

characterize. The products are stable for only short periods of time, even in the solid state under rigorously anaerobic conditions. The nature of the decomposition pathway is not clear; however, the ability of vanadocene dithiolates species to undergo facile reduction to vanadocene and disulfide has been previously described.<sup>27</sup> Despite these difficulties, the thiolato-bridged V(IV)/Cu(I) complexes were characterized by EPR spectroscopy. Each spectrum shows an eight-line pattern due to coupling of the unpaired electron to the vanadium nucleus with additional hyperfine coupling. The observed *g* values were typical of V(IV) species. Computer simulations of the spectra were consistent with the presence of hyperfine couplings of 9.5 G to Cu and 8.0 G to P for both **5** and **6** (Figure 4). The simulations fit well for the central lines. Broadening observed for the outer lines is typical of V(IV) compounds and arises from the anisotropy in the hyperfine interactions as a result of inhibited molecular tumbling caused by solute-solvent interactions.<sup>27</sup> Nonetheless, the spectral are clearly consistent with V-Cu-P couplings. We have previously reported similar coupling between the Ti(III) d<sup>1</sup> metal center and the Rh and P nuclei of [Cp<sub>2</sub>Ti(μ-SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>)<sub>2</sub>Rh]<sup>0,4</sup>. Although the line widths of the eight resonances for **7** and **8** are comparable to those of **5** and **6**, distinct hyperfine couplings are not resolved for **7** or **8**. Presumably, additional coupling to the quadrupolar N atoms of the coordinated acetonitriles contributes to the diminished resolution. The mechanism by which V-Cu-L couplings occur is not fully understood. However, molecular

orbital considerations for d<sup>1</sup> Cp<sub>2</sub>M systems suggest that the unpaired electron occupies the 1a<sub>1</sub> orbital.<sup>28</sup> Interactions between this orbital and the transannular Cu center may be mediated by the bridging sulfur atoms or may result from direct interactions between the unpaired electron and the Cu. In a related study, we have favored a direct transannular mechanism to explain the larger coupling observed for Cp<sub>2</sub>Ti(S<sub>2</sub>PR<sub>2</sub>) than for Cp<sub>2</sub>Ti(SPR<sub>2</sub>).<sup>29</sup> This suggestion was also supported by the MO calculations of Lorenz and Wasson.<sup>30</sup> A vehicle for direct electronic communication between V and Cu in the present compounds may arise from a dative donation from Cu to V similar to that inferred from the structural studies of **2**.

In summary, the data presented herein support the notion of electronic communication between disparate metal centers. Such interactions are not regarded as formal bonds; however, their influence on the structural and spectral properties of mixed-metal complexes is apparent. The effects of such interactions on the chemistry of mixed-metal systems is the subject of ongoing investigations.

**Acknowledgment.** Financial support from the NSERC of Canada is gratefully acknowledged.

**Supplementary Material Available:** Tables of crystallographic, thermal, and hydrogen atom parameters (5 pages); a table of values of 10F<sub>o</sub> and 10F<sub>c</sub> (8 pages). Ordering information is given on any current masthead page.

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## Stable Cationic 17-Electron [LM(CO)<sub>3</sub>]<sup>+</sup> Species (L = 1,4,7-Tribenzyl-1,4,7-triazacyclononane; M = Cr, Mo, W): Synthesis, Spectroscopic Properties, and Reactivity. Crystal Structure of [LMo(CO)<sub>3</sub>](PF<sub>6</sub>)-dmf

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Received September 14, 1989

The neutral 18-electron complexes LM(CO)<sub>3</sub>, where L, represents the tridentate capping ligand 1,4,7-tribenzyl-1,4,7-triazacyclononane and M is Cr, Mo, or W, were prepared from M(CO)<sub>6</sub> and L in dimethylformamide (dmf) at 150 °C. Oxidation of these diamagnetic complexes in CH<sub>2</sub>Cl<sub>2</sub> with ferrocenium hexafluorophosphate affords the cationic 17-electron species [LM(CO)<sub>3</sub>]<sup>+</sup>PF<sub>6</sub> in good yields. Magnetic susceptibility measurements and ESR spectroscopy confirm the presence of one unpaired electron per cation in these materials. The crystal structure of [LMo(CO)<sub>3</sub>]<sup>+</sup>(PF<sub>6</sub>)-dmf has been determined by X-ray crystallography (trigonal, space group R $\bar{3}$ ; *a* = 18.299 (4), *c* = 24.852 (7) Å; *Z* = 9). The molybdenum atom is in a pseudooctahedral environment comprising three facially coordinated amine nitrogen atoms and three carbonyl ligands. The cation possesses crystallographically imposed C<sub>3</sub> symmetry. Cyclic voltammetry reveals a reversible one-electron oxidation of LM(CO)<sub>3</sub> species in dmf at -0.52 V vs Fc<sup>+</sup>/Fc for the chromium complex, at -0.23 V vs Fc<sup>+</sup>/Fc for the molybdenum complex, and at -0.305 V vs Fc<sup>+</sup>/Fc for the tungsten complex. At more anodic potentials a second irreversible oxidation wave has been observed. The reactivity of the LM(CO)<sub>3</sub> species has been briefly investigated.

### Introduction

In recent years neutral organotransition-metal, 17-electron, metal-centered radicals<sup>2</sup> such as CpCr(CO)<sub>3</sub>,<sup>3</sup> Cp\*Cr(CO)<sub>3</sub>,<sup>3</sup> TpMo(CO)<sub>3</sub>,<sup>4</sup> and Tp'Mo(CO)<sub>3</sub><sup>4</sup> (Cp represents the η<sup>5</sup>-cyclo-

pentadienyl anion and Cp\* is its pentamethylated derivative, Tp is hydridotris(pyrazolyl)borate(1-), and Tp' is hydridotris(3,5-dimethylpyrazolyl)borate(1-)) have been characterized either as reactive intermediates<sup>3</sup> or in one instance as relatively stable species in the solid state.<sup>4</sup> CpCr(CO)<sub>3</sub> exists in solution in equilibrium with its dimer [CpCr(CO)<sub>3</sub>]<sub>2</sub>,<sup>3</sup> which undergoes homolytic dissociation of its weak Cr-Cr bond.<sup>3</sup> The molybdenum and tungsten analogues [CpM(CO)<sub>3</sub>]<sub>2</sub> are thermally more stable, but homolytic M-M bond cleavage has been shown to occur photochemically.<sup>5</sup> The neutral CpM(CO)<sub>3</sub> radical species (M = Mo, W) have also

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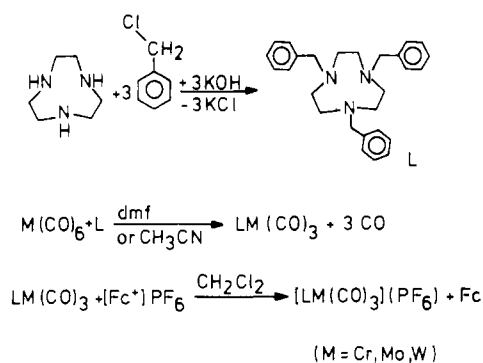
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## Scheme I

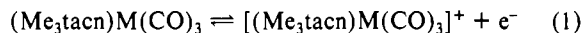


been generated electrochemically<sup>6</sup> from the dimer. In general, the CpM(CO)<sub>3</sub> radicals (M = Cr, Mo, W) are thermally quite unstable, and in no instance has the monomeric radical been isolated.

