the IR spectrum had bands in the carbonyl stretching region at 2069 w, 2014 w, 1982 s, 1938 s, 1913 w, 1897 m, 1885 m, and 1840 w cm$^{-1}$. Reflux was continued for 20 h more. The final solution was blue-green, and CO stretching bands were no longer present in the IR spectrum. The UV/visible spectrum of the solution indicated the presence of **1** as a major product, and it was isolated in 55% yield by recrystallization from *n*-hexane.

As an independent experiment, a sample of $MoI_3(PMe_3)_3$ was refluxed in toluene without $Mo(CO)_6$ for the same length of time. Except for the formation of small amounts of a brown solid, no significant change was observed during the treatment.

**X-ray Crystallography for $Mo_2I_4(PMe_3)_4 \cdot 2THF$.** The crystal was mounted in a closed capillary in the presence of THF. Data collection and the solution and refinement of the structure were routine; calculations were performed on PDP/11 and VAX computers with the Enraf-Nonius SDP software. No corrections for decay were necessary, and a semiempirical absorption correction was applied according to North, Phillips, and Mathews.[17] Crystallographic data are summarized in Table II. Final atomic positional and equivalent isotropic thermal parameters are listed in Table III, and selected bond distances and angles are given in Table IV.

## Results and Discussion

**Synthesis of $Mo_2X_4(PMe_3)_4$ by Decarbonylation of $Mo_2X_4(CO)_8$.** We reported earlier[9] that interaction of $Mo_2I_4(CO)_8$ at room temperature either in toluene or in THF (via formation of $MoI_2(CO)_3(THF)_2$ in the latter case[8b]) with 4 equiv of $PMe_3$ gave rise to gas evolution and formation of solutions whose IR spectra were consistent with the presence of $MoI_2(CO)_3(PMe_3)_2$ (**4**) as the main product. Compound **4** is apparently not reported in the literature and we were not able to isolate it, but the gross features of the spectrum that we obtained are identical with those of other reported $MoX_2(CO)_3(PR_3)_2$ compounds; see Table V. A closer examination of these spectra revealed additional features. The

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**Table V.** IR Spectra of Relevant Molybdenum Carbonyl Compounds in the Carbonyl Stretching Region

| compd | $\tilde{\nu}_{CO}$, cm$^{-1}$ | | | | solvent | ref |
|---|---|---|---|---|---|---|
| $Mo(CO)_6$ | 1982 s | | | | toluene | |
| $Mo(CO)_5(PMe_3)$ | 2073 w | 1953 m | 1945 s | | *n*-hexane | 16 |
| *cis*-$Mo(CO)_4(PMe_3)_2$ | 2019 w | 1922 m | 1905 s | 1899 m | *n*-heptane | 18 |
| *trans*-$Mo(CO)_4(PMe_3)_2$ | 1895 s | | | | *n*-heptane | 18 |
| *fac*-$Mo(CO)_3(PMe_3)_3$ | 1938 s | 1842 s | | | $CH_3OH$ | *a* |
| *fac*-$Mo(CO)_3(PMe_2Ph)_3$ | 1939 s | 1832 vs | 1824 sh | | $CHCl_3$ | *b* |
| $MoI_2(CO)_3[P(OPh)_3]_2$ | 2044 m | 1976 s | 1920 s | | $CHCl_3$ | *c* |
| $MoI_2(CO)_3[P(OMe)_3]_2$ | 1995 s | 1968 s | 1903 s | | $CHCl_3$ | *c* |
| $MoI_2(CO)_3(PPh_3)_2$ | 2020 m | 1962 s | 1926 s | | $CHCl_3$ | *d* |

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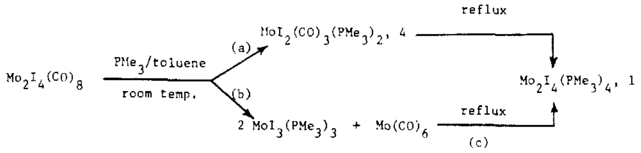
Scheme I[a]



[a] Key: (a) Decarbonylation. (b) Disproportionation; a and b are parallel paths in the same reaction mixture. (c) Presumably via intermediate formation of $Mo(CO)_n(PMe_3)_{6-n}$, $n$ = 5, 4, 3.

