Preparation of $\text{CpMoX}_3$ ($\text{Cp} = \eta^5\text{C}_5\text{H}_5$; $X = \text{Cl, Br, I}$) by Thermal Decarbonylation of $\text{CpMoX}_3(\text{CO})_2$, a Previously Overlooked Phenomenon

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Introduction

We have been recently interested in the synthesis of new molybdenum compounds that contain only halides and one cyclopentadienyl ring, $\text{CpMoX}_n$, as these are useful synths for the preparation of a variety of other organometallic products. Although the $\text{CpMoX}_3$ ($X = \text{Cl, Br, I}$) materials have been known for a long time and a variety of (ring)MoX$_n$ compounds (ring = $\text{C}_5$ or other alkyl-substituted cyclopentadienyl) rings have been more recently developed, monocyclopentadienyl halide derivatives of molybdenum(IV) were unknown until recently. We reported the preparation of $\text{CpMoCl}_3$ by either oxidation of $\text{CpMoCl}_4$ by PhICl$_2$, reduction of $\text{CpMoCl}_4$ by TiCl$_4$, or disproportionation of $\text{CpMoCl}_3$ and $\text{CpMoCl}_5$.

We wondered whether the decarbonylation of $\text{CpMoCl}_3(\text{CO})_2$ might represent a more direct route to $\text{CpMoCl}_3$ and whether this synthetic procedure could be extended to the heretofore unknown bromide and iodide analogues. $\text{CpMoX}_3(\text{CO})_2$ complexes ($X = \text{Cl, Br, I}$) were reported over 25 years ago by two research groups and were described as unstable toward loss of CO, but the nature of the decomposition products was not investigated. We report here that the decarbonylation strategy is indeed a most convenient one for the preparation of $\text{CpMoX}_3$ ($X = \text{Cl, Br, I}$) materials.

Experimental Section

General Procedures. All operations were carried out under an atmosphere of dinitrogen with standard glove-box and Schlenk-line techniques. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. Low-energy FT-IR spectra were recorded on a Perkin-Elmer 1800 spectrophotometer. NMR spectra were obtained with a Bruker WP200 spectrometer; the peak positions are reported upfield of TMS as calculated from the residual solvent peaks (H and Cl) or external 85% H$_3$PO$_4$ (1.0%). EPR spectra were recorded with a Bruker ER200 spectrometer operating with an X-band radio-frequency generator.

Room-temperature magnetic susceptibility measurements were carried out by a modified Gouy method with a Johnson Matthey balance, and low-temperature data were obtained with a computer-controlled Faraday system which consists of a Cahn 2000 microbalance, Applied Magnetics electromagnet, Lake Shore Cryotronics temperature controller, platinum resistance thermometer, and Abbes instrument cryostat. The magnetic susceptibility data were corrected for the diamagnetism of the ligands by using Pascal’s constants before conversion to magnetic moments. The elemental analyses were performed by M-H-W, Phoenix, A-Z, or Galbraith Laboratories, Inc., Knoxville, TN.

Thermal Decarbonylation of $\text{CpMoX}_3(\text{CO})_2$. Preparation of $\text{CpMoX}_3$ ($X = \text{Cl, Br, I}$). The starting materials $\text{CpMoX}_3(\text{CO})_2$ were prepared in situ by a slightly modified procedure with respect to those reported in the literature.

In each case, $\text{CpMo(OCO)}_3$ was treated in $\text{CH}_2\text{Cl}_2$ with 3 equiv of the oxidizing agent (PhICl$_2$, Br$_2$, and I$_2$, respectively). The reactions were followed by IR, showing the immediate formation of $\text{CpMoX}_3(\text{CO})_2$, followed by the slower conversion to $\text{CpMoX}_3$, which was only sparingly soluble in the $\text{CH}_2\text{Cl}_2$ solvent (overnight stirring at room temperature was necessary in each case to complete this step). For each halogen system, the nature of the precipitate obtained by filtration at this point in a separate control experiment was confirmed as the desired $\text{CpMoX}_3$ complex by its IR properties (Nujol muff and $\text{CH}_2\text{Cl}_2$ solution) with those reported in the literature.

