

(SPh)₃Cl₆]³⁻ is underscored by the large and thus strained Fe-S_b-Fe angles (139, 142°) compared to those of [Fe₂(SR)₆]²⁻ (78-79°) and [Fe₄(SR)₁₀]²⁻ (94-118°). This species undergoes structural changes in solution that, together with solid-state structural and other aspects of type 4 complexes, will be the subject of a future paper.

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Supplementary Material Available: Listings of cation and solvate atom coordinates, temperature factors of cations, anions, and solvate molecules, hydrogen atom coordinates and isotropic temperature factors, atom deviations from Fe₂(μ-S)₂ least-squares planes, and observed and calculated structure factors and a stereoview of [Fe₂(S₂-*o*-xy)₃]²⁻ (90 pages). Ordering information is given on any current masthead page.

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Reactions of LM(CO)₃ Complexes (M = Cr, Mo, W; L = 1,4,7-Triazacyclononane) with Bromine, Iodine, and Nitric Acid. Syntheses of Air-Stable Hydridocarbonyl and Hydridonitrosyl Complexes. Crystal Structure of [LMo(CO)₃Br](ClO₄)·H₂O

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LM(CO)₃ complexes (L = 1,4,7-triazacyclononane; M = Cr, Mo, W) have been synthesized, and their reactivity toward bromine, iodine, and nitric acid has been investigated. Air-stable water-soluble cationic complexes [LM(CO)₃X]⁺ (X = Br, I; M = Mo, W) have been isolated from the reaction with bromine or iodine, whereas the reaction with hydrochloric acid affords [LM(CO)₃H]⁺, the BF₄⁻ and ClO₄⁻ salts of which were isolated as crystalline solids. The reaction with HNO₃ yields cationic nitrosyl complexes [LM(CO)₂(NO)]⁺ (M = Cr, Mo, W) and [LM(NO)₂Y]⁺ (Y = Br, H); in the presence of cyanide the neutral complex [LMo(NO)(CN)₃] has been isolated. The perchlorate salt, [LMo(CO)₃Br](ClO₄)·H₂O, has been characterized by a three-dimensional X-ray diffraction study. The complex crystallizes in the triclinic space group P $\bar{1}$ with *a* = 8.375 (2) Å, *b* = 8.610 (2) Å, *c* = 13.122 (2) Å, α = 90.68 (1)°, β = 90.68 (1)°, γ = 118.24 (1)°, *V* = 833.4 Å³, and *Z* = 2. The structure was solved by conventional methods resulting in a final *R* factor of 0.043 for 2894 independent reflections. The structure consists of seven-coordinate complex cations, perchlorate anions, and one molecule of water of crystallization. The cation adopts a 4:3 piano-stool configuration.

Introduction

Many of the reactions of terdentate ligands with octahedral group 6B metal carbonyls afford simple carbonyl-substituted complexes of general formula M(CO)₃L.²⁻⁴ Rather few complexes of this type with saturated nitrogen donor ligands have been reported. If the incoming ligand is a poorer π-acceptor than CO, *fac*-M(CO)₃L (M = Cr, Mo, W) is the expected configuration, as it has been shown for Mo(CO)₃(dien) (dien = diethylenetriamine).^{5,6}

In this paper we describe the results of a study of the reactions of M(CO)₃ (M = Cr, Mo, W) with 1,4,7-triazacyclononane ([9]aneN₃ = L), a cyclic terdentate nitrogen donor ligand. This cyclic amine coordinates facially in an octahedron and has been shown to form extremely stable complexes with transition metals in different oxidation states.⁷ The stability of the complexes is believed to be due largely to the stereo-restrictive mode of coordination imposed by this ligand, although there is growing evidence that a pronounced ligand field strength of the ligand is contributing. Thus, it is possible to study the substitution of carbonyl groups by other ligands while retaining the cyclic triamine in the complex. This type of chemistry has also been developed for the more complex ligand

