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Preparation of $CpMoX_3$ ($Cp = \eta\text{-}C_5H_5$; X = Cl, Br, I) by Thermal Decarbonylation of $CpMoX_3(CO)_2$, 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, $CpMoX_n$, as these are useful synthons for the preparation of a variety of other organometallic products.[1] Although the $CpMoX_4$ (X = Cl, Br) materials have been known for a long time[2] and a variety of (ring)MoX_2 compounds (ring = Cp[3] or other alkyl-substituted cyclopentadienyl rings[4]) have been more recently developed, monocyclopentadienyl halide derivatives of molybdenum(IV) were unknown until we recently reported the preparation of $CpMoCl_3$ by either oxidation of $CpMoCl_2$ by $PhICl_2$, reduction of $CpMoCl_4$ by $TiCl_3$, or conproportionation of $CpMoCl_2$ and $CpMoCl_4$.[5]

We wondered whether the decarbonylation of $CpMoCl_3(CO)_2$ might represent a more direct route to $CpMoCl_3$ and whether this synthetic procedure could be extended to the heretofore unknown bromide and iodide analogues. $CpMoX_3(CO)_2$ complexes (X = Cl, Br, I) were reported over 25 years ago by two research groups[6,7] 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 $CpMoX_3$ (X = 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 (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P). 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 Abbess 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, AZ, or Galbraith Laboratories, Inc., Knoxville, TN.

Thermal Decarbonylation of $CpMoX_3(CO)_2$. Preparation of $CpMoX_3$ (X = Cl, Br, I). The starting materials $CpMoX_3(CO)_2$ were prepared *in situ* by a slightly modified procedure with respect to those reported in the literature.[6,7] In each case, $[CpMo(CO)_3]_2$ was treated in CH_2Cl_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 $CpMoX(CO)_3$, followed by the slower conversion to $CpMoX_3(CO)_2$, which was only sparingly soluble in the CH_2Cl_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 $CpMoX_3(CO)_2$ complex by its IR properties (Nujol mull and CH_2Cl_2 solution) with those reported in the literature.[6,7] 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 CH_2Cl_2, and dried under vacuum. Yields: 173 mg, 69% (Cl); 400 mg, 52% (Br); 669 mg, 61% (I).

The $CpMoCl_3$ material had an IR spectrum (4000–200 cm^{-1}) identical to that reported previously for the same compound obtained by a different method,[5] and a reaction with 2 equiv of $P(OCH_2)_3CEt$ proceeded to produce $CpMoCl_3[P(OCH_2)_3CEt]_2$, as expected on the basis of the previous report.[5] $\mu_{eff} = 1.25\ \mu_B$ at room temperature, decreasing to 1.12 μ_B at 80 K (see supplemental figure). Anal. Calcd. for $CpMoBr_3$, $C_5H_5Br_3Mo$: C, 14.99; H, 1.26. Found: C, 14.9; H, 1.1. Low-energy IR (400–200 cm^{-1}; Nujol mull): 245 vs, 222 s. $\mu_{eff} = 1.66\ \mu_B$. Anal. Calcd for $CpMoI_3$, $C_5H_5I_3Mo$: C, 11.09; H, 0.93. Found: C, 11.7; H, 0.8. Low-energy IR (400–200 cm^{-1}; Nujol mull): 324 w, 206 w, 188 s with sh at ca. 180. $\mu_{eff} = 1.84\ \mu_B$.

For the purpose of measuring the variable-temperature magnetic moment of $CpMoCl_3$, a sample was obtained by refluxing *isolated* $CpMoCl_3(CO)_2$ in order to avoid any possible contamination with trace amounts of $CpMoCl_2$ or $CpMoCl_4$, which may form if a nonstoichiometric amount of $PhICl_2$ is used.

