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(Pentamethylcyclopentadienyl)molybdenum(IV) Chloride. Synthesis, Structure, and Properties

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Three different syntheses of trichloro(pentamethylcyclopentadienyl)molybdenum(IV) are described, i.e. (i) thermal decarbonylation of $Cp^*MoCl_3(CO)_2$, (ii) reduction of Cp^*MoCl_4, and (iii) chlorination of $[Cp^*MoCl_2]_2$. A fourth route (conproportionation of $[Cp^*MoCl_2]_2$ and Cp^*MoCl_4) has been investigated by ^{1}H-NMR. The product has a dinuclear, dichloro-bridged structure with a four-legged piano stool geometry around each metal atom; the two piano stools have a mutual anti arrangement and the two metals are 3.888(1) Å from each other, indicating the absence of a direct metal–metal bonding interaction. Crystal data: monoclinic, space group $P2_1/n$, $a = 8.424(1)$ Å, $b = 13.323(4)$ Å, $c = 11.266(2)$ Å, $\beta = 93.87(1)°$, $V = 1261.6(8)$ Å^3, $Z = 2$, $R = 0.038$, $R_w = 0.057$ for 127 parameters and 1350 observed reflections with $F_o^2 > 3\sigma(F_o^2)$. The temperature dependent magnetic moment of the material could be fit to the sum of two Bleany–Bowers equations. $[Cp^*MoCl_3]_2$ reacts readily with CO, Cl^-, and PMe_3 to afford $Cp^*MoCl_3(CO)_2$, $[Cp^*MoCl_4]^-$, and $Cp^*MoCl_3(PMe_3)$, respectively, while the reaction with 1,2-bis(diphenylphosphino)ethane (dppe) affords the reduction product Cp^*MoCl_2(dppe).

Introduction

Monocyclopentadienyl transition metal halides have long been exploited as synthons to a wide variety of other organometallic compounds.[1] These materials are often available in oxidation states as low as II (e.g. $[Cp^*CrCl]_2$[2] or $[Cp^*RuCl]_4$[3]) and as high as V (e.g. Cp^*TaCl_4,[4] Cp^*WCl_4,[5] and Cp^*ReCl_4[6]). For a variety of transition metals, derivatives in all oxidation states within a specific range have been shown to be stable and to interconvert in a stepwise manner in the presence of suitable oxidizing or reducing agents (e.g. the series Cp^*MCl_4, $[Cp^*MCl_3]_2$, and $[Cp^*MCl_2]_2$ for M = Ta[7] and Re[8]). For molybdenum and tungsten, on the other hand, whereas compounds of M(III) and M(V) are well known,[5,9] compounds with the metal in the oxidation state IV have received little attention. (C_5R_4-*t*-Bu)WCl_3 (R = Me, Et) has been implicated as a possible intermediate during the reaction of W(C-*t*-Bu)(dme)Cl_3 with RC≡CR, ultimately leading to the disproportionation products (C_5R_4-*t*-Bu)WCl_4 and (C_5R_4-*t*-Bu)W(RC≡CR)Cl_2. Attempts to synthesize this material by reducing (C_5R_4-*t*-Bu)WCl_4 with sodium amalgam yield only products of 2-electron reduction.[9d,f] Recently, the first Mo(IV) compound of this type, $CpMoCl_3$, has been obtained in our laboratory by four independent methods and proven to be distinct from a 1:1 mixture of the dichloride and tetrachloride materials by powder X-ray diffraction and low-energy IR spectroscopy. These methods are as follows: (i) reduction of $CpMoCl_4$, (ii) oxidation of $CpMoCl_2$, (iii) conproportionation of $CpMoCl_4$ and $CpMoCl_2$,[10] and (iv) thermal decarbonylation of $CpMoCl_3(CO)_2$.[11] The last method is the most convenient one, the starting material being easily prepared in situ by chlorine oxidation of the readily available $[CpMo(CO)_3]_2$, and has the additional advantage of straightforward extension to the analogous $CpMoX_3$ (X = Br, I) compounds.[11] Unfortunately, the materials containing the unsubstituted cyclopentadienyl ligand are quite insoluble in common organic solvents; thus, their structural characterization was not conclusive. For this reason, we set out to investigate the corresponding Cp* analogues with the hope of producing more soluble compounds.

Another point of interest concerns the ability of metals to bind to each other in oligonuclear structures. For instance, possible structures for $[CpMX_3]_2$ systems are **I** and **II**, both having pseudo-square-pyramidal coordination spheres around each metal with the Cp ring in the apical position, and differing for the relative orientation of the two square pyramids in a *syn* (for **I**) or *anti* (for **II**) fashion. The only two compounds of this class that have been crystallographically characterized are $[(\eta\text{-}C_5Me_4Et)ReCl_3]_2$, a d^3–d^3 system, which is of type **I** and has the two metals bonded to each other at a distance of 3.074(1) Å,[8b] and $[(\eta\text{-}C_5Me_4Et)TaBr_3]_2$, a d^1–d^1 system, which is of type **II** and lacks any metal–metal bonding interaction (Ta···Ta: 4.1230(9) Å).[7b] The

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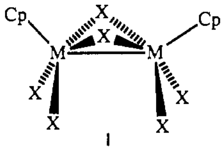
latter compound is especially interesting because the metals have electrons for potential use in the formation of a metal–metal bond, but nevertheless this is not formed. It would therefore be interesting to investigate the structure of d^2–d^2 systems such as the hypothetical $[CpMX_3]_2$ for M = Mo and W and see whether it would be of type **I** or **II** as well as whether it would contain a metal–metal bonding interaction.



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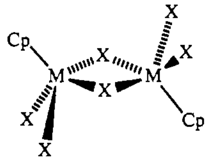

II

We report here the preparation of $[Cp^*MoCl_3]_2$ by several different methods, its structure and magnetic properties, and a few derivatization reactions. Parallel studies on the corresponding bromide and iodide systems, which exhibit a much more complex solution chemistry with respect to the chloride system, are reported separately.[12] Part of this work has been previously communicated.[13]