We did not observe decomposition of these compounds by loss of CO upon standing in solution at room temperature. Overnight reflux of the resulting mixtures yielded insoluble materials (Cl, brown; Br, dark green; I, black), which were filtered off, washed with $\text{CH}_2\text{Cl}_2$, and dried under vacuum. Yields: 173 mg, 69% (Cl); 400 mg, 52% (Br); 669 mg, 61% (I).

The $\text{CpMoCl}_3$ material had an IR spectrum (4000-200 cm$^{-1}$) identical to that reported previously for the same compound obtained by a different method and a reaction with 2 equiv of (P(OCH$_3$)$_2$Cl) to produce $\text{CpMoCl}_3(\text{PO(OCH$_3$)$_2$Cl})_2$, as expected on the basis of the previous report.

Preparation of $\text{CpMoCl}_3$ ($X = \text{Cl, Br, I}$). After complete removal of the THF solvent, each of the residual yellow materials was dissolved in 15 mL of $\text{CH}_2\text{Cl}_2$ and the solution was added Br$_2$ (50 mL, 0.16 g, 0.97 mmol), resulting in gas evolution and formation of a black precipitate. When all the PhICl$_2$ solution was added, stirring was continued for a few minutes at room temperature, during which time the color of the precipitate changed to the characteristic purple color of $\text{CpMoCl}_3$. The precipitate was filtered off, washed with n-heptane, and dried under vacuum. Yield: 1.281 g (87%). The color and EPR properties of this compound are identical with those of an authentic sample of $\text{CpMoCl}_3$.

Preparation of $\text{CpMoBr}_3$ from $\text{CpMo(CO)}_3$ and Br$_2$. $\text{CpMoBr}_3$ (0.109 g, 0.22 mmol) was dissolved in 15 mL of $\text{CH}_2\text{Cl}_2$, and to the solution was added Br$_2$ (50 mL, 0.16 g, 0.97 mmol), resulting in gas evolution and formation of a black solid. After the mixture was stirred at room temperature overnight, the solid was separated from the mother liquor, washed with heptane, and dried under vacuum. Yield: 96 mg (45%). The color of this compound is identical with that reported for a sample of $\text{CpMoBr}_3$ from $\text{CpMoBr}_3$ and Br$_2$.

Preparation of $\text{CpMoBr}_3$ from $\text{CpMo(CO)}_3$ and Br$_2$. $\text{CpMoBr}_3$-Me was prepared in situ from $\text{Mo(CO)}_3$ (1.541 g, 7.25 mmol) and NaCp as reported in the literature. After complete removal of the THF solvent, each of the residual red-orange materials was dissolved in $\text{CH}_2\text{Cl}_2$ (50 mL), and filtration of the resulting solution was slowly transferred with a cannula into a suspension of Br$_2$ (7.8 g, 18.1 mmol) in 50 mL of $\text{CH}_2\text{Cl}_2$. Gas evolution and formation of a black precipitate were observed during the transfer. The mixture was subsequently refluxed for 1.5 h. The product was recovered by filtration and washed with $\text{CH}_2\text{Cl}_2$. Yield: 2.645 g (76%). This compound has the same color and properties as that obtained from $\text{CpMo(CO)}_3$ and Br$_2$; see previous paragraphs.

Reactions of $\text{CpMoCl}_3$ and $\text{CpMoBr}_3$. Preparation of $\text{CpMoCl}_5$ ($\text{CpMo(Cl)}_3$) $\text{(305 mg, 0.622 mmol)}$ was dissolved in 20 mL of $\text{CH}_2\text{Cl}_2$, and to the resulting solution was added I$_2$ (536 mg, 2.19 mmol). Gas evolution and the formation of a dark brown suspension were observed. The mixture was refluxed for 2 days, resulting in the formation of a black solid. The mother solution of this solid had a pale blue-purple color. The solid was filtered off, washed with heptane, and then...
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dried. Yield: 560 mg (74%). Anal. Caled for C13H132MoC: 9.92; H, 0.83. Found: 9.7; H, 0.7. Low-energy IR (400–200 cm⁻¹; Nujol mull): 333 w with sh at ca. 328, 193 w. μM = 1.01 μg per [CpMoO3]⁻ unit. EPR (X-band, CH2Cl2, room temperature): γ = 2.054 (broad; peak-to-peak separation = 140 G).