Preparation of $CpMoCl_4$ from $[CpMo(CO)_3]_2$ and $PhICl_2$. $[CpMo(CO)_3]_2$ (1.187 g, 2.42 mmol) was placed in a Schlenk tube and slurried in 20 mL of CH_2Cl_2. To the resulting suspension was added via cannula a solution of $PhICl_2$ (4.0 g, 14.5 mmol) in 30 mL of CH_2Cl_2 at room temperature with stirring. During the addition, vigorous gas evolution was observed, accompanied by the formation of a brown precipitate, presumably $CpMoCl_3(CO)_2$. 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 $CpMoCl_4$. 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 $CpMoCl_4$.[8]

Preparation of $CpMoBr_4$ from $[CpMo(CO)_3]_2$ and Br_2. $[CpMo(CO)_3]_2$ (0.109 g, 0.22 mmol) was dissolved in 15 mL of CH_2Cl_2, and to the solution was added Br_2 (50 μL, 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 $CpMoBr_4$ prepared from $CpMoOBr_2$ and HBr.[2b]

Preparation of $CpMoBr_4$ from $CpMo(CO)_3Me$ and PBr_5. $CpMo(CO)_3$-Me was prepared *in situ* from $Mo(CO)_6$ (1.914 g, 7.25 mmol) and NaCp as reported in the literature.[8] After complete removal of the THF solvent, extraction of the residue with CH_2Cl_2 (50 mL), and filtration, the resulting solution was slowly transferred with a cannula into a suspension of PBr_5 (7.8 g, 18.1 mmol) in 50 mL of CH_2Cl_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 CH_2Cl_2. Yield: 2.645 g (76%). This compound has the same color and properties as that obtained from $[CpMo(CO)_3]_2$ and Br_2; see previous paragraph.

Reaction of $[CpMo(CO)_3]_2$ and I_2 in a 1:3.5 Ratio. Preparation of $CpMoI_{3.5}$. $[CpMo(CO)_3]_2$ (305 mg, 0.622 mmol) was dissolved in 20 mL of CH_2Cl_2, and to the resulting solution was added I_2 (556 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

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[†] Presidential Young Investigator 1990–1995, Alfred P. Sloan Research Fellow 1992–1994, and Alexander von Humboldt Research Fellow 1993–1994.

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dried. Yield: 560 mg (74%). Anal. Calcd for $C_5H_5I_{3.5}Mo$: C, 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. $\mu_{eff} = 1.01\ \mu_B$ per $[Cp_2Mo_2I_7]$ unit. EPR (X-band, CH_2Cl_2, room temperature): $g = 2.054$ (broad; peak-to-peak separation = 140 G).

Reactions of $CpMoX_3$ (X = Br, I) with Phosphines and Phosphites. (a) Preparation of $CpMoBr_3(dppe)$. $CpMoBr_3$ (249 mg, 0.62 mmol) and dppe (255 mg, 0.64 mmol) were introduced into a Schlenk tube and slurried in 20 mL of CH_2Cl_2. 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. Calcd for $C_{31}H_{29}Cl_3MoP_2$: C, 46.59; H, 3.66. Found: C, 46.8; H, 4.1. ^1H-NMR ($CDCl_3$): δ 8.13, 7.61, 7.24 (m, 20H, C_6H_5), 5.24 (d, $J_{PH} = 2.6$ Hz, 5H, C_5H_5), 3.45, 3.33, 3.07, 2.93 (br, 4H, CH_2). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 57.1 (d, $J_{PP} = 115$ Hz, 1P), 14.5 (d, 1P).