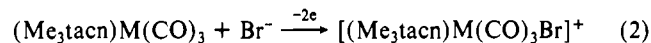
Curtis et al.<sup>4a,b</sup> have shown in an elegant study that chemical oxidation of the 18-electron anion [Tp(Mo)(CO)<sub>3</sub>]<sup>-</sup> by the Ag<sup>+</sup> ion or ferrocenium hexafluorophosphate (Fc<sup>+</sup>PF<sub>6</sub>) gives in high yields the stable monomeric 17-electron radical Tp(Mo(CO)<sub>3</sub>), which they have been able to isolate as a crystalline solid. The crystal structure of this radical has been determined.<sup>4a,b</sup> Subsequently, Shiu et al. were able to show that the thermal stability of this type of neutral radical is enhanced on going from hydridotris(pyrazolyl)borate(1<sup>-</sup>) to the bulkier 3,5-dimethylpyrazolyl derivative of the same ligand. For EHMO calculations and <sup>1</sup>H NMR studies it was concluded that the unpaired electron occupies a doubly degenerate orbital and that the odd electron is delocalized onto the pyrazolyl rings of the Tp ligand by π-bonding.<sup>4b</sup>

Common features of the CpM(CO)<sub>3</sub> and TpM(CO)<sub>3</sub> radicals are (i) they are neutral monomeric species and (ii) both the Cp<sup>-</sup> and Tp<sup>-</sup> ligands are σ-donors and good π-donors but weak π-acceptors. Increasing bulkiness of the ligands (Cp<sup>\*</sup>, Tp<sup>\*</sup>) enhances the stability of the radicals in solution because dimerization becomes an increasingly improbable (or impossible) event. Thus, both TpMo(CO)<sub>3</sub> and Tp<sup>\*</sup>Mo(CO)<sub>3</sub> do not dimerize in solution extensively. The former does form the binuclear complex Tp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>4</sub> at elevated temperatures and prolonged reaction times (note that 2 equiv of CO are cleaved off, one from each TpMo(CO)<sub>3</sub> unit).

Over the past years we have investigated the chemistry of (tacn)M(CO)<sub>3</sub> and (Me<sub>3</sub>tacn)M(CO)<sub>3</sub>, where tacn represents the saturated tridentate amine 1,4,7-triazacyclononane and Me<sub>3</sub>tacn represents its N-methylated derivative (M = Cr, Mo, W).<sup>7,8</sup> Both ligands are pure σ-donors. Cyclic voltammograms of (Me<sub>3</sub>tacn)M(CO)<sub>3</sub> (M = Mo, W) in dimethylformamide (dmf) in the absence of coordinating anions (Br<sup>-</sup>, Cl<sup>-</sup>, etc.) revealed a reversible one-electron oxidation (eq 1) whereas in the presence



of e.g. bromide ions only an irreversible oxidation occurred (eq 2), generating the seven-coordinate species [(\text{Me}\_3\text{tacn})M-



(\text{CO})\_3\text{Br}]^+.<sup>8c,d</sup> Interestingly, the redox potentials for the processes in eq 1 are in a chemically readily accessible range ( $E_{1/2}$  for the W complex is at -0.34 V vs Fc<sup>+</sup>/Fc whereas that for the Mo complex is at -0.245 V vs Fc<sup>+</sup>/Fc) and, in addition, even at very

slow scan rates (<20 mV s<sup>-1</sup>) no decomposition of the oxidized species was observed. Thus, it should be possible to chemically generate and isolate cationic 17-electron radicals [LM(CO)<sub>3</sub>]<sup>+</sup>. It is of interest to compare the spectroscopic properties and the reactivity of these complexes, which contain as capping ligand a pure σ-donor, with those of their neutral analogues, which, in contrast, contain π-acceptor ligands. Building on Curtis's and Shui's work on the TpMo(CO)<sub>3</sub> complex, we decided to synthesize the new, bulky ligand 1,4,7-tribenzyl-1,4,7-triazacyclononane and to use the readily available LM(CO)<sub>3</sub> (M = Cr, Mo, W) complexes as starting materials. Oxidation of these 18-electron species in CH<sub>2</sub>Cl<sub>2</sub> with Fc<sup>+</sup>PF<sub>6</sub> affords the yellow, air- and light-sensitive but thermally stable salts [LM(CO)<sub>3</sub>](PF<sub>6</sub>) (Scheme I). Here we report on the spectroscopic and magnetic properties of these materials. In addition, we have determined the crystal structure of [LMo(CO)<sub>3</sub>](PF<sub>6</sub>)-dmf.

## Experimental Section

**Preparation of the Ligand 1,4,7-Tribenzyl-1,4,7-triazacyclononane (L; C<sub>27</sub>H<sub>33</sub>N<sub>3</sub>).** To a solution of 1,4,7-triazacyclononane (4 g; 31 mmol) in toluene (70 mL) was added benzyl chloride (12.8 g; 93 mmol) and finely powdered potassium hydroxide (5.21 g; 93 mmol). The mixture was stirred at 80 °C for 8 h, after which time an additional amount of KOH (1 g) was added to the suspension at 20 °C. After removal of KCl by filtration, the solvent was removed under reduced pressure. A crude yellow oil of the ligand was obtained in 88% yield, which was used for the synthesis of complexes without further purification.

<sup>1</sup>H NMR (80 MHz; CDCl<sub>3</sub>; δ): 2.85 (s, 12 H), 2.68 (s, 6 H), 7.40 (m, 15 H).

**Preparation of Complexes.** All manipulations were carried out under an argon atmosphere; oxygen-free and dried solvents were used throughout.

The complexes [Et<sub>4</sub>N][TpM(CO)<sub>3</sub>] (M = Cr, Mo, W) were prepared according to published procedures.<sup>9</sup>

**LCr(CO)<sub>3</sub>.** A mixture of Cr(CO)<sub>6</sub> (3.6 g; 16.3 mmol) and the ligand L (6.5 g; 16.3 mmol) in dimethylformamide (dmf) (25 mL) was heated at 150 °C for 1.5 h. During this time the color of the solution changed to yellow-green and a yellow solid started to precipitate out. After the mixture was cooled to 0 °C for 2 h, the yellow precipitate was filtered off, washed with ether, and dried (yield: 5.4 g; 62%). The product is soluble in dmf, CH<sub>2</sub>Cl<sub>2</sub>, acetone, and dimethyl sulfoxide (dmsO).

<sup>1</sup>H NMR (80 MHz; dmsO-*d*<sub>6</sub>; δ): 7.4 (s, 15 H), 4.7 (s, 6 H), 3.0–3.5 (m, 6 H), 2.0–2.5 (m, 6 H). Anal. Calcd for C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>Cr: C, 67.3; H, 6.2; N, 7.8. Found: C, 67.1; H, 6.4; N, 7.8.

**[LCr(CO)<sub>3</sub>](PF<sub>6</sub>)·CH<sub>2</sub>Cl<sub>2</sub>.** To a solution of LCr(CO)<sub>3</sub> (0.3 g; 0.5 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) was added ferrocenium hexafluorophosphate (Fc<sup>+</sup>PF<sub>6</sub>) (0.186 g; 0.5 mmol) with stirring at room temperature. After 5 min the violet color of the solution had changed to yellow. Argon was slowly passed through this solution until the volume was reduced 15 mL and a yellow precipitate had formed. Yellow microcrystals were collected by filtration, washed with ether, and dried (yield: 0.28 g; 73%).

Anal. Calcd for [C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>Cr]PF<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub>: C, 48.6; H, 4.6; N, 5.5. Found: C, 48.4; H, 4.7; N, 5.6.

**LMo(CO)<sub>3</sub> and LW(CO)<sub>3</sub>.** A mixture of Mo(CO)<sub>6</sub> (2 g; 7.6 mmol) and L (3.1 g; 7.8 mmol) in acetonitrile (60 mL) was heated to reflux for 5 h. During the reaction of yellow precipitate formed. After cooling of the solution to 5 °C, this precipitate was filtered off, washed with ether, and dried (yield: 3.3 g; 75%).