Experimental Section

General Data. Unless otherwise stated, all operations were carried out under an atmosphere of dinitrogen with standard Schlenk-line and glovebox techniques. Solvents were purified by conventional methods and distilled under dinitrogen prior to use. FT-IR spectra were recorded on a Perkin-Elmer 1800 spectrophotometer with 0.1 mm KBr liquid-sample cells (solutions) or KBr disks (Nujol mulls). NMR spectra were obtained with Bruker WP200 and AF200 spectrometers; the peak positions are reported upfield of TMS as calculated from the residual solvent peaks (^1H) or upfield of external 85% H_3PO_4 (^{31}P). For each ^{31}P-NMR spectrum, a sealed capillary containing H_3PO_4 and immersed in the same NMR solvent that had been used for the measurement was used as a reference. EPR spectra were recorded on a Bruker ER200 spectrometer equipped with an X-band microwave generator. Cyclic voltammograms were recorded with an EG&G 362 potentiostiat connected to a Macintosh computer through MacLab hardware/software; the electrochemical cell was a locally modified Schlenk tube with a Pt counterelectrode sealed through uranium glass/Pyrex glass seals. The cell was fitted with a Ag/AgCl reference electrode and a Pt working electrode. All measurements were carried out with n-Bu_4NPF_6 (ca. 0.1 M) as the supporting electrolyte. All potentials are reported vs the Cp_2Fe/Cp_2Fe^+ couple which was introduced into the cell at the end of each measurement. The elemental analyses were by M-H-W Laboratories, Phoenix, AZ, or Galbraith Laboratories, Inc., Knoxville, TN. Cp^*MoCl_4 was prepared by the standard PCl_5 method,[5] although $[Cp^*Mo(CO)_3]_2$ and 2 equiv of PCl_5 were used rather than $Cp^*Mo(CO)_3(CH_3)$ and 2.5 equiv of PCl_5 (yield 97% on a 20-g scale). $[Cp^*MoCl_2]_2$[9o] was prepared by Na/Hg reduction of Cp^*MoCl_4 by analogy to the corresponding η-C_5H_4R (R = Me, i-Pr) compounds[9i] (87% yield on a 3-g scale, ^1H-NMR: δ 1.84 in $CDCl_3$. Anal. Calcd for $C_{10}H_{15}Cl_2Mo$: C, 39.76; H, 5.01. Found: C, 40.2; H, 5.0). $PhICl_2$ was prepared according to the known procedure,[14] and $[Cp^*Mo(CO)_3]_2$ was prepared by a method identical to that reported for $[(C_5H_4Me)Mo(CO)_3]_2$.[15]

Synthesis of $Cp^*Mo(CO)_2Cl_3$. CH_2Cl_2 (50 mL) was added to a mixture of $[Cp^*Mo(CO)_3]_2$ (0.93 g, 1.48 mmol) and $PhICl_2$ (1.21 g, 4.44 mmol) resulting in a vigorous reaction during which the solution darkened in color (from orange to red) and a precipitate formed. The reaction mixture was allowed to stir for 3 days, after which time, heptanes (10 mL) were added with stirring until the layers mixed. The orange-red solid was allowed to settle, collected by filtration, washed with heptanes until the washings were colorless, and dried under vacuum. Yield: 0.84 g (74%). IR (ν_{CO}, cm^{-1}, CH_2Cl_2): 2087 s, 2044 s. ^1H NMR (δ, $CDCl_3$) 2.18 (s). Anal. Calcd for $C_{12}H_{15}MoO_2Cl_3$: C, 36.62; H, 3.84. Found C, 36.3; H, 4.0.

Thermal Decarbonylation of $Cp^*MoCl_3(CO)_2$. Preparation of $[Cp^*MoCl_3]_2$. $Cp^*MoCl_3(CO)_2$ (0.84 g, 2.18 mmol) was placed in a Schlenk tube equipped with a magnetic stirrer bar and a reflux condenser. Heptane (20 mL) was added, and the suspension was refluxed overnight, yielding a brownish solid which was collected by filtration. An IR spectrum on an aliquot of the solid (Nujol mull) showed carbonyl stretching vibrations attributable to unreacted $Cp^*MoCl_3(CO)_2$. The solid was then placed back in the Schlenk and refluxed for one more day in toluene (8 mL). At the end of this treatment the solid had changed its color to olive green. The solid was filtered, washed with heptane (2 × 10 mL) and dried under vacuum. An IR spectrum on this solid did not show any residual CO stretching vibration. Yield: 0.44 g, 60%. The compound was recrystallized from CH_2Cl_2/heptane, yielding air-stable black crystals. These yielded a green microcrystalline powder when crushed, and a brown solution when dissolved in CH_2Cl_2 or $CHCl_3$. Anal. Calcd for $C_{10}H_{15}Cl_3Mo$: C, 35.58; H, 4.48. Found: C, 35.3; H, 4.6. Low-energy IR (Nujol mull): 380 w, 372 w, 328 m, 291 w, 283 w cm^{-1}. ^1H-NMR (δ, room temperature, $CDCl_3$): –3.87 (broad singlet, $w_{1/2}$ = 64 Hz). This resonance was observed at δ –4.23 in CD_2Cl_2 and at δ –4.04 in C_6D_6. A minor sharp singlet at δ 1.98 was also observed, its relative intensity varying among batches obtained in different runs.

The same product could also be obtained by carrying out the reflux in CH_2Cl_2. $Cp^*MoCl_3(CO)_2$ was made in situ as described above from $[Cp^*Mo(CO)_3]_2$ (0.431 g, 0.684 mmol) and $PhICl_2$ (593 mg, 2.157 mmol) in CH_2Cl_2 (20 mL). Upon completion of this step, reflux for 5 h led to loss of all CO (by solution IR). Evaporation of the solution to dryness followed by washing with heptane (2 × 10 mL) gave 394 mg of solid (85.3% yield), which exhibited ^1H-NMR properties identical to those of the product obtained by reflux in toluene.

Alternative Syntheses of $[Cp^*MoCl_3]_2$. (a) Sodium Reduction of Cp^*MoCl_4. Cp^*MoCl_4 (959 mg, 2.57 mmol) was introduced into a Schlenk tube which already contained amalgamated sodium (61 mg, 2.65 mmol in ca. 10 g of Hg) and 40 mL of toluene. The purple suspension was allowed to stir at room temperature for 6 h. During this time, the initial precipitate was replaced by a greenish-grey precipitate. The mixture was evaporated to dryness and the residue was extracted with CH_2Cl_2 (60 mL) to afford an olive green solution, which was filtered and evaporated to dryness to leave a dark microcrystalline crude product, which was confirmed by ^1H-NMR and analytical data (Found: C, 35.8; H, 4.5) to be identical with the product obtained by decarbonylation of $Cp^*MoCl_3(CO)_2$. Yield: 649 mg, 75%.

A similar synthetic procedure was also carried out in THF as solvent (84% yield), although the material obtained from toluene was spectroscopically purer.

(b) From $[Cp^*MoCl_2]_2$ and $PhICl_2$. $[Cp^*MoCl_2]_2$ (255 mg, 0.42 mmol) and $PhICl_2$ (117 mg, 0.43 mmol) were placed together in a Schlenk tube and then dissolved in 10 mL of CH_2Cl_2. Stirring at room temperature overnight gave rise to a color change from brown to olive green. The product was isolated in 41% yield (118 mg) by evaporation to dryness, washing with toluene (10 mL), and recrystallization by diffusion of a heptane layer into a CH_2Cl_2 solution. The material was identified as $[Cp^*MoCl_3]_2$ by comparison of the ^1H-NMR spectrum with that of the material obtained as described above.

This reaction was also carried out on a smaller scale [10 mg (0.033 mmol) of $[Cp^*MoCl_2]_2$ and 4.5 mg (0.016 mmol) of $PhICl_2$ in ca. 1 mL of $CDCl_3$) with ^1H-NMR monitoring. The evolution of the ^1H-NMR spectrum is presented in the Results and Discussion section.