(b) Preparation of $CpMoBr_3[P(OCH_2)_3CEt]_2$. $CpMoBr_3$ (420 mg, 1.05 mmol) and $P(OCH_2)_3CEt$ (343 mg, 2.12 mmol) were introduced into a Schlenk tube and slurried with 20 mL of CH_2Cl_2. 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. Calcd for $C_{17}H_{27}Br_3MoP_2O_2$: C, 28.16; H, 3.75. Found: C, 27.7; H, 4.0. ^1H-NMR (CD_2Cl_2): δ 5.75 (t, $J_{PH} = 3.8$ Hz, 5H, C_5H_5), 4.33 (vt, $J_{PH} = 2.1$ Hz, 12H, OCH_2), 1.25 (q, $J_{HH} = 7.4$ Hz, 4H, CH_2CH_3), 0.83 (t, $J_{HH} = 7.5$ Hz, 6H, CH_2CH_3). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 128.1.

(c) Reaction of $CpMoBr_3$ with PMe_3. $CpMoBr_3$ (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 PMe_3 (135 μL, 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 $CpMoBr_3$. ^1H-NMR inspection of an aliquot of the solution showed no evidence for a diamagnetic $CpMoBr_3(PMe_3)_2$ 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 $CpMoBr_3(PMe_3)$ adduct.

(d) Reaction of $CpMoI_3$ with Dppe. $CpMoI_3$ (536 mg, 0.989 mmol) and dppe (399 mg, 1.00 mmol) were introduced into a Schlenk tube and slurried with 10 mL of CH_2Cl_2. A deep red-brown 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 $CpMoI_2(dppe)$, 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. Calcd for $C_{31}H_{29}I_2MoP_2$: C, 45.78; H, 3.59. Found: C, 45.4; H, 3.8. This solid had an EPR spectrum identical to that reported previously for $CpMoI_2(dppe)$.[8]

(e) Reaction of $CpMoI_3$ with PMe_3 and Then with I_2. $CpMoI_3$ (160 mg, 0.295 mmol) was slurried in a Schlenk tube with 10 mL of CH_2Cl_2. PMe_3 (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 spectum of an aliquot of the supernatant liquid indicated the presence of $CpMoI_2(PMe_3)_2$ by comparison with the literature spectrum.[9] To the reaction mixture was added I_2 (112 mg, 0.441 mmol), and the resultant mixture was stirred at room temperature. Once all the I_2 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 CD_2Cl_2 confirmed the presence of the $[CpMoI_2(PMe_3)_2]^+$ ion.[10]

Reaction of $CpMoX_3$ with CO. For each halide system, a small amount (ca. 50 mg) of the compound was suspended in CH_2Cl_2 (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 $CpMoX_3(CO)_2$ (IR (cm^{-1}): $CpMoBr_3(CO)_2$, 2095 s, 2061 vs; $CpMoI_3(CO)_2$, 2071 s, 2039 vs). The chloride analogue was not sufficiently soluble for an IR investigation in CH_2Cl_2, 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 $CpMoCl_3(CO)_2$ and $CpMoBr_3(CO)_2$, whereas $CpMoI_3(CO)_2$ was totally transformed to $CpMoI(CO)_3$ within 3 days (IR: 2042 s, 1966 vs, br cm^{-1}).

Results and Discussion

The Mo(IV) carbonyl compounds $CpMoX_3(CO)_2$ (X = Cl, Br, I) appear to be stable toward CO loss at room temperature, but they can be completely decarbonylated in refluxing CH_2Cl_2 to afford insoluble materials that analyze correctly for $CpMoX_3$. The $CpMoCl_3$ material obtained by this route shows physical and chemical properties identical with those of the same compound obtained by other routes.[5] 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 $CpMoCl_3$ (eq 1) and also represents a convenient route to the previously unknown $CpMoBr_3$ and $CpMoI_3$ materials. For the chloride system, the stoichiometric reagent $PhICl_2$ was used rather than gaseous Cl_2.

$$[CpMo(CO)_3]_2 + 3X_2 \xrightarrow{CH_2Cl_2} 2CpMoX_3(CO)_2 \xrightarrow[\Delta]{CH_2Cl_2} 2CpMoX_3 \qquad (1)$$