<sup>1</sup>H NMR (80 MHz; CD<sub>2</sub>Cl<sub>2</sub>; δ): 7.4 (s, 15 H), 4.7 (s, 6 H), 3.1–3.6 (m, 6 H), 2.2–2.7 (m, 6 H). Anal. Calcd for C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>Mo: C, 62.2; H, 5.7; N, 7.3. Found: C, 61.1; H, 5.0; N, 6.9.

The yellow complex LW(CO)<sub>3</sub> was prepared analogously by using W(CO)<sub>6</sub>. The reaction mixture was heated to reflux for 14 h. Yield: 3.8 g; 67%.

<sup>1</sup>H NMR (80 MHz; CH<sub>3</sub>NO<sub>2</sub>; δ): 7.3–7.7 (m, 15 H), 4.7 (s, 6 H), 3.2–3.8 (m, 6 H), 2.4–2.9 (m, 6 H). Anal. Calcd for C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>W: C, 53.9; H, 4.9; N, 6.3. Found: C, 54.1; H, 4.9; N, 6.2.

**[LM(CO)<sub>3</sub>]PF<sub>6</sub> (M = Mo, W).** To a solution of LM(CO)<sub>3</sub> (M = Mo, W) (0.34 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added Fc<sup>+</sup>PF<sub>6</sub> (0.114 g; 0.34 mmol) with stirring at ambient temperature. Within 5 min the color of the solution changed from deep violet to yellow. Argon was passed slowly through this solution until the volume was reduced to half by evaporation. A yellow precipitate was collected by filtration, washed with *n*-hexane, and dried under argon. The materials are air- and light-sensitive but can be stored under argon in the dark for many weeks without detectable decomposition. The yields were ca. 75%.

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**Table I.** Crystallographic Data for [LMo(CO)<sub>3</sub>](PF<sub>6</sub>)-dmf

| formula           | C <sub>30</sub> H <sub>33</sub> MoN <sub>3</sub> O <sub>3</sub> -PF <sub>6</sub> C <sub>3</sub> H <sub>7</sub> NO | radiation<br>(monochromator;<br>λ, Å)     | Mo Kα<br>(graphite;<br>0.71069) |
|-------------------|---|---|---------------------------------|
| space group       | R $\bar{3}$ (No. 148)   |   |                                 |
| a, Å              | 18.299 (4)  | $\rho_{\text{calc}}$ , g cm <sup>-3</sup> | 1.50                            |
| c, Å              | 24.852 (7)  | abs coeff, mm <sup>-1</sup>               | 0.52                            |
| V, Å <sup>3</sup> | 7205 (3)  | temp, K                                   | 225                             |
| Z                 | 9   | R(F)                                      | 0.085                           |
|                   |   | R <sub>w</sub> (F <sup>2</sup> )          | 0.078                           |

Anal. Calcd for C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>MoPF<sub>6</sub>: C, 49.5; H, 4.5; N, 5.7. Found: C, 49.3; H, 4.6; N, 5.5.

Anal. Calcd for C<sub>30</sub>H<sub>33</sub>N<sub>3</sub>O<sub>3</sub>WPF<sub>6</sub>: C, 44.3; H, 4.1; N, 5.2. Found: C, 44.6; H, 4.2; N, 5.3.

[LM(CO)<sub>2</sub>NO]BF<sub>4</sub> (M = Mo, W). To a solution of LM(CO)<sub>3</sub> (M = Mo, W) (0.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added [NO]BF<sub>4</sub> (0.035 g, 0.3 mmol) with stirring at 20 °C. After 30 min the volume of the reaction mixture was reduced to half by passing argon through the solution. The yellow precipitates were collected by filtration, washed with ether, and air-dried (yield: ≈50%).

Anal. Calcd for C<sub>29</sub>H<sub>33</sub>N<sub>4</sub>O<sub>4</sub>MoBF<sub>4</sub>: C, 52.2; H, 4.9; N, 8.3. Found: C, 51.8; H, 4.7; N, 8.1. <sup>1</sup>H NMR (80 MHz; acetone-d<sub>6</sub>; δ): 2.8–3.5 (m, 6 H), 3.51–4.1 (m, 6 H), 4.45 (s, 2 H), 4.75 (d, 4 H), 7.3–7.8 (m, 15 H).

Anal. Calcd for C<sub>29</sub>H<sub>33</sub>N<sub>4</sub>O<sub>4</sub>WBF<sub>4</sub>: C, 46.0; H, 4.3; N, 7.4. Found: C, 45.8; H, 4.2; N, 7.2. <sup>1</sup>H NMR (80 MHz; acetone-d<sub>6</sub>; δ): 2.9–4.0 (m, 12 H), 4.45 (s, 2 H), 4.75 (d, 4 H), 7.4–7.8 (m, 15 H).

**Reactivity Studies.** To a solution [LMo(CO)<sub>3</sub>](PF<sub>6</sub>) (0.073 g; 0.1 mmol) in degassed CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added PPh<sub>3</sub> (0.262 g). The solution was heated to reflux under an argon atmosphere for 1 h. The solution infrared spectrum in the CO stretch region indicated the quantitative reduction of [LMo(CO)<sub>3</sub>]<sup>+</sup> to yield the neutral species LMo(CO)<sub>3</sub>. No disproportionation products such as [LMo(CO)<sub>3</sub>X]<sup>+</sup> were detected. It is not clear to us what the oxidation product is since the oxidation potential of the cation does not appear to be sufficient to oxidize triphenylphosphine. On the other hand, in a similar control experiment we were able to show that PPh<sub>3</sub> reduces under the same reaction conditions the ferrocenium cation to ferrocene.

To a solution of [LMo(CO)<sub>3</sub>](PF<sub>6</sub>) (0.073 g; 0.1 mmol) in degassed CH<sub>3</sub>CN (25 mL) was added (CH<sub>3</sub>)<sub>3</sub>NO (0.037 g; 0.5 mmol). The solution was stirred under an argon atmosphere for 24 h at ambient temperature. Addition of degassed diethyl ether initiated the quantitative precipitation of LMo(CO)<sub>3</sub>.

To a solution of LMo(CO)<sub>3</sub> (0.058 g; 1 mmol) in degassed CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added [Fc](PF<sub>6</sub>) (0.033 g; 0.1 mmol). Within 10 min at ambient temperature the color of the solution turned orange. Quantitative formation of [LMo(CO)<sub>3</sub>]<sup>+</sup> and Fc was indicated by a solution infrared spectrum. Then [TBA]Br (0.065 g; 0.2 mmol) was added and the solution was stirred for 10 min. A solution infrared spectrum in the CO stretch region showed the presence of LMo(CO)<sub>3</sub> and [LMo(CO)<sub>3</sub>Br]<sup>+</sup> in equal amounts. Further addition of 0.1 mmol of [Fc](PF<sub>6</sub>) produced within 10 min quantitatively [LMo(CO)<sub>3</sub>Br]<sup>+</sup>, which was precipitated as a PF<sub>6</sub> salt by addition of diethyl ether in 80% yield.

**Electrochemistry.** The apparatus used for electrochemical measurements has been described previously.<sup>8c</sup> Cyclic voltammograms were recorded in dmf solution (0.1 M tetra-*n*-butylammonium hexafluorophosphate (TBA)PF<sub>6</sub>, as supporting electrolyte) under an argon atmosphere. At the beginning of each experiment a cyclic voltammogram of the solution containing only the supporting electrolyte was recorded. To this solution were then added solid samples, and these were dissolved to yield ≈10<sup>-3</sup> M concentrations of the respective complex. Then a nearly equimolar amount of ferrocene was added as internal standard. Formal redox potentials are given vs the reference electrode system ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) in volts. The working reference electrode used was an Ag/AgCl (saturated LiCl in ethanol) and a Pt-wire auxiliary electrode; the working electrode was a glassy-carbon electrode in all cases.