tris(1-pyrazolyl)borate—a uninegative tridentate nitrogen donor ligand.⁸

Nyholm et al.⁹ have extensively studied halogen oxidations of group 6B metal tricarbonyl-tris(tertiary arsine) complexes. Since analogous halogen oxidations of tricarbonyl complexes containing terdentate saturated nitrogen donor ligands have not been studied in great detail,^{4,8} we have also examined the reactions of our M(CO)₃L complexes with bromine and iodine. Seven-coordinate metal(II) complexes of molybdenum and tungsten have been isolated. As these compounds provide examples of the [M(terdentate)(monodentate)₄] seven-coordinate stereochemistry,¹⁰ we have determined the crystal structure of [Mo([9]aneN₃)(CO)₃Br]ClO₄·H₂O prepared in this study.

The employment of nitric acid as a preparative reagent for metal nitrosyl compounds has been quite limited.¹¹ Obviously, nitrosyl complexes containing metals in relatively high oxidation states are produced. However, Piper et al.¹² used nitric acid to produce C₅H₅Mn(CO)₂(NO)⁺ in low yield from C₅H₅Mn(CO)₃. We found that the M(CO)₃([9]aneN₃) (M = Cr, Mo, W) complexes react readily with aqueous HNO₃ in good yields to give [LM(CO)₂(NO)]⁺, [LM(NO)₂X]⁺, and [M₂O₅L₂]²⁺ where M = Mo or W and X = H or Br.

(1) (a) Ruhr-Universität. (b) Max-Planck-Institut für Kohlenforschung.
(2) Chatt, J.; Watson, H. R. *J. Chem. Soc.* 1961, 4980.
(3) Howell, I. V.; Venanzi, L. M. *Inorg. Chim. Acta* 1969, 3, 121.
(4) Dunn, J. G.; Edwards, D. A. *J. Chem. Soc. A* 1971, 988.
(5) Abel, E. W.; Bennett, M. A.; Wilkinson, G. *J. Chem. Soc.* 1959, 2323.
(6) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* 1965, 4, 314.
(7) (a) Zompa, L. J.; Young, R. *Inorg. Chem.* 1976, 15, 1499. (b) Wieghardt, K.; Küppers, H. J.; Herrmann, W. *Ibid.* 1983, 22, 2953.

(8) Trofimenko, S. *J. Am. Chem. Soc.* 1969, 91, 588; *Acc. Chem. Res.* 1971, 4, 17; *Inorg. Chem.* 1979, 18, 2675.
(9) Nyholm, R. S.; Snow, M. R.; Stiddard, M. H. B. *J. Chem. Soc.* 1965, 6570.
(10) Drew, M. G. B. *Prog. Inorg. Chem.* 1977, 23, 67.
(11) Caulton, K. G. *Coord. Chem. Rev.* 1975, 14, 317.
(12) Piper, T. S.; Cotton, F. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* 1955, 1, 165.

Table II. Selected IR Spectral Data (KBr Pellet)