reaction was cleaner in THF [the three bands of **4** (at 2023 s, 1953 s, and 1910 s cm$^{-1}$) being the prominent ones immediately after the room-temperature treatment], whereas in the toluene reaction the solution also showed other major bands that appeared to be due to $Mo(CO)_6$ (1982 cm$^{-1}$) and to $Mo(CO)_4(PMe_3)_2$, on the basis of a comparison with spectra reported in the literature[18] and with those taken on solutions of authentic samples. However, the toluene solution behaved under the subsequent thermal treatment as if it contained pure **4**: prolonged reflux resulted in complete decarbonylation with production of a blue solution whose visible properties were in accordance with the presence of $Mo_2I_4(PMe_3)_4$ (**1**) as the sole product. When the reaction was stopped after a short reflux and an IR spectrum was taken on the solution, the compounds $Mo(CO)_6$ and $Mo(CO)_5(PMe_3)$ were identified, in addition to unreacted **4**. The assignments were again based on the comparison with IR spectra of pure samples.[16] Also, the band due to $Mo(CO)_6$ was found to disappear upon evaporating the solution to dryness (see Experimental Section), in agreement with the known high volatility of $Mo(CO)_6$.

Carbonyl compounds of molybdenum(0) were not present in the final mixture. This suggested that a disproportionation reaction had occurred at intermediate stages, and since no metallic deposit was present at the end of the treatment, it also suggested that these disproportionation products had comproportionated back to the decarbonylated dimer of molybdenum(II), **1** (see Scheme I). This suggestion is supported by the results of the comproportionation reaction between $MoI_3(PMe_3)_3$ and $Mo(CO)_6$, vide infra.

It is noteworthy that the disproportionation reaction takes place at room temperature as soon as $PMe_3$ is added to $Mo_2I_4(CO)_8$ and the resulting solution does not change its IR spectroscopic properties with time, whereas subsequent thermal treatment changes the nature of the molybdenum(0) complexes [from a mixture of $Mo(CO)_6$ and *cis*-$Mo(CO)_4(PMe_3)_2$ to $Mo(CO)_6$ and $Mo(CO)_5(PMe_3)$]. The earlier assumption[10] that the decarbonylation reaction proceeds via $MoI_2(CO)_3(PR_3)_2$ and perhaps $MoI_2(CO)_2(PR_3)_2$ then does not take into account all the observations. The data suggest that (at least when $PR_3$ = $PMe_3$) there are other, independent pathways. It has been found[8b,c] that $Mo_2I_4(CO)_8$ disproportionates upon thermal treatment and can be reduced by a number of agents. It is then possible that some of the unreacted $Mo_2I_4(CO)_8$ is engaged in redox reactions with the products of CO substitution, leading to Mo(0) and Mo(III) species.

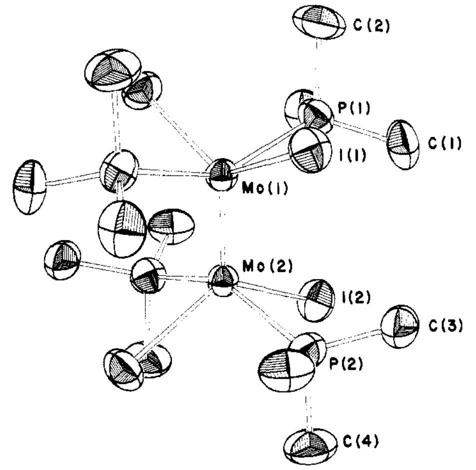


**Figure 1.** ORTEP view of the $Mo_2I_4(PMe_3)_4$ molecule.

Compound **1** could also be obtained from the reaction performed in THF, but carbonyl compounds were still present after several hours of reflux, as shown by IR spectroscopy. The observed bands were assigned to *cis*-$Mo(CO)_4(PMe_3)_2$ (2011 w, 1907 sh, 1897 m, and 1880 sh cm$^{-1}$; probably containing small amounts of the trans isomer[18]) and *fac*-$Mo(CO)_3(PMe_3)_3$ (1939 m and 1841 w cm$^{-1}$), by comparison with literature spectra (see Table V) and with the results obtained by using other phosphines and published elsewhere.[10] Compound **1**, as obtained from THF, formed better single crystals, and one of these was subjected to an X-ray crystallographic study.[9] The compound contained interstitial THF, which is disordered among two equally populated orientations. The presence of THF is confirmed by IR spectroscopy (band at 1070 cm$^{-1}$ not present in the specimen obtained from toluene, assigned to a C–O–C stretching vibration) and by $^1$H NMR spectroscopy (see Experimental Section).