Reduction of $[Cp^*MoCl_3]_2$ with Sodium Amalgam. $[Cp^*MoCl_3]_2$ (246 mg, 0.364 mmol) was dissolved in THF (30 mL) and the resulting solution transferred over amalgamated sodium (19 mg, 0.83 mmol, in ca. 2 g of Hg). After an overnight stirring at room temperature, an aliquot of the solution was evaporated to dryness and the residue redissolved in 1 mL of $CDCl_3$ for inspection by ^1H-NMR spectrometry. A single resonance at 1.83 δ indicated the quantitative conversion to $[Cp^*MoCl_2]_2$.

Reaction between $[Cp^*MoCl_2]_2$ and Cp^*MoCl_4. This reaction was only investigated by ^1H-NMR, both in a 1:1 and in a 1:2 molar ratio. Appropriate amounts of the two solid compounds were introduced in a Schlenk tube and dissolved in ca. 1 mL of $CDCl_3$. In each case, the resulting solution was transferred into a thin-walled 5 mm NMR tube and used for the NMR monitoring.

Reaction between $[Cp^*MoCl_3]_2$ and Donor Ligands L. (a) L = PMe_3. Preparation of $Cp^*MoCl_3(PMe_3)$. $[Cp^*MoCl_3]_2$ (338 mg, 1.00 mmol)

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Table 1. Crystal Data for $[Cp^*MoCl_3]_2$

formula	$C_{30}H_{45}Cl_6Mo_2$
fw	810.28
space group	$P2_1/n$
a, Å	8.424(1)
b, Å	13.323(4)
c, Å	11.266(2)
β, deg	93.87(1)
V, Å^3	1261.6(8)
Z	2
d_{calcd}, g/cm^3	2.13
μ(Mo Kα), cm^{-1}	16.31
radiation (monochromated in incident beam)	Mo Kα (λ = 0.710 73 Å)
temp, °C	23
T_{max}/T_{min}	1.16
R^a	0.038
$R_w{}^b$	0.057

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

was placed in a Schlenk tube with a magnetic stirrer bar and dissolved in CH_2Cl_2 (10 mL). PMe_3 (103 μL, 1.03 mmol) was added, and the mixture was stirred at room temperature for ca. 30 m, during which time the color changed from olive green to brown. The solution was evaporated to dryness and the residue extracted with toluene (2 × 10 + 5 mL). After filtration, the solution was concentrated by evaporation at reduced pressure to ca. one-fourth of its original volume and kept at −80°C. After 3 days the dark brown microcrystalline solid was filtered off, washed with pentane (5 mL), and dried under vacuum. Yield: 210 mg. From the mother liquor, which was layered with 30 mL of pentane and kept at −80°C, an additional crop of 30 mg was obtained to bring the total yield to 240 mg, 58%. The two crops had identical ^{1}H-NMR spectra, which were also identical with that previously reported for $Cp^*MoCl_3(PMe_3)$.[16]

(b) L = 1,2-Bis(diphenylphosphino)ethane (dppe). Preparation of $Cp^*MoCl_2(dppe)$. $[Cp^*MoCl_3]_2$ (771 mg, 1.14 mmol) was placed in a Schlenk tube with a magnetic stirrer bar and dissolved in CH_2Cl_2 (20 mL). Then dppe (910 mg, 2.28 mmol) was added, and the olive green solution was stirred at room temperature. No color change was initially noted. However, continued stirring at room temperature for ca. 4 days produced a yellow-brown solution. The solution was concentrated to ca. one-third of its original volume, and a layer of heptane (30 mL) was carefully placed on top. Diffusion at room temperature over 5 days produced brown crystals, which were separated by decanting off the mother liquor and then washed with heptane (10 mL) and dried under vacuum. Yield: 859 mg, 53.8%. Anal. Calcd for $C_{36}H_{39}P_2Cl_2Mo$: C, 61.73; H, 5.61. Found: C, 61.9; H, 5.2. EPR (CH_2Cl_2, room temperature): g = 1.957 (triplet with Mo satellites, a_P = 24 G, a_{Mo} = 47 G).

(c) L = CO. Formation of $Cp^*MoCl_3(CO)_2$. A 50-mg sample of $[Cp^*MoCl_3]_2$ was introduced in a Schlenk tube with a magnetic stirrer bar and dissolved in CH_2Cl_2 (5 mL). The solution was then put under 1 atm of CO. An immediate reaction was noted as evidenced by the formation of an orange solid. Solution IR confirmed the formation of $Cp^*MoX_3(CO)_2$ (2085, 2043 cm^{-1}).

(d) L = Cl^-. Preparation of $PPN[Cp^*MoCl_4]$. $[Cp^*MoCl_3]_2$ (375 mg, 0.55 mmol) and PPNCl (637 mg, 1.11 mmol) were placed in a Schlenk tube and treated with CH_2Cl_2 (50 mL). A green solution formed immediately. After the solution was stirred at room temperature overnight, the volume was reduced to ca. 30 mL by evaporation at reduced pressure and diethyl ether (50 mL) was added. The green microcrystalline precipitate that formed was filtered off, washed with Et_2O, and dried under vacuum. Yield: 632 mg (65%). Anal. Calcd for $C_{46}H_{45}Cl_4MoNP_2$: C, 60.61; H, 4.98; Cl, 15.56. Found: C, 61.4; H, 5.1; Cl, 15.2. ^{1}H-NMR ($CDCl_3$, δ): 7.48 (broad m, 30H, PPN), −13.5 (broad s, $w_{1/2}$ = 190 Hz, 15H, Cp*).

X-ray Crystallography for $[Cp^*MoCl_3]_2$. A crystal suitable for an X-ray structural investigation was obtained by cutting a bigger chunk and mounted on the tip of a glass fiber with epoxy cement. Selected crystal, data collection and refinement parameters are collected in Table 1. The unit cell parameters and the orientation matrix for data collection were obtained from the least-squares fit of the setting angles of 25 reflections. During the unit cell determination procedure, three out of the 25 original orientation reflections could not be indexed, indicating that one or more smaller crystals had remained attached to the major single crystal. Axial photographs confirmed the good quality of the major crystal and the random orientation of the minor one(s). The data were corrected for Lorentz and polarization factors, and for absorption by the semiempirical ψ-scan method. A total of 41 reflections in the data showed either a very asymmetric background or a peak position deviating from the calculated position by more than 0.1°, probably due to accidental overlap with reflections from the minor crystal(s), and were therefore eliminated from the data. The systematic absences from the data uniquely established the space group as $P2_1/n$. The structure was solved by direct methods which located the central Mo_2Cl_2 core, and the remaining non-hydrogen atoms were located by alternating full-matrix least-squares refinement and difference Fourier syntheses. All hydrogen atoms were included as idealized isotropic contributions (d_{CH} = 0.960 Å, $U = 1.2U$ for attached C). All non-hydrogen atoms were refined with anisotropic thermal parameters. The software used and the sources of the scattering factors are contained in the TEXSAN(2.0) program library.[17] Positional and isotropic equivalent thermal parameters are given in Table 2, and selected bond distances and angles are collected in Table 3.