**Instrumentation.** Infrared spectra of complexes were recorded on a Perkin-Elmer FTIR 720 X spectrometer both as KBr disks of solid samples and in CH<sub>2</sub>Cl<sub>2</sub> solution. Magnetic susceptibilities of powdered samples were measured by using the Faraday method in the temperature range 90–298 K. Diamagnetic corrections were applied with use of Pascal's constants. ESR spectra were measured at X-band frequency on frozen glasses (dmf) at -196 °C or in case of [LCr(CO)<sub>3</sub>](PF<sub>6</sub>) as powdered sample at 10 K.

**X-ray Crystallography.** Yellow single crystals suitable for an X-ray structure determination were obtained in the following fashion. To a solution of LMo(CO)<sub>3</sub> (0.35 g) in a mixture of CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and dmf (5 mL) was added Fc<sup>+</sup>PF<sub>6</sub> (0.2 g) under an argon atmosphere at room temperature. After the color of the solution had changed to yellow the solution was kept at -30 °C for 3 days, after which time yellow translucent crystals of [LMo(CO)<sub>3</sub>](PF<sub>6</sub>)-dmf had formed. These crystals lose

**Table II.** Atomic Coordinates (×10<sup>4</sup>) and Equivalent Isotropic Displacement Factors (Å<sup>2</sup> × 10<sup>3</sup>)

|        | x         | y          | z         | U <sub>eq</sub> <sup>a</sup> |
|--------|-----------|------------|-----------|------------------------------|
| Mo     | 0         | 0          | 3474 (1)  | 40 (1)*                      |
| N      | -1048 (4) | -524 (4)   | 2845 (2)  | 42 (3)*                      |
| C(1)   | -494 (6)  | -984 (7)   | 3942 (3)  | 62 (5)*                      |
| O(1)   | -757 (5)  | -1516 (5)  | 4259 (3)  | 102 (5)*                     |
| C(2)   | -1888 (5) | -944 (6)   | 3111 (3)  | 62 (5)*                      |
| C(3)   | -947 (6)  | -1156 (7)  | 2519 (5)  | 101 (7)*                     |
| C(4)   | -949 (6)  | 196 (6)    | 2516 (5)  | 93 (6)*                      |
| C(6)   | -3047 (6) | -2181 (6)  | 2601 (4)  | 67 (5)*                      |
| C(7)   | -3745 (7) | -2536 (8)  | 2286 (5)  | 91 (7)*                      |
| C(8)   | -4116 (7) | -2105 (11) | 2124 (4)  | 98 (8)*                      |
| C(9)   | -3771 (8) | -1259 (12) | 2272 (5)  | 107 (9)*                     |
| C(10)  | -3035 (6) | -862 (7)   | 2606 (4)  | 70 (5)*                      |
| C(5)   | -2672 (5) | -1337 (6)  | 2748 (3)  | 53 (4)*                      |
| P      | 0         | 5000       | 5000      | 151 (5)                      |
| F(1)   | 1 (14)    | 5793 (11)  | 4969 (9)  | 147 (7)                      |
| F(2)   | 217 (14)  | 5067 (13)  | 4433 (6)  | 254 (12)                     |
| F(3)   | -890 (10) | 4546 (14)  | 4861 (9)  | 224 (10)                     |
| F(4)   | -349 (20) | 4031 (19)  | 4776 (14) | 223 (13)                     |
| F(5)   | -453 (31) | 5617 (29)  | 4808 (20) | 329 (23)                     |
| C(01)  | 2097 (35) | 3159 (36)  | 263 (21)  | 225 (20)                     |
| O(01)  | 1632 (22) | 3472 (22)  | 71 (14)   | 230 (13)                     |
| N(01)  | 1378 (18) | 2809 (17)  | 631 (12)  | 140 (8)                      |
| C(02)  | 856 (35)  | 2404 (32)  | 1053 (20) | 211 (19)                     |
| C(02A) | 1583 (32) | 2349 (30)  | 1038 (19) | 203 (18)                     |

<sup>a</sup> Asterisk indicates equivalent isotropic U defined as one-third of the trace of the orthogonalized U<sub>ij</sub> tensor.

**Table III.** Bond Distances (Å) and Selected Angles (deg) of the Cation in [LMo(CO)<sub>3</sub>](PF<sub>6</sub>)-dmf

|                        |            |                     |            |
|------------------------|------------|---------------------|------------|
| Mo-N                   | 2.281 (6)  | C(2)-C(5)           | 1.53 (1)   |
| Mo-C(1)                | 1.946 (10) | C(4)-C(3a)          | 1.36 (1)   |
| N-C(2)                 | 1.49 (1)   | C(5)-C(6)           | 1.39 (1)   |
| N-C(4)                 | 1.48 (1)   | C(8)-C(9)           | 1.40 (3)   |
| C(10)-C(5)             | 1.38 (2)   | C(1)-O(1)           | 1.15 (1)   |
| N-C(3)                 | 1.50 (2)   | C(3)-C(4a)          | 1.365 (18) |
| C(6)-C(7)              | 1.36 (14)  | C(7)-C(8)           | 1.33 (3)   |
| C(9)-C(10)             | 1.43 (2)   |                     |            |
| N-Mo-C(1)              | 96.7 (3)   | C(1a)-Mo-C(1b)      | 87.9 (4)   |
| C(1)-Mo-N <sub>a</sub> | 96.9 (4)   | N-Mo-N <sub>a</sub> | 78.2 (2)   |
| C(1)-Mo-N <sub>b</sub> | 173.4 (3)  | Mo-C(1)-O(1)        | 173.7 (8)  |

dmf upon removal of the solvent at room temperature and become turbid and amorphous. Therefore, a single crystal from the above solution was transferred into a glass fiber and protected by a capillary at -30 °C and mounted on the diffractometer where it was cooled to 225 K. Measurements of the lattice parameters and intensities were carried out at this temperature, the details of which are summarized in Table I and SI (supplementary material). The structure was solved by standard Patterson and difference Fourier methods and refined<sup>10</sup> with anisotropic thermal parameters for Mo, N, O, and C atoms of the cation whereas atoms of the disordered PF<sub>6</sub> and dmf molecule were refined with isotropic thermal parameters. All attempts failed to model the disorder of the PF<sub>6</sub> and dmf molecules satisfactorily. Neutral-atom scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref 11. Methylene and phenyl ring hydrogen atoms were placed at calculated positions and refined as rigid bodies (C-H = 0.96 Å; C-C-H and H-C-H = 109.5 and 120°, respectively).

The function minimized during full-matrix least-squares refinement was  $\sum w(|F_o| - |F_c|)^2$ , where  $w = [\sigma^2(F_o) + 0.0005F_o^2]^{-1}$ . Final atom coordinates are given in Table II, and selected bond distances and angles, in Table III.

## Results

The transformations observed in this work are summarized in Scheme I. A structure study was undertaken for [LMo(CO)<sub>3</sub>](PF<sub>6</sub>)-dmf, whose results are presented in Tables I–III. Finally, infrared, magnetic, electrochemical, and reactivity studies

(10) (a) Boese, R.; Bläser, D. *J. Appl. Crystallogr.* **1989**, *22*, 394. (b) All computations were carried out on a Micro VAX II computer by using the SHELXTL-PLUS program package.

(11) (a) Cromer, D. R.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321 (and SHELXTL). (b) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891.