A view of the dimer is shown in Figure 1. The molecule has imposed $C_{2v}$ symmetry, the Mo–Mo vector lying along the twofold axis. The structural parameters are very similar, with the exception of the Mo–X distances, to those of $Mo_2Cl_4(PMe_3)_4$,[19] which, although not crystallographically isostructural, exhibits the same coordination geometry. As already found for the $Mo_2X_4(dppm)_2$ [dppm = bis(diphenylphosphino)methane][20] and the $Mo_2X_4(dppe)_2$ [dppe = bis(diphenylphosphino)ethane][21] series (X = Cl, Br, I), the Mo–Mo distance [2.129 (1) Å] is insensitive to the halogen change from chloride to iodide. The ligand dependence of the molecular and electronic structures of the $Mo_2X_4(PMe_3)_4$ complexes has recently been studied by Gray et al.,[22] who also reported the crystal structure of a different crystalline form of $Mo_2I_4(PMe_3)_4$.

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Once we had realized that the thermal interaction between $Mo_2I_4(CO)_8$ and $PMe_3$ is a good synthetic method for compound **1**, we wondered if the same method could be applied to the preparation of the other halides. This indeed proved to be the case, as $Mo_2Br_4(PMe_3)_4$ (**2**), and $Mo_2Cl_4(PMe_3)_4$ (**3**) could be obtained in excellent yields from $Mo_2X_4(CO)_8$ (X = Br, Cl) and $PMe_3$ with reaction conditions identical with those employed for the synthesis of compound **1**. Compounds **2** and **3** have been previously described.[19,22,23] The spectroscopic properties of the $Mo_2X_4(PMe_3)_4$ (X = Cl, Br, I) series are reported in Table I. The $^1H$ NMR spectra present a broad peak with some emerging fine structure because of coupling to the $^{31}P$ nuclei system. The chemical shift moves downfield on going from chloride to iodide, which is opposite to what is expected from simple electronegativity considerations. This can possibly be attributed, according to a recent suggestion based on electrochemical work,[24] to an increased $\pi$-acceptor ability of the heavier halide. The $^{31}P$ NMR spectra show a singlet in the region between $-9$ and $-15$ ppm, which is quite typical for transition-metal-coordinated phosphines.[25]

**Comproportionation Reactions between $MoX_3(PMe_3)_3$ and $Mo(CO)_6$.** The identification of $Mo(CO)_6$ among the disproportionation products of the $Mo_2I_4(CO)_8$–$PMe_3$ system made us consider the disproportionation stoichiometry represented in eq 1.

$$^3/_2Mo_2I_4(CO)_8 + 6PMe_3 \rightarrow Mo(CO)_6 + 2MoI_3(PMe_3)_3 + 6CO \quad (1)$$

The identification of $Mo(CO)_5(PMe_3)$ among the products could be ascribed to the presence of an excess of $PMe_3$, although we cannot rule out that other Mo(III) products with a lower phosphine content are also formed during the disproportionation reaction. We were not able to isolate $MoI_3(PMe_3)_3$, nor other Mo(III) compounds, from the mixture arising from the interaction between $Mo_2I_4(CO)_8$ and $PMe_3$. If one considers, however, eq 1 to be a good approximation to the actual disproportionation process, one would expect the comproportionation of $Mo(CO)_6$ and $MoI_3(PMe_3)_3$ in a 1:2 molar ratio to afford compound **1** when conditions are such that CO is forced out of the equilibrium (eq 2, X = I).