Table 2. Positional and Equivalent Isotropic Thermal Parameters for $[Cp^*MoCl_3]_2$

atom	x	y	z	B(eq), Å^2
Mo	0.04652(6)	0.48003(4)	0.66969(5)	1.94(3)
Cl(1)	−0.1591(2)	0.4448(1)	0.5077(2)	2.90(7)
Cl(2)	−0.1839(3)	0.5060(2)	0.7771(2)	4.6(1)
Cl(3)	0.1451(3)	0.6296(2)	0.7606(2)	4.6(1)
C(1)	0.2835(7)	0.3822(5)	0.6738(6)	2.6(3)
C(2)	0.1527(7)	0.3250(5)	0.6236(6)	2.4(3)
C(3)	0.0442(8)	0.3093(5)	0.7140(6)	2.5(3)
C(4)	0.1090(9)	0.3590(5)	0.8189(6)	2.9(3)
C(5)	0.2563(8)	0.4026(5)	0.7934(6)	3.0(3)
C(6)	0.432(1)	0.4066(7)	0.6157(8)	4.8(4)
C(7)	0.141(1)	0.2795(6)	0.5035(7)	3.9(4)
C(8)	−0.099(1)	0.2464(6)	0.7041(8)	4.4(4)
C(9)	0.045(1)	0.3528(7)	0.9386(7)	4.8(5)
C(10)	0.369(1)	0.4543(7)	0.8823(8)	4.8(4)

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Cp^*MoCl_3]_2$

(a) Distances^a			
Mo–Cl(1)	2.475(2)	Mo–Cl(3)	2.366(2)
Mo–Cl(1)′	2.481(2)	Mo–CNT	2.028(7)
Mo–Cl(2)	2.381(2)	Mo···Mo	3.888(1)
(b) Angles^a			
Cl(1)–Mo–Cl(1)′	76.66(6)	Cl(1)–Mo–CNT	112.8(2)
Cl(2)–Mo–Cl(2)	81.27(7)	Cl(1)′–Mo–CNT	112.2(2)
Cl(1)–Mo–Cl(3)	133.41(8)	Cl(2)–Mo–CNT	112.3(2)
Cl(1)′–Mo–Cl(2)	136.04(8)	Cl(3)–Mo–CNT	113.5(2)
Cl(1)′–Mo–Cl(3)	82.33(7)	Mo–Cl(1)–Mo	103.34(6)
Cl(2)–Mo–Cl(3)	86.10(9)		

^{a} CNT = centroid of atoms C(1) to C(5).

Variable Temperature Magnetic Studies on $[Cp^*MoCl_3]_2$. The magnetic susceptibilities were measured between 80 and 295 K on 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. A Data Translation A/D board and AT computer were used to monitor the microbalance output and temperature readings. The instrument was calibrated with $HgCo(SCN)_4$. The raw data were corrected for the susceptibility of the holder and the diamagnetism of the ligand atoms by Pascal's constants, and converted to molar susceptibilities from which the magnetic moments were calculated as $\mu_{eff} = 2.828(\chi_M T)^{1/2}$. The experimental data were fitted to the appropriate theoretical equations by a nonlinear least-squares fitting program, GraFit, as described previously.[18]

Results and Discussion

(a) Syntheses. All the synthetic work reported in this contribution is summarized in Scheme 1. The sodium amalgam reduction of Cp^*MoCl_4 has previously been reported to afford

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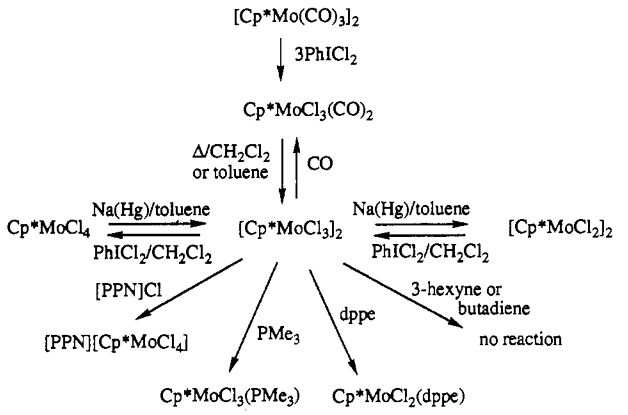
Scheme 1



$[Cp^*MoCl_2]_2$ in good yields.[9c] We have reinvestigated this reaction and found that when only 1 equiv of reducing agent is employed, a new broad and paramagnetically shifted resonance in the ^{1}H-NMR spectrum due to the $[Cp^*MoCl_3]_2$ product is observed at δ −3.87 in $CDCl_3$ (−4.23 in CD_2Cl_2). This reduction can be carried out both in THF and toluene as solvent, although the latter affords cleaner results. A minor sharp resonance at δ 1.98 is also observed during the ^{1}H-NMR monitoring of the reduction process. Compound $[Cp^*MoCl_3]_2$ can also be obtained by oxidation of $[Cp^*MoCl_2]_2$ with 1 equiv of $PhICl_2$, in which case the ^{1}H-NMR resonance at δ 1.98 is not observed, and by thermal decarbonylation of $Cp^*MoCl_3(CO)_2$ in toluene or CH_2Cl_2. The latter compound is obtained by oxidation of $[Cp^*Mo(CO)_3]_2$ with 3 equiv of $PhICl_2$ and its properties are as expected in comparison with the previously reported Cp analogue (CO stretching vibration at 2087 and 2044 cm^{-1} for the Cp* compound, vs 2105 and 2063 cm^{-1} for the Cp analogue).[19,20] The thermal decarbonylation route is the most convenient one given the ready availability of the starting material. The analogous thermal decarbonylation of $CpMoCl_3(CO)_2$ affords $CpMoCl_3$.[11] From each of these three synthetic procedures, $[Cp^*MoCl_3]_2$ can be isolated as a green-brown crystalline material, which is soluble in organic solvents (CH_2Cl_2, THF, toluene) to afford brown solutions. Thus, as we expected, this material is more soluble than the previously reported $CpMoCl_3$.[10,11] The formation of $[Cp^*MoCl_3]_2$ has also been observed spectroscopically (^{1}H-NMR) from the reaction of Cp^*MoCl_4 and $[Cp^*MoCl_2]_2$. The time evolution of this reaction, which gives useful insights into the chemical and redox behavior of this system, is described in detail later.