Reactions of CpMoX3 (X = Br, I) with Phosphines and Phosphites. (a) Preparation of CpMoBr3(dppe). CpMoBr3 (249 mg, 0.62 mmol) and dppe (255 mg, 0.64 mmol) were introduced into a Schlenk tube and slurried in 20 mL of CH2Cl2. The immediate formation of a red-purple solution was observed, followed by the slow precipitation of a red-brown solid. More precipitate formed after 20 mL of n-heptane was added to the mixture. The solid was filtered off, washed with n-heptane (5 mL), and dried under vacuum. Yield: 64.3%. Anal. Caled for C13H14Cl2MoC: 46.59; H, 3.66. Found: C, 46.8; H, 4.1. 1H-NMR (CDCl3): δ 8.13, 7.61, 7.24 (m, 20H, C5H5H), 5.24 (d, JHH = 2.6 Hz, 5H, CH2), 3.45, 3.33, 3.07, 2.93 (br, 4H, CH2). 131P[1H]-NMR (CDCl3): δ 57.1 (d, JPH = 115 Hz, 1P), 14.5 (d, 1P).

(b) Preparation of CpMoBr3[P(OCH2)3CEt]2. CpMoBr3 (420 mg, 1.03 mmol) and P(OCH2)3CEt (343 mg, 2.12 mmol) were introduced into a Schlenk tube and slurried with 20 mL of CH2Cl2. The solution immediately turned brown. A minor amount of insoluble solid was eliminated by filtration, and from the solution, the product was crystallized by diffusion of a heptane layer (15 mL). The resulting crystals were filtered off, washed with heptane, and dried under vacuum. Yield: 503 mg, 70.7%. Anal. Caled for C13H132Br2MoP2C: 28.16; H, 3.75. Found: C, 27.7; H, 4.0. 1H-NMR (CDCl3): δ 7.55 (t, JHH = 3.8 Hz, 5H, CH2), 3.33 (d, JHP = 2.1 Hz, 12H, OCH3), 2.52 (q, JHP = 7.4 Hz, 4H, C5H5CH2), 0.83 (t, JHH = 7.5 Hz, 6H, CH2CH3). 31P[1H]-NMR (CDCl3): δ 128.1.

(c) Reaction of CpMoBr3 with PMe2. CpMoBr3 (172 mg, 0.64 mmol) was suspended in THF (10 mL). The suspension was cooled to −78 °C in a dry ice/acetone bath, and then PMe2 (135 mL, 1.28 mmol) was added. The mixture allowed to slowly warm to room temperature under magnetic stirring. At −5 °C the formation of a pale pink-red solution was noted. Further warming deepened the color of the solution to purple while a cream-white precipitate had replaced the initial insoluble solid. 1H-NMR analysis of an aliquot of the solution showed no evidence for a diamagnetic CpMoBr3(PMe2)2 product and revealed the presence of several paramagnetically shifted resonances in the δ = 2 to 50 region, two prominent resonances in an approximate 1:1 ratio being observed at δ = −38 and −40, but none of these could be assigned to a paramagnetic CpMoBr3(PMe2)2 adduct.