$$Mo(CO)_6 + 2MoX_3(PMe_3)_3 \rightarrow {}^3/_2Mo_2X_4(PMe_3)_4 + 6CO \quad (2)$$

$$X = Cl, I$$

We actually find this to be the case, as refluxing $Mo(CO)_6$ and $MoI_3(PMe_3)_3$[15] (1:2 molar ratio) in toluene as solvent affords a solution containing no more carbonyl compounds, from which compound **1** could be isolated in about 55% yield. This reaction seems to take place about as fast as the synthesis of **1** from $Mo_2I_4(CO)_8$ and $PMe_3$. IR and UV/visible monitoring has also established the same behavior for the reaction between $Mo(CO)_6$ and $MoCl_3(PMe_3)_3$, where compound **3** is formed (eq 2, X = Cl).

IR monitoring of these reactions shows the presence, after short reflux, of all of the known $Mo(CO)_{6-n}(PMe_3)_n$ ($n$ = 0, 1, 2, 3) compounds of molybdenum(0) (see Scheme I). Their formation as intermediates in this reaction seems perhaps too fast to be the result of CO substitution on $Mo(CO)_6$ by free $PMe_3$. Also, independent observations are not consistent with dissociation of the phosphine from $MoI_3(PMe_3)_3$ in refluxing toluene.[15] A possible mechanism by which these intermediates could form involves oxidation of $Mo(CO)_6$ to a 17-electron (17-e) radical cation by the Mo(III) species. It is, in fact, well-known that CO substitutions on 18-e compounds are greatly accelerated by either chemical[26] or electrochemical[27] oxidation to 17-e intermediates. The Mo(II) anion resulting from this electron-transfer reaction could then eliminate iodide and dimerize to the product while the 17-e Mo(I) cations could be neutralized by $I^-$, lose CO, and further react with Mo(III) to again produce the observed Mo(II) dimers.

## Concluding Remarks

The molybdenum–iodide–phosphine–CO system appears to be a very complex one. Perhaps the most interesting result of this study is that our observations have allowed us to encompass in one scheme three of the different major areas of inorganic chemistry, i.e., carbonyl chemistry, classical Wernerian coordination chemistry, and the chemistry of multiple metal–metal bonds.

Evidence for disproportionation of $PMe_3$-containing molybdenum(II) carbonyl complexes to Mo(0) and Mo(III) complexes has been found. This has led to the design of the comproportionation reaction between $Mo(CO)_6$ and $MoX_3(PMe_3)_3$ that is also a new synthetic route to $Mo_2X_4(PMe_3)_4$ complexes.

We finally observe that the exploitation of the comproportionation reaction described in this paper should provide new synthetic routes to mixed-metal multiply bonded systems.

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**Registry No.** **1**, 89637-15-0; **1**·2THF, 104010-56-2; **2**, 89707-70-0; **3**, 67619-17-4; $Mo_2I_4(CO)_8$, 22547-54-2; $Mo_2Br_4(CO)_8$, 80594-72-5; $Mo_2Cl_4(CO)_8$, 104815-65-8; *mer*-$MoI_3(PMe_3)_3$, 107680-53-5; $Mo(CO)_6$, 13939-06-5; Mo, 7439-98-7.

**Supplementary Material Available:** Full tables of bond distances, bond angles, and anisotropic displacement parameters for **1**·THF (3 pages); a listing of observed and calculated structure factors for **1**·THF (8 pages). Ordering information is given on any current masthead page.

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# Late-Transition-Metal $\mu$-Oxo and $\mu$-Imido Complexes. 1. $\mu$-Oxo Complexes of Rhodium and Iridium

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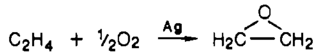
The chemical properties of oxygen atoms absorbed on metal surfaces (oxygen adatoms) are important in many catalytic processes. Several metal-catalyzed reactions where adsorbed oxygen plays an important role are given below.[1–4]



(1)

$$4NH_3 + 5O_2 \xrightarrow{Pt} 4NO + 6H_2O \quad (2)$$

$$O_2 + 4e^- + 4H^+ \xrightarrow{Pt} 2H_2O \quad (3)$$

$$2NO + 2CO \xrightarrow{Rh} N_2 + 2CO_2 \quad (4)$$

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