complex	color	freq, α cm $^{-1}$	
Cr(CO) $_3$ L	yellow	ν (CO)	1880 (vs), 1740–1700 (vs, br)
Mo(CO) $_3$ L	yellow	ν (CO)	1850 (vs), 1740–1700 (vs, br)
W(CO) $_3$ L	yellow	ν (CO)	1840 (vs), 1730–1690 (vs, br)
[Mo $_2$ O $_5$ L $_2$](ClO $_4$) $_2$	pale yellow	ν (Mo=O)	920–910 (vs)
[W $_2$ O $_5$ L $_2$](ClO $_4$) $_2$	colorless	ν (Mo–O)	780–750 (vs, br)
		ν (W=O)	900 (vs)
		ν (W–O)	790–770 (vs, br)
[LMo(CO) $_3$ Br]Br $_3$	brown	ν (CO)	2020 (vs), 1960 (vs), 1920 (vs)
[LMo(CO) $_3$ Br]PF $_6$	orange	ν (CO)	2020 (vs), 1950 (vs), 1940 (vs), 1910 (vs)
[LMo(CO) $_3$ Br]ClO $_4$ ^a	orange	ν (CO)	2020 (vs), 1950 (vs), 1900 (vs)
[LMo(CO) $_3$ I]ClO $_4$ ^b	orange	ν (CO)	2000 (vs), 1920 (vs), 1900 (vs)
[LW(CO) $_3$ I]PF $_6$ ·H $_2$ O	golden brown	ν (CO)	2010 (vs), 1930 (vs), 1900 (vs)
[LMo(CO) $_3$ H]BF $_4$	yellow-brown	ν (CO)	1990 (vs), 1890 (vs), 1860 (vs)
[LW(CO) $_3$ H]BF $_4$	yellow-green	ν (CO)	2000 (vs), 1930 (vs), 1890 (vs), 1870 (vs)
[LW(CO) $_3$ H]ClO $_4$ ^b	yellow	ν (CO)	1980 (vs), 1870 (vs), 1830 (vs)
[LCr(CO) $_2$ (NO)]ClO $_4$	red-orange	ν (CO)	2020 (vs), 1920–1910 (vs)
		ν (NO)	1670 (vs)
[LMo(CO) $_2$ (NO)]ClO $_4$	yellow-orange	ν (CO)	2000 (vs), 1900 (vs)
		ν (NO)	1640 (vs)
[LW(CO) $_2$ (NO)]BF $_4$	yellow	ν (CO)	1990 (vs), 1870 (vs)
		ν (NO)	1630 (vs)
[LMo(NO) $_2$ Br]Br	green	ν (NO)	1750 (vs), 1650 (vs)
[LW(NO) $_2$ Br]Br	green	ν (NO)	1730 (vs), 1630 (vs)
[LMo(NO) $_2$ H]ClO $_4$	green	ν (NO)	1770 (vs), 1690 (s), 1640 (vs)
[LMo(NO)(CN) $_3$]·H $_2$ O	colorless	ν (NO)	1660 (vs)

^a vs = very strong; s = strong; br = broad. ^b Highly explosive.

Experimental Section

The ligand 1,4,7-triazacyclononane has been prepared by procedures described in the literature.¹³ All other starting materials were commercially available. Microchemical analyses were performed by Beller Microanalytical Laboratory, Göttingen, West Germany, and by the Microanalytical Laboratory of the Inorganic Chemistry Department, Ruhr-University, Bochum, West Germany. UV-vis spectra were recorded on a Unicam SP8-100 at 20 °C in aqueous solutions. Infrared spectra were recorded on a Beckman Acculab 10 or Perkin-Elmer 225 infrared spectrophotometer. The magnetic susceptibilities of powdered samples were measured by the Faraday method between 100 and 300 K. All complexes of this study were found to be diamagnetic. Acid dissociation constants were determined potentiometrically by using a Metrohm E536 potentiograph. Analytical data for the compounds isolated are given in Table I (supplementary material). IR spectral data are listed in Table II.

Preparation of Complexes

M(CO) $_3$ L (M = Cr, Mo, W). M(CO) $_6$ and 1,4,7-triazacyclononane (11 mmol) were heated together in 50 mL of Decalin (or mesitylene) under gentle reflux for 1 h under argon. After cooling, the yellow solid was filtered off, washed several times with small portions of benzene, ethanol, and ether, successively, and air-dried. The yield was between 60 and 80%. During the reaction, sublimation of M(CO) $_6$ occurred, varying the percentage of yield.

Mo(CO) $_3$ L was also obtained with a relatively constant yield (~75%) by refluxing a solution of Mo(CO) $_6$ (1.3 g) and 1,4,7-triazacyclononane (0.7 g) in 20 mL of benzene and 20 mL of glacial acetic acid for 24 h under argon. After cooling, the yellow Mo(CO) $_3$ (C $_6$ -H $_5$ N $_3$) was filtered off, washed with ethanol and ether, and air-dried. The yield of the preparation was 1.15 g.