(d) Reaction of CpMo3 with Dppe. CpMo3 (536 mg, 0.989 mmol) and dppe (399 mg, 1.00 mmol) were introduced into a Schlenk tube and slurried with 10 mL of CH2Cl2. As this reaction solution immediately formed, and large amounts of a brown solid were also noted. After being stirred overnight at room temperature, the mixture had not changed in appearance. After the solid was filtered off, concentration of the mother solution, addition of toluene, and cooling to −80 °C produced crystalline CpMo(dppe), which was separated from the solution, washed with n-heptane, and dried under vacuum. Yield: 218 mg (40.7% based on the stoichiometry of eq 4; see Results and Discussion). Anal. Caled for C13H132MoP2C: 45.78; H, 3.59. Found: C, 45.6; H, 3.8. This solid had an EPR spectrum identical to that reported previously for CpMo- dppe.14

(e) Reaction of CpMo3 with PMe2 and Then with I2. CpMo3 (160 mg, 0.295 mmol) was slurried in a Schlenk tube with 10 mL of CH2Cl2. PMe2 (61 mL, 0.589 mmol) was added with a microsyringe while the suspension was kept at room temperature with magnetic stirring. An immediate reaction took place with formation of a green solution and a gray-green solid. An EPR spectrum of an aliquot of the supernatant liquid indicated the presence of CpMo3(PMe2)3 by comparison with the literature spectrum.9 To the reaction mixture was added I2 (112 mg, 0.441 mmol), and the resultant mixture was stirred at room temperature. Once the I2 dissolved, the solution became noticeably darker green, while a green precipitate remained. At this point, an aliquot of the solution showed no residual EPR signal, while 1H-NMR spectroscopy after evaporation to dryness and redissolution in CD2Cl2 confirmed the presence of the [CpMo3(PMe2)3]+ ion.10

Reactions of CpMoX3 with CO. For each halide system, a small amount (ca. 50 mg) of the compound was suspended in CH2Cl2 (5–10 mL), and the suspension was stirred at room temperature under an atmosphere of CO. The solid rapidly reacted to afford a solution of sparingly soluble CpMoX3(CO)2 (IR cm−1; CpMoBr3(CO)2, 2059 s, 2061 vs; CpMoI3(CO)2, 2071 s, 2039 vs). The chloride analogue was not sufficiently soluble for an IR investigation in CH2Cl2, and it was identified from its Nujol IR spectrum (2116 s, 2076 vs cm−1). Continued stirring at room temperature under CO with IR monitoring indicated no further change for CpMoCl3(CO)2 and CpMoBr3(CO)2, whereas CpMoI3(CO)2 was totally transformed to CpMoI3(CO)3 within 3 days (IR: 2042 s, 1966 vs, br cm−1).

Results and Discussion

The Mo(IV) carbonyl compounds CpMoX3(CO)2 (X = Cl, Br, I) appear to be stable toward CO loss at room temperature, but they can be completely decarbonylated in refluxing CH2Cl2 to afford insoluble materials that analyze correctly for CpMoX3. The CpMoCl3 material obtained by this route shows physical and chemical properties identical with those of the same compound obtained by other routes.9 Considering that [CpMo(CO)3]2 is commercially available or can easily be prepared from Mo(CO)6, the procedure reported here represents by far the most convenient method for the preparation of CpMoCl3 (eq 1) and also represents a convenient route to the previously unknown CpMoBr3 and CpMoI3 materials. For the chloride system, the stoichiometric reagent PhICl3 was used rather than gaseous Cl2.

CH3Cl

\[ \text{CpMo(OCO)3I_2 + 3X_2} \rightarrow \text{CpMoX_3(CO)2} \]

Use of an excess of PhICl3 or Br2 affords a straightforward synthesis of the previously reported CpMoCl4 and CpMoBr4, respectively (see eq 2), and is comparable in simplicity to the recently reported PF3 (X = Cl, Br) method.11

\[ \text{CpMoCl_3 + 4X_2} \rightarrow \text{CpMoCl_4} \]

The identity of the bromide compound is verified by derivatization reactions analogous to those previously run on the chloride system (eqs 3 and 4).

\[ \text{CpMoBr_3 + dppe} \rightarrow \text{CpMoBr_3(dppe)} \]

\[ \text{CpMoBr_3 + 2P(OCH_2)CEt} \rightarrow \text{CpMoBr_3[P(OCH_2)CEt]_2} \]