**Table IV.** IR Data for 18- and 17-Electron Complexes Containing the *cis*-Tricarbonylmethyl Entity (Metal = Cr, Mo, W)

| complex <sup>f</sup>                     | $\nu(\text{CO}), \text{cm}^{-1}$                 | ref         |
|--|--|-------------|
| LCr(CO) <sub>3</sub>                     | 1889, 1758, 1737 <sup>a</sup>                    | } this work |
| [LCr(CO) <sub>3</sub> ]PF <sub>6</sub>   | 1903, 1762 <sup>b</sup>                          |             |
|  | 2026, 1876 (b) <sup>a</sup>                      |             |
|  | 2027, 1909, 1865 <sup>b</sup>                    |             |
| LMo(CO) <sub>3</sub>                     | 1895, 1759, 1729 <sup>a</sup>                    |             |
|  | 1907, 1768 <sup>b</sup>                          |             |
| [LMo(CO) <sub>3</sub> ]PF <sub>6</sub>   | 2017, 1909, 1873 <sup>b</sup>                    |             |
| LW(CO) <sub>3</sub>                      | 1886, 1747, 1718 <sup>a</sup>                    |             |
|  | 1897, 1757 <sup>b</sup>                          |             |
| [LW(CO) <sub>3</sub> ]PF <sub>6</sub>    | 1998, 1875, 1790 <sup>a</sup>                    |             |
|  | 2001, 1878, 1830 <sup>b</sup>                    |             |
| [LMo(CO) <sub>2</sub> NO]BF <sub>4</sub> | 2025, 1932 ( $\nu(\text{NO})$ 1667) <sup>a</sup> |             |
| [LW(CO) <sub>2</sub> NO]BF <sub>4</sub>  | 2011, 1913 ( $\nu(\text{NO})$ 1652) <sup>a</sup> |             |
| [TpMo(CO) <sub>3</sub> ] <sup>-</sup>    | 1897, 1761 <sup>c</sup>                          | 9           |
| TpMo(CO) <sub>3</sub>                    | 2010, 1885 <sup>b</sup>                          | 4b          |
| [Tp'Mo(CO) <sub>3</sub> ] <sup>-</sup>   | 1891, 1751 <sup>c</sup>                          | 9           |
| Tp'Mo(CO) <sub>3</sub>                   | 1998, 1864 <sup>b</sup>                          | 4c          |
| [CpCr(CO) <sub>3</sub> ] <sup>-</sup>    | 1897, 1795 <sup>d</sup>                          | 3e          |
| CpCr(CO) <sub>3</sub>                    | 2012, 1896 <sup>d</sup>                          | 3c          |
| Cp'Cr(CO) <sub>3</sub>                   | 1999, 1849 <sup>e</sup>                          | 3g          |

<sup>a</sup>KBr disk. <sup>b</sup>CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>c</sup>CH<sub>3</sub>CN solution. <sup>d</sup>Tetrahydrofuran solution. <sup>e</sup>Hexane solution. <sup>f</sup>Ligand abbreviations: L = 1,4,7-tribenzyl-1,4,7-triazacyclononane; Tp = hydridotris(pyrazolyl)borate(1-); Tp' = hydridotris(3,5-dimethylpyrazolyl)borate(1-); Cp = cyclopentadienyl(1-); Cp' = pentamethylcyclopentadienyl(1-).

**Table V.** Summary of Electrochemical Data<sup>a,d</sup>

| complex  | $E_{1/2}, \text{V}$ | $E_{p,ox}, \text{V}$ | $E_{p,red}, \text{V}$ | ref          |
|--|---------------------|----------------------|-----------------------|--------------|
| LCr(CO) <sub>3</sub> <sup>b</sup>                      | -0.52               | r +0.32              | no                    | ir this work |
| LMo(CO) <sub>3</sub> <sup>b</sup>                      | -0.23               | r +0.68              | -0.75                 | ir this work |
| LW(CO) <sub>3</sub> <sup>b</sup>                       | -0.30               | r +0.74              | -0.92                 | ir this work |
| (Me <sub>3</sub> tacn)Cr(CO) <sub>3</sub> <sup>b</sup> | -0.57               | r +0.39              | -1.35                 | ir this work |
| (Me <sub>3</sub> tacn)Mo(CO) <sub>3</sub> <sup>c</sup> | -0.24               | r ni                 |                       | 8c           |
| (Me <sub>3</sub> tacn)W(CO) <sub>3</sub> <sup>c</sup>  | -0.34               | r ni                 |                       | 8d           |
| [TpCr(CO) <sub>3</sub> ] <sup>-b</sup>                 | -0.84               | r -0.02              | -1.50                 | ir this work |
| [TpMo(CO) <sub>3</sub> ] <sup>-b</sup>                 | -0.53               | r +0.21              | no                    | this work    |
| [TpW(CO) <sub>3</sub> ] <sup>-b</sup>                  | -0.62               | r +0.14              | -1.24                 | ir this work |
| [LMo(CO) <sub>2</sub> NO] <sup>+b</sup>                | -2.02               | qr                   |                       | this work    |
| [LW(CO) <sub>2</sub> NO] <sup>+b</sup>                 | -2.13               | qr                   |                       | this work    |

<sup>a</sup>Potentials are referenced versus the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc) couple. <sup>b</sup>dmf solution (0.1 M [TBA]PF<sub>6</sub>). <sup>c</sup>CH<sub>3</sub>CN solution (0.1 M [TBA]PF<sub>6</sub>). <sup>d</sup> $E^\circ(\text{Fc}^+/\text{Fc})^b = 0.64 \text{ V vs Ag/AgCl (saturated LiCl in C}_2\text{H}_5\text{OH)}$ . Abbreviations: r = reversible, ir = irreversible, qr = quasireversible, ni = not investigated, no = not observed.

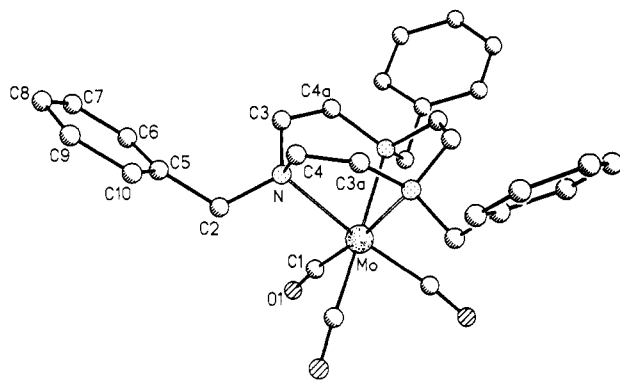
were undertaken whose results are presented in Tables IV and V. These will be introduced at appropriate places in the sections that follow.

## Discussion

**Syntheses.** The reaction of 1,4,7-triazacyclononane with 3 equiv of benzyl chloride in toluene in the presence of potassium hydroxide (3–4 equiv) affords in good yields the ligand 1,4,7-tribenzyl-1,4,7-triazacyclononane (Scheme 1). The hexacarbonylmetal complexes of chromium, molybdenum, and tungsten dissolved in dmf or acetonitrile react with this ligand to give in excellent yields the yellow, air- and moisture-stable, diamagnetic 18-electron species LM(CO)<sub>3</sub>. These complexes are soluble in organic solvents but insoluble in water.

In solution the N<sub>3</sub>M(CO)<sub>3</sub> core possesses local C<sub>3v</sub> symmetry, as is readily deduced from the solution infrared spectrum, which exhibits two  $\nu(\text{CO})$  stretching frequencies (A<sub>1</sub> and E), respectively. In contrast, solid-state spectra of LM(CO)<sub>3</sub> complexes show three  $\nu(\text{CO})$  frequencies (Table IV). The degeneracy of the E mode is lifted probably to a lower symmetry of the neutral species in the solid state.