Reactions of M(CO) $_3$ L with Nitric Acid. [M $_2$ O $_5$ L $_2$](ClO $_4$) $_2$ (M = Mo, W). A suspension of 3 mmol of Mo(CO) $_3$ L in 30 mL of 1.5 M HNO $_3$ was stirred at 50 °C for 2 h, until a clear solution was obtained. To this clear solution (if necessary, filtered) was added solid NaClO $_4$. Pale yellow crystals separated after cooling, which were filtered off, washed with ethanol and ether, and air-dried; yield 0.2 g (~9%).

The preparation of the corresponding tungsten compound is straightforward and very similar to the above procedure.

[ML(NO) $_2$ Br]Br (M = Mo, W). A suspension of 3 mmol of M(CO) $_3$ L in 15 mL of 0.4 M HNO $_3$ was stirred at room temperature

for 2 h until a clear yellow-green solution was obtained. A small amount of solid NaBr was added to this solution, and the solution was filtered through a G4 filtering crucible to eliminate any solid particles. When the filtrate was cooled in a refrigerator overnight, green crystals precipitated, were filtered out, washed with ethanol and ether, and air-dried; yield 40% (Mo) and 30% (W). UV-vis spectra in 0.1 M HBr: [LMo(NO) $_2$ Br]Br 418 nm (1.48×10^3 L mol $^{-1}$ cm $^{-1}$), 690 (41); [LW(NO) $_2$ Br]Br 419 nm (1.5×10^3 L mol $^{-1}$ cm $^{-1}$), 695 (43).

[LMo(NO) $_2$ H]ClO $_4$. The preparation of this compound is exactly the same as that for [LMo(NO) $_2$ Br]Br; instead of NaBr, solid NaClO $_4$ was used to precipitate the hydrido complex out of the solution; yield 30%. UV-vis spectra in 0.1 M HClO $_4$: 418 nm (520 L mol $^{-1}$ cm $^{-1}$), 701 (20).

[ML(CO) $_2$ (NO)]X (M = Cr, Mo, W; X = BF $_4^-$, ClO $_4^-$). Dissolution of M(CO) $_3$ L (3 mmol) in 0.07 M HNO $_3$ (~15 mL) at room temperature yielded yellow solutions. HBF $_4$ (50%) solution or solid NaClO $_4$ was added to this clear solution, and the mixture was cooled. Crystals of [ML(CO) $_2$ (NO)]X separated out; they were filtered off, washed with a minimum amount of ethanol and then with ether, and air-dried; yield ~40%.

Reaction of [ML(CO) $_3$] with Nitrous Acid. [ML(CO) $_2$ (NO)]X (M = Cr, Mo, W; X = BF $_4^-$, ClO $_4^-$) (Vide Infra). Mo(CO) $_3$ L (1 g) was suspended in a solution of NaNO $_2$ (1 g) in 40 mL of water, and 4 mL of 1.2 M HCl was added dropwise with constant stirring at room temperature over a period of 15 min. The stirring was continued until an orange-yellow solution was obtained. The solution was filtered to remove any unreacted starting material, to the filtrate was added solid NaClO $_4$ (~2 g), and the mixture was cooled. The resulting orange-yellow precipitate was filtered off, washed with a minimum amount of ethanol and then with ether, and air-dried; yield 0.5 g (~38%).

Similar experiments performed by using CrL(CO) $_3$ or WL(CO) $_3$ afforded the analogous orange-red [CrL(CO) $_2$ (NO)]ClO $_4$ or yellow [WL(CO) $_2$ (NO)]BF $_4$. The yields were 50% and 30% for the Cr and W complexes, respectively.