Use of an excess of $PhICl_2$ or Br_2 affords a straightforward synthesis of the previously reported $CpMoCl_4$ and $CpMoBr_4$,[2] respectively (see eq 2), and is comparable in simplicity to the recently reported PX_5 (X = Cl, Br) method.[8,11]

$$[CpMo(CO)_3]_2 + 4X_2 \xrightarrow{CH_2Cl_2} 2CpMoX_4 \qquad (2)$$

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

$$CpMoBr_3 + dppe \rightarrow CpMoBr_3(dppe) \qquad (3)$$

$$CpMoBr_3 + 2P(OCH_2)_3CEt \rightarrow CpMoBr_3[P(OCH_2)_3CEt]_2 \qquad (4)$$

The $CpMoBr_3(dppe)$ 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 ^{31}P-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 ^{31}P-NMR spectrum, possibly indicating equilibration with other isomers, as was also suggested for the analogous $CpMoCl_3(dppe)$ and $CpMoClBr_2(dppe)$ compounds.[13] In particular, a ^{31}P-NMR singlet resonance at δ 39.3 is assigned to structure II [compare with δ 38.6 for $CpMoCl_3(dppe)$ and δ 39.1 for $CpMoClBr_2(dppe)$].[13] Structure I was found in the solid state for both $CpMoCl_3(dppe)$[13] and $CpMoCl_3(dmpe)$.[14]

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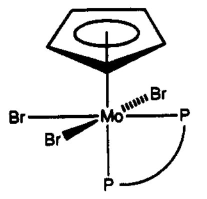
$CpMoBr_3[P(OCH_2)_3CEt]_2$ has NMR properties that perfectly match these previously reported for the trichloride analogue.[5]



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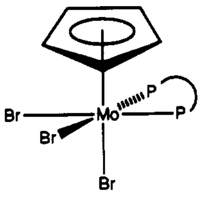


II

The reaction between $CpMoBr_3$ and PMe_3 did not produce the expected $CpMoBr_3(PMe_3)_2$ or the corresponding paramagnetic $CpMoBr_3(PMe_3)$ 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 $CpMoCl_3/PMe_3$ reaction.[5] $CpMoI_3$ rapidly reacted with dppe and PMe_3, but 18-electron adducts were not obtained in these cases. Rather, the previously reported[9] $CpMoI_2(dppe)$ complex was isolated in the dppe reaction and the known[10] $CpMoI_2(PMe_3)_2$ and $[CpMoI_2(PMe_3)_2]^+I_3^-$ complexes were identified by EPR in the PMe_3 reaction. These reduction reactions probably occur as illustrated in eq 5, since the proposed intermediate ($L = PMe_3$)

$$3CpMoI_3 + 3L_2 \rightarrow \{3[CpMoI_2L_2]I\} \rightarrow 2CpMoI_2L_2 + [CpMoI_2L_2]I_3 \quad (5)$$

$$L_2 = \text{dppe or } (PMe_3)_2$$

was obtained earlier by interaction of $CpMoI_2(PMe_3)_2$ and $^1/_2$ equiv of I_2 and shown to rapidly rearrange to the products of eq 5.[10,15] 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 $CpMoX_3$ compounds promptly react with CO at room temperature to regenerate the 18-electron precursors, $CpMoX_3(CO)_2$, showing the reversibility of the decarbonylation process (eq 6). Whereas the chloride and bromide $CpMoX_3(CO)_2$

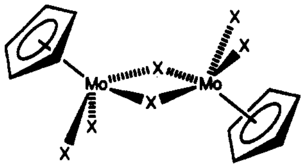
$$CpMoX_3 + 2CO \underset{\Delta/N_2}{\overset{rt/p_{CO} = 1\text{ atm}}{\rightleftarrows}} CpMoX_3(CO)_2 \quad (6)$$

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

$$CpMoI_3(CO)_2 + CO \rightleftarrows CpMoI(CO)_3 + I_2 \quad (7)$$

reversible. Under CO (1 atm), equilibrium 7 is completely shifted toward the right whereas, under N_2, 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 $CpMoX_3$ 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 $CpMoX_3$ 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^*MoX_3 ($Cp^* = \eta$-C_5Me_5; X = Cl, Br), e.g. **III**.