Comparison of the  $\nu(\text{CO})$  frequencies observed for the neutral LM(CO)<sub>3</sub> compounds with those of isoelectronic anionic species CpM(CO)<sub>3</sub><sup>-</sup> and TpM(CO)<sub>3</sub><sup>-</sup> reveals that, in general, the  $\nu(\text{CO})$  stretching frequencies of LM(CO)<sub>3</sub> complexes are only slightly shifted to higher wavenumbers (6–10 cm<sup>-1</sup>). The increased overall

**Figure 2.** Structure of the cation in crystals of [LM(CO)<sub>3</sub>](PF<sub>6</sub>)·dmf.

negative charge of the anions and the fact that Cp<sup>-</sup> and Tp<sup>-</sup> are weak  $\pi$ -acceptors but good  $\pi$ -donors whereas L has neither property are proposed to be the origin of this observation.

The LM(CO)<sub>3</sub> complexes in CH<sub>2</sub>Cl<sub>2</sub> are readily oxidized under an argon atmosphere at room temperature by the ferrocenium ion. The yellow salts [LM(CO)<sub>3</sub>](PF<sub>6</sub>) (M = Cr, Mo, W) have been isolated as air- and light-sensitive solid materials, which, in the absence of both, could be stored without decomposition for days. In all three cases the solution infrared spectra display three carbonyl stretching frequencies (Figure 1, supplementary material) that are shifted by  $\approx 100 \text{ cm}^{-1}$  to higher wavenumbers as compared to their neutral 18-electron analogues. This is due to reduced  $\pi$ -back-bonding in the oxidized forms. The shift is of the same magnitude as has been reported for the [TpMo(CO)<sub>3</sub>]<sup>-</sup>/TpMo(CO)<sub>3</sub> and [CpCr(CO)<sub>3</sub>]<sup>-</sup>/CpCr(CO)<sub>3</sub> couples (Table IV). Interestingly, for the radicals TpMo(CO)<sub>3</sub> and CpCr(CO)<sub>3</sub> only two  $\nu(\text{CO})$  frequencies are observed in solution, which indicates that in these cases the C<sub>3v</sub> symmetry of the molecules is retained whereas in the [LMo(CO)<sub>3</sub>]<sup>+</sup> cations this symmetry is lowered.

The LMo(CO)<sub>3</sub> complexes (M = Mo, W) react with [NO]BF<sub>4</sub> in CH<sub>2</sub>Cl<sub>2</sub> smoothly, affording yellow diamagnetic complexes of the type [LMo(CO)<sub>2</sub>NO]BF<sub>4</sub>.<sup>8a,d</sup>

### Description of the Crystal Structure of [LMo(CO)<sub>3</sub>](PF<sub>6</sub>)·dmf.

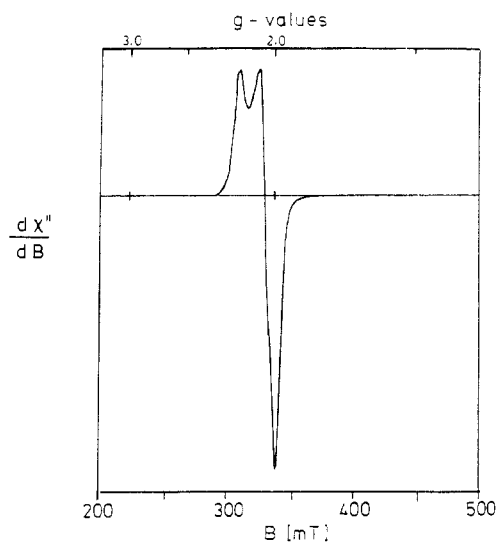
Figure 2 shows a perspective view of the cation in crystals of [LMo(CO)<sub>3</sub>](PF<sub>6</sub>)·dmf. Bond distances and angles are summarized in Table III. The most important feature of this structure determination is the confirmation that, indeed, a pseudooctahedral [LMo(CO)<sub>3</sub>]<sup>+</sup> radical cation and an uncoordinated PF<sub>6</sub><sup>-</sup> anion (ratio 1:1) are present in the solid state. The cation has imposed C<sub>3</sub> symmetry (the N<sub>3</sub>Mo(CO)<sub>3</sub> core has apparent C<sub>3v</sub> symmetry). This is in contrast to the infrared and ESR spectra (see below) of [LMo(CO)<sub>3</sub>]<sup>+</sup> in solution, where clearly a lower symmetry of this core prevails.

The bond distances and angles in the ligand L are unremarkable. The Mo–C distance, 1.95 (1) Å, is only slightly longer than the average Mo–C distance in (tasn)Mo(CO)<sub>3</sub>,<sup>12</sup> 1.925 (3) Å, where tasn represents the ligand 1-thia-4,7-diazacyclononane. The overall accuracy of the crystal structure determination is rather low due to the disorder of the PF<sub>6</sub><sup>-</sup> anion and the dmf molecule, and consequently, this difference is still within the experimental uncertainty and may not be significant. On the other hand, the difference of Mo–C distances in [Tp'Mo(CO)<sub>3</sub>]<sup>-</sup><sup>13</sup> and TpMo(CO)<sub>3</sub><sup>4b</sup> of  $\approx 0.07 \text{ Å}$  is significant and more pronounced. Similarly, the C–O distance in [LMo(CO)<sub>3</sub>]<sup>+</sup>, 1.15 (1) Å, is only marginally (if at all) shorter than in (tasn)Mo(CO)<sub>3</sub> (1.17 Å). In contrast, the C–O bond lengths in [Tp'Mo(CO)<sub>3</sub>]<sup>-</sup> and TpMo(CO)<sub>3</sub> differ more markedly by 0.037 Å.

The C–Mo–C angle of 87.9 (4)° is slightly smaller than the ideal octahedral angle of 90°; the N–Mo–N angle, 78.2°, is rather small due to the steric constraint of the 1,4,7-triazacyclononane backbone.<sup>7</sup> This has been observed in many octahedral complexes containing this ligand.<sup>7</sup>

(12) Hoffmann, P.; Steinhoff, A.; Mattes, R. Z. Naturforsch. 1987, 42B, 867.

(13) Maraballa, C. D.; Enemark, J. H. J. Organomet. Chem. 1982, 226, 57.



**Figure 3.** X-Band ESR spectrum of a powdered sample of  $[\text{LCr}(\text{CO})_3](\text{PF}_6)$  at 10 K ( $2.0 \mu\text{W}/50 \text{ dB}$ ; microwave frequency 9.4228 GHz).

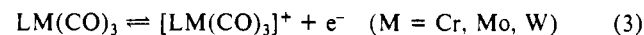
We conclude that the geometry and metrical details of the neutral molecule  $\text{LMo}(\text{CO})_3$  do not change dramatically upon one-electron oxidation to  $\text{LMo}(\text{CO})_3^+$ . The small changes that do occur are reflected more accurately in the infrared spectra than by X-ray structure determinations.

**Magnetic Properties and ESR Spectra.** Magnetic susceptibilities of powdered samples of  $[\text{LM}(\text{CO})_3](\text{PF}_6)$  complexes were measured in the temperature range 90–298 K by using the Faraday method. Temperature-independent magnetic moments of  $1.82 \mu_{\text{B}}$  (Cr),  $1.94 \mu_{\text{B}}$  (Mo), and  $1.93 \mu_{\text{B}}$  (W) were derived, which are in good agreement with the spin-only value of  $1.73 \mu_{\text{B}}$  for one unpaired electron.