The CpMoBr3(dppe) compound had been previously described,12 but only a 1H-NMR characterization was given, which was not sufficient for a complete structural assignment. We find by 1H- and 31P-NMR that freshly prepared solutions of this compound contain isomer I as the major species but that, upon standing at room temperature, the samples exhibit other peaks in the 31P-NMR spectrum, possibly indicating equilibration with other isomers, as was also suggested for the analogous CpMoCl3(dppe) and CpMoClBr2(dppe) compounds.13 In particular, a 31P-NMR singlet resonance at δ 39.3 is assigned to structure II (compare with δ 38.6 for CpMoCl3(dppe) and δ 39.1 for CpMoClBr2(dppe)).13 Structure I was found in the solid state for both CpMoI3(dppe)13 and CpMoI3(dpme).14


CpMoBr₃[P(OCH₃)₂CH₂] has NMR properties that perfectly match those previously reported for the trichloro analogue.⁵

The reaction between CpMoBr₃ and PMe₅ did not produce the expected CpMoBr₃(PMe₅)₂ or the corresponding paramagnetic CpMoBr₃(PM₂₅)₂ adduct but rather produced a mixture of other paramagnetic products, as shown by ¹H-NMR, and thus takes a course rather similar to that of the previously investigated CpMoCl₃(PM₃)₂ reaction.⁴ CpMoI₃ rapidly reacted with dppe and PMe₅, but 18-electron adducts were not obtained in these cases. Rather, the previously reported CpMoI₃(dppe) complex was isolated in the dppe reaction and the known¹⁰ CpMoI₃(PM₃)₂ and [CpMoI₂(PM₃)₂]⁺I⁻ complexes were identified by EPR in the PMe₅ reaction. These reduction reactions probably occur as illustrated in eq 5, since the proposed intermediate (L = PMe₅)

$$3\text{CpMoI}_3 + 3\text{L}_2 \rightarrow [3\text{[CpMoI}_2\text{L}_2]\text{I}] \rightarrow 2\text{CpMoI}_2\text{L}_2 + [\text{CpMoI}_2\text{L}_2]\text{I}_2$$

was obtained earlier by interaction of CpMoI₃(PM₃)₂ and 1/₂ equiv of I₂ and shown to rapidly rearrange to the products of eq 5.¹⁰ ¹² Two possible reasons for the different reactivities of the tribromide and triiodide compounds are the greater steric requirements of the three iodide ligands and the greater reducing power of I⁻ versus the corresponding Br⁻ ion.

All three CpMoX₃ compounds promptly react with CO at room temperature to regenerate the 18-electron precursors, CpMoX₃(CO)₂, showing the reversibility of the decarboxylation process (eq 6). Whereas the chloride and bromide CpMoX₃(CO)₂

$$\text{CpMoX}_3 + 2\text{CO} \rightarrow \text{CpMoX}_3(\text{CO})_2$$

systems are stable under CO, the iodide analogue reacts further to quantitatively (by IR) produce the monoiodide tricarbonyl complex (eq 7), demonstrating that this step is also completely

$$\text{CpMoI}_3(\text{CO})_2 + \text{CO} \rightarrow \text{CpMoI}(\text{CO})_3 + \text{I}_2$$

reversible. Under CO (1 atm), equilibrium 7 is completely shifted toward the right whereas, under N₂, the triiodide derivative can be made from the monoiodide complex in good yields. The lower solubility of the triiodide compound presumably contributes to shift this equilibrium toward the left under low CO pressure conditions.

A point of interest concerns the structure of the CpMoX₃ compounds. As these are all highly insoluble materials, solution spectroscopic methods cannot be applied. The sparing solubility also prevented recrystallization in the form of single crystals for an X-ray analysis. On the basis of the reactivity of these materials (see above) and parallels with the corresponding Cp* analogues,¹⁶ it seems most likely that the CpMoX₃ species are dinuclear or oligonuclear covalent species. Physical studies are also in accord with this view and point more directly to a dinuclear structure as found for Cp*MoX₃ (Cp* = μ₂-C₅H₄Mo₂, X = Cl, Br), e.g. III.