III

The low-energy IR spectra of $CpMoCl_3$ and Cp^*MoCl_3 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 $CpMoX_3$ increases in the order Cl > Br < I, with the moment for the iodide complex (1.84 μ_B/Mo) being still substantially smaller than the value found for magnetically diluted d^2 Mo(IV), for instance 2.63 μ_B (temperature independent) for $Cp^*MoCl_3(PMe_3)$.[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 "$Cp^*MoI_{3.5}$" exists but it in fact consists of a $Mo^{III}Mo^{IV}$ system, e.g. $[Cp^*Mo_2I_4]^+I_3^-$. Electrochemical work has established that further addition of I_2 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 $CpMoI_3$ as a neutral Mo(IV) compound. It is worth mentioning here that $CpVI_3$ has also been shown to adopt a solid-state structure consisting of a molecular triiodo material of the metal in the +IV oxidation state whereas considerations of oxidation potentials as a function of halide for the $CpVX_3$ (X = Cl, Br, I) series would lead to the prediction of an internal redox process with production of polyiodides.[18] The related Cp^*CrI_3 and $Cp^*CrI_{5.5}$ 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 $CpMoI_3$ is its rapid reaction with CO, which is analogous to those of $CpMoX_3$ (X = Cl, Br) (vide supra) and to those of the structurally characterized (see **III**) $[Cp^*MoX_3]_2$ (X = Cl, Br).[16,20] "$Cp^*MoI_{3.5}$", on the other hand, does not react with CO.[21] As further support for this argument, we have prepared a compound of stoichiometry $CpMoI_{3.5}$ by the reaction between $[Cp^*Mo(CO)_3]_3$ and I_2 in a 1:3.5 ratio, followed by reflux of the resulting mixture that presumably contains $Cp^*MoI_3(CO)_2$ and unreacted I_2 in a 4:1 molar ratio (eq 8). This product has

$$CpMoI_3(CO)_2 + {}^1/_4I_2 \xrightarrow{\Delta/CH_2Cl_2} CpMoI_{3.5} + 2CO \quad (8)$$

properties substantially different from those of $CpMoI_3$. For instance, the two materials have different low-energy IR spectra, and while $CpMoI_3$ is completely insoluble in organic solvents, $CpMoI_{3.5}$ is sparingly soluble in CH_2Cl_2, generating deep violet solutions. While $CpMoI_3$ rapidly reacts with CO to regenerate $CpMoI_3(CO)_2$, $CpMoI_{3.5}$ does not react with CO over several days at room temperature and therefore behaves identically to "$Cp^*MoI_{3.5}$".

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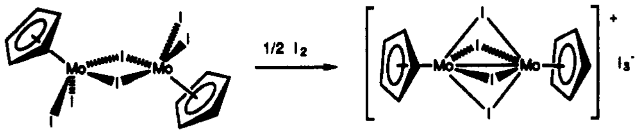
Scheme I



We propose therefore that the structure of $CpMoI_{3.5}$ is analogous to that of its more soluble Cp* analogue, i.e. $[Cp_2Mo_2I_4]^+I_3^-$, and that the affinity of I_2 for I^- induces this curious rearrangement with formal reduction of the metal by action of the oxidizing agent I_2 (see Scheme I). For the proposed structure of $CpMoI_{3.5}$, a single unpaired electron per dimeric unit is expected since theoretical calculations on this system[22] suggest a $\sigma^2\delta^{*2}\delta^1$ configuration. Consistent with this view, $CpMoI_{3.5}$ 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 $CpMoCl_3$ (1 page). Ordering information is given on any current masthead page.

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