The broad ^{1}H-NMR resonance observed at δ ca. −4 for $[Cp^*MoCl_3]_2$ is fully consistent with the structural and magnetic properties of this material (vide infra). The byproduct with the sharp resonance at δ 1.98 probably arises from partial replacement of chlorine with oxygen atoms. This conclusion is based on the observation that this resonance has a small and variable relative intensity with respect to that of the product and is not present within the first 24 h when the product is obtained from $[Cp^*MoCl_2]_2$ and $PhICl_2$ in CD_2Cl_2. The deliberate addition of water to this solution causes the growth of several new resonances, including that at δ 1.98. The possibility that this minor compound is an isomeric, diamagnetic form of $[Cp^*MoCl_3]_2$ such as that having structure **I**, which we initially suspected, seems therefore excluded. From a batch of crystals obtained from the decarbonylation route, the majority of them being large black agglomerates of $[Cp^*MoCl_3]_2$, a smaller red crystal was investigated and found to correspond to the formulation $[(Cp^*Mo)_3(\mu\text{-}Cl)_5(\mu\text{-}O)][MoOCl_4]\cdot C_7H_{16}$,[13] but whether this is the source of the sharp NMR resonance at δ 1.98 has not been established. The oxophilicity of high oxidation state Mo compounds is well-known, and we have previously reported that the related $CpMoCl_3$ compound reacts with warm THF to produce the oxo-centered cluster $Cp_3Mo_3Cl_7O$ and $Cl(CH_2)_4Cl$.[21]

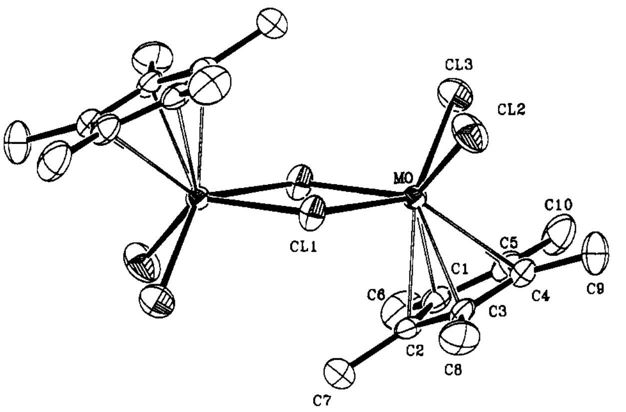


Figure 1. ORTEP view of the $[Cp^*MoCl_3]_2$ molecule. Ellipsoids are drawn at the 40% probability level. Hydrogen atoms are omitted for clarity.

Reduction of $[Cp^*MoCl_3]_2$ with amalgamated sodium produces, as expected, $[Cp^*MoCl_2]_2$, whereas oxidation with 1 equiv of $PhICl_2$ regenerates the tetrachloride compound Cp^*MoCl_4. The decarbonylation of $Cp^*MoCl_3(CO)_2$ also appears to be reversible, as was the case for $CpMoCl_3(CO)_2$,[11] since exposure of $[Cp^*MoCl_3]_2$ to 1 atm of CO quickly regenerates the dicarbonyl precursor. The central $Mo_2(\mu\text{-}Cl)_2$ unit of the compound (see X-ray analysis below) is easily split also by other nucleophiles such as Cl^- and PMe_3. The cyclic voltammogram of $PPN^+[Cp^*MoCl_4]^-$, isolated from the reaction of $[Cp^*MoCl_3]_2$ with PPNCl, shows a reversible one-electron oxidation in CH_2Cl_2 at $E_{1/2} = -0.16$ V vs Cp_2Fe/Cp_2Fe^+. The neutral Mo(V) compound, Cp^*MoCl_4, shows a reversible reduction at the same potential under the same conditions. The $[Cp^*MoCl_4]^-$ ion shows a paramagnetically shifted NMR resonance for the Cp* protons at −13.5 δ, consistent with the presence of two unpaired electrons in the ion. When the interaction between $[Cp^*MoCl_3]_2$ and PPNCl was carried out with ^{1}H-NMR monitoring on a sample containing the impurity with the resonance at δ 1.98, it was observed that only the resonance of the trichloride dimer at δ ca. −4 was rapidly consumed and was replaced by the resonance of the product, while the δ 1.98 resonance remained unchanged over several hours. This represents further evidence against the assignment of this resonance to a compound in chemical equilibrium with the trichloride dimer.

Trimethylphosphine adds to $[Cp^*MoCl_3]_2$ to produce the monophosphine adduct, $Cp^*MoCl_3(PMe_3)$, which was previously obtained by the direct reduction of $Cp^*MoCl_4(PMe_3)$.[16] We have previously analyzed the steric requirements around the Mo(IV) center in both $CpMoCl_3$ and Cp^*MoCl_3 adducts and concluded that there is no room around Cp^*MoCl_3 for more than one tertiary phosphine ligand. This is perhaps the reason why an adduct with the large chelating diphosphine dppe does not form. Rather, a reduction process slowly affords Cp^*MoCl_2(dppe) in moderate yields. The source of the reducing equivalent has not been identified. This product is analogous to the previously reported $CpMoCl_2$(dppe).[22] It is interesting to note, however, that the corresponding dppe Mo(IV) complex with the less sterically hindered Cp ligand exists.[23] No reaction occurs between $[Cp^*MoCl_3]_2$ and butadiene (6 days in THF at room temperature) or 3-hexyne (overnight reflux in CH_2Cl_2).

(b) Molecular Structure. The structure of the $[Cp^*MoCl_3]_2$ molecule is shown in Figure 1 and is analogous to the type **II**

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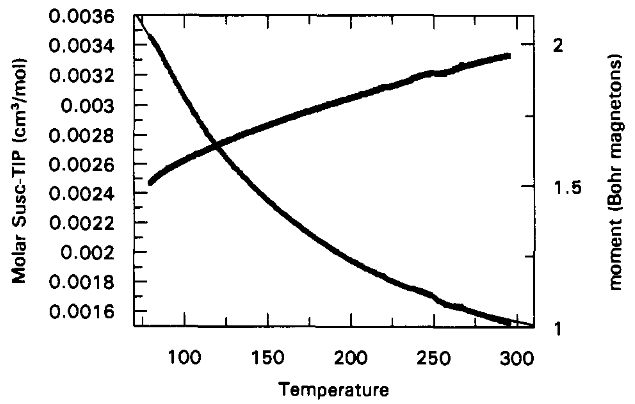

Figure 2. Temperature variation of the magnetic moment for $[Cp^*MoCl_3]_2$.

structure previously reported for $[Cp^*TaBr_3]_2$.[7b] The metals are separated by a distance of 3.888(1) Å, which indicates the absence of direct metal–metal bonding. The slightly shorter metal–metal separation with respect to that found in $[Cp^*TaBr_3]_2$ (4.1230(9) Å) may be attributed to the slightly smaller radius of Mo(IV) with respect to Ta(IV) and to the smaller size of Cl with respect to Br. The geometry around each metal center can be described as a four-legged piano stool or as a square pyramid with the ring in the apical position if the Cp* ring is considered to occupy a single coordination position. The two square pyramids share a basal edge. The two Mo–Cl(bridging) distances are, as expected, significantly longer than the Mo–Cl(terminal) distances. The latter ones compare better with the Mo–Cl distances in the 16-electron mononuclear $[CpMoCl_2(PMe_3)_2]^+$ complex (average 2.372(3) Å)[24] than with those in the isoelectronic $Cp^*MoCl_3(PMe_3)$ complex (average 2.406(12) Å).[16] The Mo–CNT distance is not significantly different than that found in the $Cp^*MoCl_3(PMe_3)$ complex (2.038(9) Å). The Cp* ring deviates more from an ideal η^5 coordination than Cp and Cp* rings in other 16-electron Mo(IV) complexes, the difference between the longest and the shortest Mo–C bonds being 0.083(7) Å as compared with 0.042(8) Å in $Cp^*MoCl_3(PMe_3)$ and 0.01(1) Å in $[CpMoCl_2(PMe_3)_2]^+$. However, this parameter is even larger for the 18-electron $CpMoCl_3(PMe_2Ph)_2$ (0.192(4) Å),[16] and for 17-electron $CpMoX_2(PR_3)_2$ compounds, e.g. 0.138(8) Å in $CpMoCl_2(PMe_3)_2$.[24]