The low-energy IR spectra of CpMoCl₃ and Cp*MoCl₃ are similar,¹⁶ and the two compounds also have a similar temperature dependences of their magnetic moments, which has been attributed to antiferromagnetic coupling.¹⁶ The room-temperature magnetic moment for CpMoX₃ increases in the order Cl > Br > I, with the moment for the iodide complex (1.84 μₜ/Mo) being still substantially smaller than the value found for magnetically diluted d₃ Mo(IV), for instance 2.63 μₜ (temperature independent) for Cp*MoCl₃(PM₃).¹⁶ This trend indicates stronger antiferromagnetic coupling for the lighter halide system, in accord with the presumed smaller separation of the metals in the halide-bridged dinuclear structure.

It is interesting to observe that a compound of empirical formula "Cp*MoI₃I" exists but it in fact consists of a Mo₁⁰I₁⁰ system, e.g. [Cp*Mo₂I₄]⁺I⁻. Electrochemical work has established that further addition of I₂ would not produce a complex of the metal in a higher oxidation state.¹⁷ Consequently, a question arises as to whether it is legitimate to describe CpMoI₃ as a neutral Mo(IV) compound. It is worth mentioning here that CpV₂I₇ has also been shown to adopt a solid-state structure consisting of a molecular triiodide material of the metal in the IV oxidation state whereas considerations of oxidation potentials as a function of halide for the CpVX₃ (X = Cl, Br, I) series would lead to the prediction of an internal redox process with production of polyiodides.¹⁸ The related Cp*Crl₃ and Cp*Crl₄ compounds, on the other hand, have been shown to be polyiodide complexes of Cr(III).¹⁹

Support for the assignment of a neutral structure to CpMoI₃ is its rapid reaction with CO, which is analogous to those of CpMoX₃ (X = Cl, Br) (vide supra) and to those of the structurally characterized (see III) [Cp*MoX₃I]⁺ (X = Cl, Br).²¹ "Cp*MoI₃I" on the other hand, does not react with CO.²¹ As further support for this argument, we have prepared a compound of stoichiometry CpMoI₅ by the reaction between [Cp*Mo(CO)₃I]⁺ and I₂ = 1 in a 1:3.5 ratio, followed by reflux of the resulting mixture that presumably contains Cp*MoI₅(CO)₃ and unreacted I₂ in a 4:1 molar ratio (eq 8). This product has properties substantially different from those of CpMoI₃. For instance, the two materials have different low-energy IR spectra, and while CpMoI₅ is completely insoluble in organic solvents, CpMoI₅ is sparingly soluble in CH₂Cl₂, generating deep violet solutions. While CpMoI₃ rapidly reacts with CO to regenerate CpMoI₅(CO)₂, CpMoI₅ does not react with CO over several days at room temperature and therefore behaves identically to "Cp*MoI₃I".

We propose therefore that the structure of CpMoI\textsubscript{3.5} is analogous to that of its more soluble Cp\textsuperscript{*} analogue, i.e. [Cp\textsubscript{2}Mo\textsubscript{2}I\textsubscript{4}]\textsuperscript{+13-}, and that the affinity of I\textsubscript{2} for I\textsuperscript{-} induces this curious rearrangement with formal reduction of the metal by action of the oxidizing agent I\textsubscript{2} (see Scheme I). For the proposed structure of CpMoI\textsubscript{3.5}, a single unpaired electron per dimeric unit is expected since theoretical calculations on this system\textsuperscript{22} suggest a $\sigma^{2}\delta^{181}$ configuration. Consistent with this view, CpMoI\textsubscript{3.5} shows a broad EPR resonance at room temperature at $g = 2.054$.

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Supplementary Material Available: A figure showing the variable-temperature magnetic moment of CpMoCl\textsubscript{3} (1 page). Ordering information is given on any current masthead page.