The X-band ESR spectrum of a solid sample of  $[\text{LCr}(\text{CO})_3](\text{PF}_6)$  at 10 K is shown in Figure 3. A rhombic signal with  $g_x = 2.158$ ,  $g_y = 2.040$ , and  $g_z = 1.992$  is observed, indicating again that the symmetry of the  $\text{N}_3\text{Cr}(\text{CO})_3$  core cannot be  $\text{C}_{3v}$ . For  $[\text{LMo}(\text{CO})_3](\text{PF}_6)$  the X-band ESR spectrum of a frozen glass (dmf) at 77 K also shows a rhombic signal with  $g_x = 2.188$ ,  $g_y = 2.045$ , and  $g_z = 1.906$ , as does the spectrum of  $[\text{LW}(\text{CO})_3](\text{PF}_6)$  with  $g_x = 1.80$ ,  $g_y = 1.76$ , and  $g_z = 1.68$  under the same conditions. In the spectrum of  $[\text{LMo}(\text{CO})_3](\text{PF}_6)$  no hyperfine splitting from the Mo isotopes with spin  $5/2$  has been detected.

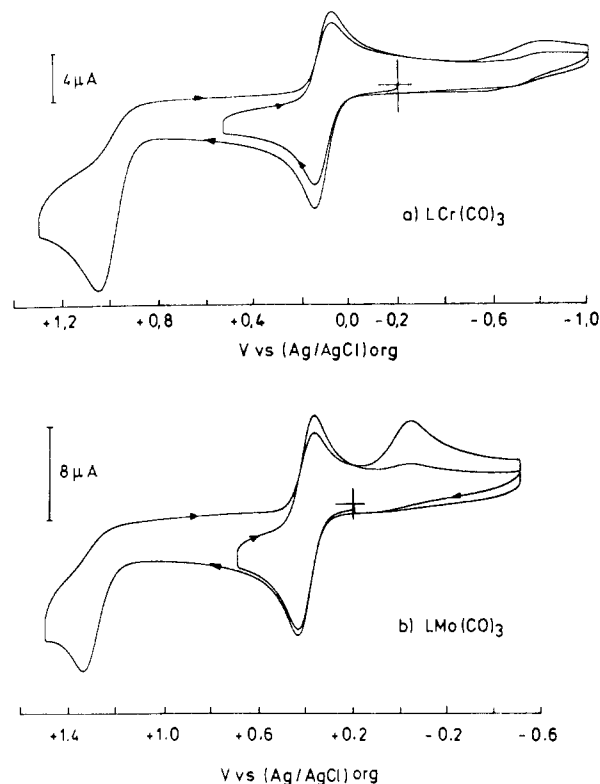
**Electrochemistry.** Cyclic voltammograms (CVs) of  $\text{LCr}(\text{CO})_3$  and  $\text{LMo}(\text{CO})_3$  in dmf, with 0.1 M  $[\text{TBA}]\text{PF}_6$  as supporting electrolyte, are shown in Figure 4. The CV of  $\text{LW}(\text{CO})_3$  is very similar to that of  $\text{LMo}(\text{CO})_3$  and is therefore not shown. In the potential range  $-2.0$  to  $+1.7$  V vs Ag/AgCl four peaks are observed. Identical CVs are observed when the  $[\text{LM}(\text{CO})_3](\text{PF}_6)$  salts were used as starting materials.

When the CVs are scanned in the potential range  $-2.0$  to  $+0.7$  V, only one oxidation and one reduction peak at a peak-potential difference,  $|E_{\text{p,ox}} - E_{\text{p,red}}|$ , of  $\approx 60$  mV is observed (Figure 4). Since this difference and the ratio  $I_{\text{p,red}}/I_{\text{p,ox}}$  of 1.0 are independent of the scan rate  $20$ – $400 \text{ mV s}^{-1}$ , it is concluded that the criteria of Nicholson and Shain<sup>14</sup> for a reversible one-electron-transfer process are met. We assign this process to the reversible oxidation of  $\text{LM}(\text{CO})_3$  species to the corresponding radical cations  $[\text{LMo}(\text{CO})_3]^+$  according to eq 3. This assignment was further cor-



roborated by controlled-potential coulometry of  $\text{LM}(\text{CO})_3$  species at a potential slightly more positive ( $0.3$  V) than the corresponding  $E_{1/2}$  potential given in Table V for the respective  $[\text{LM}(\text{CO})_3]^+/\text{LM}(\text{CO})_3$  couple. In each case the transfer of  $1.0 \pm 0.1$  electron/molecule was determined.

Upon expansion of the potential range of  $+1.7$  V vs Ag/AgCl, a second irreversible oxidation peak is observed in all three cases;



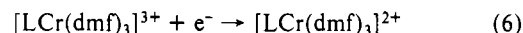
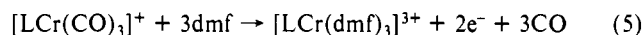
**Figure 4.** Cyclic voltammograms at 20 °C of (a)  $\text{LCr}(\text{CO})_3$  and (b)  $\text{LMo}(\text{CO})_3$  (dmf; glassy-carbon working electrode; 0.1 M  $[\text{TBA}]\text{PF}_6$  supporting electrolyte;  $[\text{complex}] = 0.6 \times 10^{-3} \text{ M}$ ; scan rate  $200 \text{ mV s}^{-1}$ ).

the corresponding reduction peak appears at quite negative potentials (see Table V). The reduction peak is rather ill-defined in the case of  $\text{LCr}(\text{CO})_3$ . This process is probably due to the formation of seven-coordinate  $\text{Mo}(\text{II})$  and  $\text{W}(\text{II})$  species  $[\text{LM}(\text{CO})_3\text{dmf}]^{2+}$  (eq 4). It has previously been shown that in the



presence of bromide ions the structurally characterized species  $[(\text{Me}_3\text{tacn})\text{Mo}(\text{CO})_3\text{Br}]^+$  forms from  $(\text{Me}_3\text{tacn})\text{Mo}(\text{CO})_3$ .<sup>8a,d</sup> The analogous tungsten chemistry has also been demonstrated.<sup>8d</sup>

In the case of  $\text{LCr}(\text{CO})_3$  it is suggested that the second oxidation is an irreversible two-electron process with concomitant loss of CO yielding  $[\text{LCr}(\text{dmf})_3]^{3+}$ , which is then reduced to a chromium(II) species at a very negative potential (eqs 5 and 6). We

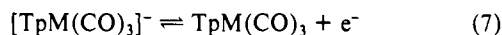


have not investigated these second oxidation processes in more detail, but exhaustive oxidative decarbonylation of (triamine)- $\text{Cr}(\text{CO})_3$  species in the presence of coordinating ligands is a well-established reaction in this chemistry.<sup>7</sup>

The redox potentials of the  $[(\text{amine})\text{M}(\text{CO})_3]^+ / (\text{amine})\text{M}(\text{CO})_3$  couples do not vary greatly when the benzyl groups of L are substituted by methyl groups. Thus,  $(\text{Me}_3\text{tacn})\text{M}(\text{CO})_3$  complexes are oxidized to  $[(\text{Me}_3\text{tacn})\text{M}(\text{CO})_3]^+$  radicals at nearly the same potentials as the corresponding  $\text{LM}(\text{CO})_3$  complexes. We have also investigated (or reinvestigated<sup>9</sup> for the sake of consistency) the electrochemistry of Trofimenko's  $[\text{TpM}(\text{CO})_3]^-$  complexes.<sup>15</sup> Figure 5 (supplementary material) shows the CVs

(15) In Trofimenko's original publication<sup>9</sup> it was stated that the  $[\text{Et}_3\text{N}][\text{TpM}(\text{CO})_3]^-$  complexes dissolved in acetonitrile (tetrabutylammonium perchlorate as supporting electrolyte) exhibited "two well-defined oxidation waves". The potentials given were unreferenced, and no further details of the electrochemical study was given. This is in contrast to our observation of one reversible one-electron process and a second irreversible one. We have repeated the measurements in  $\text{CH}_3\text{CN}$  (0.1 M  $[\text{TBA}]\text{PF}_6$  as supporting electrolyte) and find exactly the same behavior as reported here for dmf solutions.

for [TpCr(CO)<sub>3</sub>]<sup>-</sup> and [TpW(CO)<sub>3</sub>]<sup>-</sup>. The pattern of the CVs obtained is very similar to that of LM(CO)<sub>3</sub> and (Me<sub>3</sub>tacn)M(CO)<sub>3</sub> (M = Cr, Mo, W). Interestingly, the redox potentials,  $E_{1/2}$ , for the reversible one-electron oxidation (eq 7) are shifted by  $\approx 20$

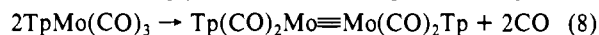


mV to less positive potentials in comparison with those of the corresponding [LM(CO)<sub>3</sub>]<sup>+</sup>/LM(CO)<sub>3</sub> couples. Thus, the anions [TpM(CO)<sub>3</sub>]<sup>-</sup> are more easily oxidized than their neutral LM(CO)<sub>3</sub> analogues.