(c) Magnetic Properties. The magnetic properties of $[Cp^*MoCl_3]_2$ have been investigated in the 80–295 K range. The plot of moment/Mo atom vs temperature shown in Figure 2 reveals (*i*) a reduced moment from that expected for a d^2 mononuclear system and (*ii*) a temperature dependence. These observations could be due to either very strong spin orbital effects or antiferromagnetic exchange. To determine the effect of the former, which is known to be strong for *octahedral* Mo(IV) compounds, the magnetism of a related mononuclear Mo(IV) complex, $Cp^*MoCl_3(PMe_3)$, was investigated and found to have a temperature independent moment of 2.63 μ_B which is close to the spin only value.[25] The geometry of $Cp^*MoCl_3(PMe_3)$ has previously been shown by a single crystal X-ray investigation to be that of a four-legged piano stool, that is identical to that found in the present study around each Mo atom in $[Cp^*MoCl_3]_2$. All four-legged piano stool Mo(IV) compounds reported to date have been found by ^{1}H-NMR to be paramagnetic and therefore to presumably contain two unpaired electrons.[16,24,26] No other variable temperature magnetic studies on four-legged piano stool organometallic Mo(IV) complexes appear to have previously been published. The result of the magnetic investigations on $Cp^*MoCl_3(PMe_3)$ therefore suggest that the four-legged piano stool geometry for Mo(IV) does not lead to strong spin–orbit coupling effects and that the behavior of $[Cp^*MoCl_3]_2$ is due to antiferromagnetic exchange.

Attempts to fit the magnetic susceptibility of this compound to the $S_1 = S_2 = 1$ interacting dimer equation[27] were completely unsuccessful. The Ginsberg modifications of this equation[28] which allow for zero field splitting and/or interdimer coupling also proved unsuccessful. In search for a model to fit the magnetic data of $[Cp^*MoCl_3]_2$, we considered that the electronic structure of four-legged piano stool geometries calls for the two independent electrons to be located on very different metal orbitals, that is d_{xy} and d_{z^2}.[29] It is thus possible that the two different electrons could undergo magnetic exchange with their counterpart on the adjacent Mo at different levels of strength. A similar situation has been described for face-sharing bioctahedral $Mo_2X_9^{3-}$ (X = halogen) systems where coupling of the two octahedral t_{2g}^3 systems was best interpreted as occurring through two independent interaction pathways, a very strong one for one electron per Mo atom, and a weaker one for the other two pairs of electrons.[30] For $Mo_2X_9^{3-}$ the strong coupling could be totally neglected for the purpose of the fitting of magnetic data. We thus tested our system for the $S_1 = S_2 = {}^1/_2$ model equation. This model also proved unsuccessful. The obvious next step is to consider the general situation of two independent magnetic exchange pathways of different strength. We could not find a literature precedent for a treatment of this nature. For a coupling model consisting of two independent J pathways, the susceptibility of the system is just the sum of two Bleany–Bowers equations[27] in which the J parameters are different; see eq 1.

$$\chi = \frac{0.375g^2}{T}\left(\frac{e^{2J_1/kT}}{1 + 3e^{2J_1/kT}} + \frac{e^{2J_2/kT}}{1 + 3e^{2J_2/kT}}\right) + \text{TIP} \qquad (1)$$

The experimental data were fit to the above equation using a TIP of 100×10^{-6}. This treatment gave an excellent fitting of the experimental data. Theoretical curve and experimental points are shown in Figure 2. An unconstrained fit gives $J_1 = -308(2)$ and $J_2 = -31.7(2)$ cm^{-1} with $g = 2.118(2)$ and a reduced χ^2 of 1.9×10^{-10}. Fixing g at 2.00 gives $J_1 = -362(2)$ and $J_2 = -29.11(6)$ cm^{-1} without significantly affecting the quality of the fit (reduced $\chi^2 = 1.3 \times 10^{-10}$). A physical interpretation for these two J values is not completely clear at the moment. For the time being, the conclusions that we can draw from our magnetic studies are as follows: (i) the two metal centers in this complex are antiferromagnetically coupled; (ii) the exchange mechanism is complex and gives rise to magnetic data that are fit in a novel fashion by a $2J$ equation. It should be possible in the future to find other examples of antiferromagnetic dimers that can be analyzed in a similar way.

(d) ^{1}H-NMR Characterization. As mentioned above, $[Cp^*MoCl_3]_2$ exhibits a broad and paramagnetically shifted ^{1}H-NMR resonance at δ −3.87 at room temperature in $CDCl_3$. The value of this resonance is in agreement with the measured magnetic properties and molecular structure of the compound and therefore suggests that the observed solid state geometry remains intact in solution. This is so because antiferromagnetic coupling reduces the magnetic moment of the material with respect to the value expected for two unpaired electrons per metal atom, and the paramagnetic shift is correspondingly reduced with respect to the value which is observed at δ −13.5 for the mononuclear ($S = 1$) $[Cp^*MoCl_4]^-$ complex, which has the same metal oxidation state, geometry, and number and type of ligands around the central metal atom as $[Cp^*MoCl_3]_2$. All other reasonable alternatives

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are excluded by the data. A mononuclear Cp^*MoCl_3 structure in solution is not likely because there are no examples of three-legged piano stool, 14-electron Mo(IV) complexes whereas the four-legged piano stool, 16-electron structure is common for Mo(IV).[16,24] Furthermore, a mononuclear structure is excluded by the observation of over 10 resonances for the mixture of mixed-halide complexes $Cp^*_2Mo_2Cl_xBr_{6-x}$, which is obtained by conproportionation of $Cp^*_2Mo_2Cl_4$ and Cp^*MoBr_4.[31] A trinuclear $[Cp^*MoCl_2(\mu\text{-}Cl)]_3$ structure is also not possible, because this would lead to two Cp* resonances in a 2:1 ratio (as found for instance for $[Cp^*TaCl(\mu\text{-}N)]_3)$[32] if at least one of the three Mo atoms adopts the more favored *cis*-$Cp^*MoCl_2(\mu\text{-}Cl)_2$ geometry, whereas only one resonance is observed. A structure with all *trans*-$Cp^*MoCl_2(\mu\text{-}Cl)_2$ units (D_{3h} symmetry with all magnetically equivalent Cp* ligands) is shown by a molecular model to be sterically too strained, having six intramolecular Cl···Cl contacts at ca. 2.30 Å. The analogous $Cp^*_2Mo_2X_6$ (X = Br, I) also shows only a single paramagnetically shifted resonance.[12]

Upon changing the temperature in the 208–355 K, the chemical shift of the broad resonance at –3.87 δ remains practically unchanged, while its intensity decreases both upon warming and upon cooling, until it disappears below 250 K and above 330 K. Both these phenomena are reversible; that is, the original room temperature spectrum is restored after the temperature change is reversed. The reasons for these temperature dependent changes are not clear at this time, although we may advance the possibility of the intervention of a dimer–monomer equilibrium at high temperatures. The little sensitivity of the chemical shift to the temperature change is indication that the species does not exhibit Curie-type paramagnetism, in further disagreement with a mononuclear solution structure and in at least qualitative agreement with the structure observed in the solid state.

(e) ^{1}H-NMR Monitoring of the $[Cp^*MoCl_2]_2/Cp^*MoCl_4$ and $[Cp^*MoCl_2]_2/PhICl_2$ Reactions. Since we found earlier that $CpMoCl_3$ can easily be synthesized by conproportionation of $CpMoCl_2$ and $CpMoCl_4$, we have investigated the same reaction for the Cp* system, with the advantage that the higher solubility of the Cp* system allows NMR monitoring and also an electrochemical investigation. It is convenient to first analyze the electrochemical properties of the two starting materials. As discussed above, the Cp^*MoCl_4 compound exhibits a reversible reduction process at –0.16 V vs Cp_2Fe/Cp_2Fe^+. The cyclic voltammogram of $[Cp^*MoCl_2]_2$, which has not previously been reported, shows a reversible one-electron oxidation to the $[Cp^*_2Mo_2Cl_4]^+$ cation at –0.33 V and a second chemically irreversible one-electron oxidation with $E_{p,a}$ = +0.76 V on the same scale (see Figure 3). For comparison, the same redox processes for the tetraiodo analogue are observed at –0.381 and +0.475 V, respectively, both these values being $E_{1/2}$ of electrochemically reversible processes.[33] According to the observed redox properties, therefore, the interaction between Cp^*MoCl_4 and $[Cp^*MoCl_2]_2$ should first generate a solution of $[Cp^*_2Mo_2Cl_4]^+[Cp^*MoCl_4]^-$.

When the interaction between these two materials is carried out in a 1:1 molar ratio, a broad resonance ($w_{1/2}$ = 90 Hz) is immediately observed at δ 6.0, but this rapidly disappears within 2 h at room temperature while the resonance assigned to $[Cp^*MoCl_3]_2$ (δ –3.87), which is already dominant in the spectrum recorded immediately after mixing, continues to grow. The sharp resonance at δ 1.98 due to the impurity in the isolated trichloride dimer is also observed to grow. Another broad resonance (at δ 1.3, $w_{1/2}$ = 40) also grows together with that of the trichloride dimer and remains unchanged in the final spectrum. When the interaction is carried out in a 1:2 molar ratio, the initial development of the ^{1}H-NMR spectrum is identical to that described for the 1:1 reaction. However, the broad resonance at δ 1.3 ultimately decreases in intensity and almost completely disappears.

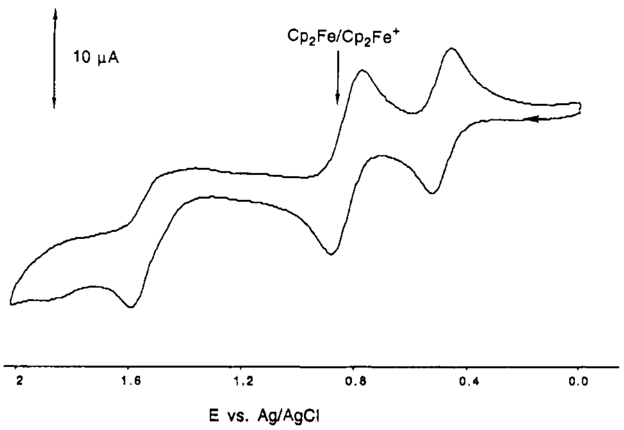
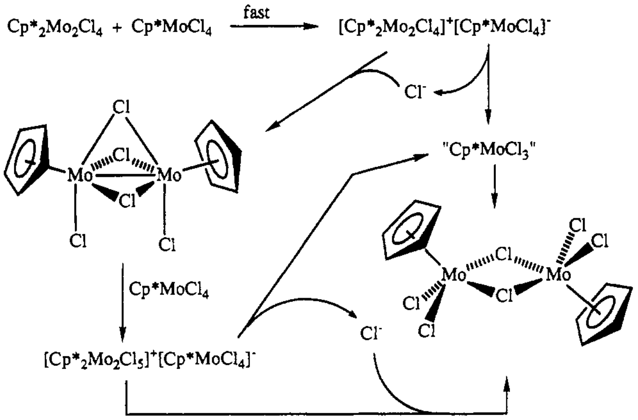


Figure 3. Room temperature cyclic voltammogram of a solution containing $[Cp^*MoCl_2]_2$ and the ferrocene standard. Solvent = CH_2Cl_2. Scan rate = 200 mV s^{-1}.

Scheme 2



Given the stoichiometries of these reactions, we assign the broad resonance at δ 1.3 to the mixed valence neutral compound $Cp^*_2Mo_2Cl_5$ and we propose the series of events illustrated in Scheme 2 to rationalize all the above observations. The assignment of the broad resonance at δ 6.0 to the mixed-valence $[Cp^*_2Mo_2Cl_4]^+$ species is consistent with the trend of chemical shifts observed for the analogous bromide (δ 4.3) and iodide (δ 2.7) cations.[12] The resonance of the transient $[Cp^*MoCl_4]^-$ ion (which should be observed around δ –13.5) is not observed, perhaps because of a rapid self-exchange with the parent Mo(V) complex whose slow electronic relaxation time broadens the ^{1}H-NMR resonance beyond detection. The absence of the $[Cp^*MoCl_4]^-$ ^{1}H-NMR resonance could also be explained by a rapid dissociation of Cl$^-$ followed by slow incorporation into the $[Cp^*_2Mo_2Cl_4]^+$ ion. We have independent evidence that the incorporation of Cl$^-$ into the coordination sphere of $[Cp^*_2Mo_2Cl_4]^+$ is slow: the cyclic voltammogram of $[Cp^*MoCl_2]_2$ did not significantly change upon introduction of one equivalent of PPN$^+$Cl$^-$. However, parallel studies on mixed-halide conproportionation reactions (e.g. $Cp^*_2Mo_2X_4 + 2Cp^*MoY_4$; X $\neq$ Y) that have been reported separately prove that the halide transfer from the anion to the cation must be associative.[31] These studies also revealed an interesting halide scrambling process for the $[Cp^*_2Mo_2X_4]^+[Cp^*MoY_4]^-$ salts.