Finally, the CVs of the [LM(CO)<sub>2</sub>(NO)]BF<sub>4</sub> (M = Mo, W) complexes in dmf in the potential range +1.6 to -2.0 V vs Ag/AgCl exhibit one quasi-reversible one-electron process at  $R_{1/2}$  of -2.13 V for the tungsten and at -2.02 V vs F<sup>+</sup>/Fc for the molybdenum complex. It is conceivable that 19-electron species, LM(CO)<sub>2</sub>NO, are formed, but up to now we have not been able to isolate and characterize such a species and, therefore, the above interpretation is tentative.

**Reactivity Study.** The most pertinent feature of the reactivity of the CpCr(CO)<sub>3</sub> radical appears to be the enormously enhanced substitution lability of the carbonyl groups as compared to its 18-electron [CpCr(CO)<sub>3</sub>]<sup>-</sup> counterpart.<sup>2,3e</sup> Thus, it has been shown to readily react with monodentate tertiary phosphines to form radicals of the type CpCr(CO)<sub>2</sub>L.<sup>3e</sup> In contrast, [LMo(CO)<sub>3</sub>]<sup>+</sup> was found to react with PPh<sub>3</sub> or PMe<sub>3</sub> in refluxing CH<sub>2</sub>Cl<sub>2</sub> within 1 h to yield solely the neutral 18-electron species LMo(CO)<sub>3</sub>. Thus, no substitution of carbonyl ligands has been observed but, instead, a one-electron reduction of the cation. P(OMe)<sub>3</sub> did not react at all under the same conditions. [LW(CO)<sub>3</sub>]<sup>+</sup> and [LCr(CO)<sub>3</sub>]<sup>+</sup> proved also to be substitution inert toward phosphines. CpCr(CO)<sub>3</sub> reacts with CH<sub>3</sub>I, affording CpCr(CO)<sub>3</sub>I and CpCr(CO)<sub>3</sub>Me.<sup>3e</sup> This reaction has again not been observed to take place with [LM(CO)<sub>3</sub>]<sup>+</sup> species—the radical cations could be recovered quantitatively.

The TpMo(CO)<sub>3</sub> radical is also much more substitution inert, but in refluxing acetonitrile or toluene it rapidly loses 1 mol of CO and forms a triply bonded dimer in quantitative yield.<sup>4a,b</sup>

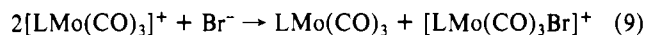


The cationic radicals [LM(CO)<sub>3</sub>]<sup>+</sup> (M = Cr, Mo, W) do not react under the same conditions. This may be due to the fact that a bimolecular reaction between two cations is a less favorable process than that between two neutral species or, alternatively, to an increased stability of the Mo-CO bonds in [LMo(CO)<sub>3</sub>]<sup>+</sup> as compared to TpMo(CO)<sub>3</sub>.

Tp'Mo(CO)<sub>3</sub> was shown to react with elemental sulfur to yield the dimer [Tp'Mo(CO)<sub>2</sub>]<sub>2</sub>S. LMo(CO)<sub>3</sub><sup>+</sup> dissolved in dry tetrahydrofuran did not react with S<sub>8</sub> even at prolonged (3–5 h) reaction times, although (Me<sub>3</sub>tacn)M(CO)<sub>3</sub> complexes do react with S<sub>8</sub> and [(Me<sub>3</sub>tacn)<sub>2</sub>M<sub>2</sub>(CO)<sub>4</sub>S]<sup>2+</sup> cations are produced (M = Mo, W).<sup>16</sup>

Trimethylamine *N*-oxide is known to be a gentle decarbonylation reagent in organometallic chemistry.<sup>17</sup> Koelle has derived the empirical rule that metal carbonyl complexes with the (CO) stretching frequency at wavenumbers >2000 cm<sup>-1</sup> should be susceptible to attack by (CH<sub>3</sub>)<sub>3</sub>NO.<sup>18</sup> Therefore, LMo(CO)<sub>3</sub><sup>+</sup> should be a suitable candidate, but the reaction in acetonitrile produced only the neutral species LMo(CO)<sub>3</sub> and no decarbonylation products have been identified.

Obviously, the [LM(CO)<sub>3</sub>]<sup>+</sup> radicals do not display the same substitution lability of CpCr(CO)<sub>3</sub> and related species. They are redox reactive, as is demonstrated in the following experiment. LMo(CO)<sub>3</sub> dissolved in CH<sub>2</sub>Cl<sub>2</sub> reacts with an equimolar amount of Fc<sup>+</sup>PF<sub>6</sub> to produce quantitatively [LMo(CO)<sub>3</sub>]<sup>+</sup>. Addition of tetra-*n*-butylammonium bromide initiates a rapid disproportionation reaction and LMo(CO)<sub>3</sub> and [LMo(CO)<sub>3</sub>Br]<sup>+</sup> are generated in equal amounts.



When the same amount of Fc<sup>+</sup>PF<sub>6</sub> was then added to this solution, [LMo(CO)<sub>3</sub>Br]PF<sub>6</sub> was generated quantitatively.

Finally, we have tested the stability of [LMo(CO)<sub>3</sub>]<sup>+</sup> toward light in a preliminary experiment. A CH<sub>2</sub>Cl<sub>2</sub> solution of [LMo(CO)<sub>3</sub>]<sup>+</sup>PF<sub>6</sub> was illuminated with a Hg lamp at room temperature for 4 h. Addition of diethyl ether initiated the precipitation of a brownish powder, the infrared spectrum of which do not display any bands in the 2200–1600-cm<sup>-1</sup> region. We conclude that under these conditions photochemically induced Mo-CO cleavage occurs. The neutral LMo(CO)<sub>3</sub> complex does not react under these conditions.

### Summary

We have shown in this study that persistent pseudooctahedral, cationic radicals are generated by chemical or electrochemical oxidation of LM(CO)<sub>3</sub> species (M = Cr, Mo, W). [LM(CO)<sub>3</sub>](PF<sub>6</sub>) salts are readily isolated; they are oxygen- and light-sensitive materials. In contrast to the known reactivity of neutral organometallic radicals of this type, the [LM(CO)<sub>3</sub>]<sup>+</sup> cations are substitution inert but redox reactive.

**Acknowledgment.** This work was supported by the Fonds der Chemischen Industrie. We thank Professor A. X. Trautwein and Dr. E. Bill (Medizinische Universität, Lübeck, FRG) for measuring the ESR spectra.

**Supplementary Material Available:** Figures 1 and 5, showing infrared spectra and cyclic voltammograms, and listings of crystallographic details of the crystal structure determination (Table S1), anisotropic displacement factors (Table S2), H atom coordinates (Table S3), and bond lengths and angles (Tables S4 and S5) (5 pages); a listing of observed and calculated structure factors (Table S6) (9 pages). Ordering information is given on any current masthead page.

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