After transfer of a chloride ion from the $[Cp^*MoCl_4]^-$ anion to the $[Cp^*_2Mo_2Cl_4]^+$ cation, the "Cp^*MoCl_3" species dimerizes. If a second equivalent of Cp^*MoCl_4 is *not* present, the reaction stops with the formation of $Cp^*_2Mo_2Cl_5$ and $Cp^*_2Mo_2Cl_6$ in a 2:1 ratio. According to the electrochemical results, a second equivalent of Cp^*MoCl_4 is not able to oxidize the $[Cp^*_2Mo_2Cl_4]^+$ species to the corresponding dication. However, coordina-

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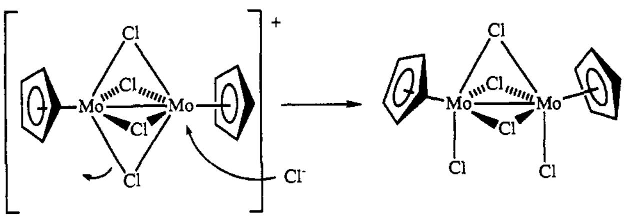
Scheme 3



tion of a chloride ion to form neutral $Cp^*_2Mo_2Cl_5$ should lower the oxidation potential of the metal so that Cp^*MoCl_4 may be able to oxidize this molecule to produce the second proposed intermediate salt. At this point, chloride transfer may occur in the same way as proposed above for the first intermediate salt. The consumption of the $Cp^*_2Mo_2Cl_5$ intermediate in the 1:2 reaction is rather slow, indicating that the electron transfer is probably endoergic and is thermodynamically driven by the subsequent chloride transfer reaction.[37]

The structure proposed for the mixed-valence $Cp^*_2Mo_2Cl_5$ (cis configuration of the terminal chloride ligands) is the only one that allows the geometry around each metal atom to remain of the four-legged piano stool type and it derives in a straightforward manner from the rupture of one of the four $Mo(\mu\text{-}Cl)$-Mo units in the $[Cp^*_2Mo_2Cl_4]^+$ cation (see Scheme 3). Since the structure of compounds of the type $[(ring)MoX_2]_2$ has been shown to contain a quadruply-bridged $Mo(\mu\text{-}X)_4Mo$ moiety [e.g. for X = Cl, ring = $C_5H_4\text{-}i\text{-}Pr$,[9g] C_5Me_4Et;[34] X = Br, ring = C_5Ph_4-(2,5-$(MeO)_2C_6H_3$)[35]] and the one-electron oxidation of $Cp^*_2Mo_2Cl_4$ is electrochemical reversible (see Figure 3), it is logical to propose a quadruply-bridged structure for the monocation as well. In addition, the structure observed for the $[Cp^*_2Mo_2X_4]^+$ (X = Br, I) analogues[12] is also of the quadruply-bridged type and the ^{1}H-NMR chemical shift of the three species (Cl, Br, and I) follows a regular trend as discussed above. A structural similar to that proposed for the $Cp^*_2Mo_2Cl_5$ has been reported for the $[Cp_2Mo_2(CO)_2(\mu\text{-}SMe)_3]^+$ ion.[36]

The results of the ^{1}H-NMR monitoring of the $[Cp^*MoCl_2]_2$/$PhICl_2$ reaction can also be understood on the basis of Scheme 2 with minor modifications. A broad resonance at δ 6.0 developed immediately but soon disappeared (ca. 1 h at room temperature), while the broad resonances at δ 1.3 and -3.87, assigned to $Cp^*_2Mo_2Cl_5$ and $Cp^*_2Mo_2Cl_6$, grew. Thus, this reaction proceeded in a similar manner to the previously discussed oxidation of $[Cp^*MoCl_2]_2$ by Cp^*MoCl_4. We have investigated the cyclic voltammogram of $PhICl_2$ and found that its reduction its highly irreversible, occurring at -0.36 V vs ferrocene and producing Cl^- ions, which are reoxidized at +0.61 V (by comparison with a control CV experiment on PPN^+Cl^-). It is therefore probable that one electron oxidation ultimately produces the $[Cp^*_2Mo_2Cl_4]^+Cl^-$ ion pair, whose cation is responsible for the broad ^{1}H-NMR resonance at δ 6.0. The followup of this oxidation process is the same as discussed earlier for the $Cp^*_2Mo_2Cl_4$/Cp^*MoCl_4 reaction. It was observed that when 1 equiv of $PhICl_2$ per $Cp^*_2Mo_2Cl_4$ was used, which should result in the stoichiometric formation of the trichloride dimer, the resonance at δ 1.3 assigned to $Cp^*_2Mo_2Cl_5$ persists in the final solution. Since the one electron reduction of $PhICl_2$ is expected to produce $Cl^\cdot$ radicals as well as Cl^-, it is not unlikely that part of the $PhICl_2$ is consumed in typical radical chlorination reactions, such as oxidation of the solvent or Cp* ligands. Treatment of this final solution with additional $PhICl_2$ resulted in the eventual disappearance of the broad δ 1.3 resonance. The observed accumulation of $Cp^*_2Mo_2Cl_5$ in solution could not be due to a conproportionation between $[Cp^*MoCl_2]_2$ and $[Cp^*MoCl_3]_3$, since an independent control experiment shows that such a reaction is very slow (<20% conversion in 4 days at room temperature in THF).

Conclusions

We have described the preparation, structure, magnetic behavior, and a few reactions of the novel $[Cp^*MoCl_3]_2$ compound, as well as electrochemical and ^{1}H-NMR experiments that tie together the chemical and redox reactivity of the $Cp^*_2Mo_2Cl_n$ (n = 4, 5, 6) and Cp^*MoCl_4 complexes. In particular, we have learned that $[Cp^*MoCl_2]_2$ and Cp^*MoCl_4 engage in a redox process to afford $[Cp^*_2Mo_2Cl_4]^+$ and $[Cp^*MoCl_4]^-$ and that the $[Cp^*_2Mo_2Cl_4]^+$ ion is quite reactive and abstracts a Cl^- ion from $[Cp^*MoCl_4]^-$. We shall show later that this behavior changes dramatically in the corresponding bromo system.[12] Addition of neutral ligands to $[Cp^*MoCl_3]_2$ easily splits the di-μ-chloro bridge system with the formation of either diamagnetic, 18-electron bis adducts with CO or paramagnetic, 16-electron monoadducts with Cl^- and PMe_3. No tendency for this compound to bind olefins or alkynes was observed. The structure of this d^2–d^2 compound is analogous to that of the corresponding d^1–d^1 hexabromoditantalum compound (type **II**),[7b] and different than that of the metal–metal-bonded d^3–d^3 hexachlorodirhenium analogue (type **I**). It is at present unclear whether this structural change is caused by the change of electron count on the metal from d^2 to d^3 or by the change from a 4d to a 5d row metal, since structure **I** has a better disposition than structure **II** for the formation of metal–metal bonds and it is well-known that metals of the 5d series form stronger metal–metal bonds. In the case of the tantalum compound, structure **I** may be enforced by either the electron count or by the presence of the larger bromide bridging group. To resolve this question, the synthesis of the corresponding tungsten chloride and bromide systems is currently being pursued in this laboratory.

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Supplementary Material Available: Full tables of crystal and refinement parameters, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom positions (6 pages). Ordering information is given on any current masthead page.

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(37) Note added in proof: The $[Cp^*_2Mo_2Cl_5]^+$ ion has now been isolated as the $[AlCl_4]^-$ salt. It shows a reversible reduction at $E_{1/2}$ = -0.13 V: Abugideiri, F.; Fettinger, J. C.; Poli, R. Manuscript in preparation.