Reaction of the [Mo(NO) $_2$] $_6$ Unit with KCN. [MoL(NO)(CN) $_3$]. A 1-g sample of MoL(CO) $_3$ was dissolved in 30 mL of 0.5 M HNO $_3$ with stirring at room temperature. The pH of the resultant yellow-green solution was adjusted to 9.0 with a solution of NaOH (1 M), and the solution was filtered to eliminate any solid particles. Solid KCN (0.6 g) was added to the stirred filtrate at ~40 °C; the stirring was continued for 30 min, during which a colorless crystalline solid separated out. The crystals were filtered off, washed with ethanol and ether, and air-dried; yield 0.3 g (~26%).

(13) (a) Richman, J. E.; Atkins, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2268. (b) Wieghardt, K.; Schmidt, W.; Nuber, B.; Weiss, J. *Chem. Ber.* **1979**, *112*, 2220.

Table III. Summary of Crystal Data and Intensity Collection of [Mo([9]aneN₃)(CO)₃Br](ClO₄)·H₂O

(A) Crystal Parameters at 22 °C	
$a = 8.375 (2) \text{ \AA}$	$V = 833.4 \text{ \AA}^3$
$b = 8.610 (2) \text{ \AA}$	$Z = 2$
$c = 13.122 (2) \text{ \AA}$	space group: $P\bar{1}$ (No. 2)
$\alpha = 90.68 (1)^\circ$	mol wt: 506.55
$\beta = 90.68 (1)^\circ$	mol formula: [C ₉ H ₁₅ N ₃ BrMoO ₃](ClO ₄)·H ₂ O
$\gamma = 118.24 (1)^\circ$	$\rho_{\text{calcd}} = 2.018 \text{ g cm}^{-3}$

(B) Measurement of Intensity Data
 diffractometer: CAD 4
 radiation: Mo K α ($\lambda = 0.7107 \text{ \AA}$)
 data collection: θ - 2θ range 2-60°
 reflens collected: 3790; 2894 ($I \geq 3\sigma(I)$)
 no. of parameters: 208
 abs coeff: 33.4 cm⁻¹; empirical absorption correction carried out

Reaction of ML(CO)₃ with Hydrochloric Acid. [ML(CO)₃H]X (M = Mo, W; X = ClO₄⁻, BF₄⁻). A suspension of 1 g of ML(CO)₃ in 40 mL of 1 M HCl was stirred at 50 °C until a clear yellow-brown solution was obtained. Solid NaClO₄ was added to this clear solution, and the mixture was cooled. Precipitated yellow compound was filtered off, washed with ethanol and ether, and air-dried (caution! very explosive; never handle more than ~10 mg of dry substance at a time).

An experiment similar to that described above was performed for the preparation of [ML(CO)₃H]BF₄ using HBF₄ solution (50%) instead of NaClO₄; yield ~60%.

Oxidation Reaction of MoL(CO)₃ with Bromine. [MoL(CO)₃Br]X (X = Br₃⁻, PF₆⁻, ClO₄⁻). A 1-g sample of Mo(CO)₃L in 40 mL of chloroform was treated with 1 mL of bromine in 10 mL of chloroform, and the mixture was refluxed for 0.5 h. The resulting red-brown product was filtered off, washed several times with chloroform, and air-dried; yield 1.9 g (~90%).

The hexafluorophosphate salt [MoL(CO)₃Br]PF₆ was obtained by treating a hot solution of brown in ethanol with an aqueous solution of NaPF₆. On cooling, orange crystals of [MoL(CO)₃Br]PF₆ precipitated out.

X-ray-quality orange crystals of the perchlorate salt were obtained by dissolving the brown [MoL(CO)₃Br]Br₃ crystals in very dilute sodium perchlorate solution and cooling the mixture at 5 °C for several hours (danger! very explosive).

The color of [LMo(CO)₃Br]Br₃ changed from brown to green upon standing for ca. 3 weeks at room temperature. This green substance was dissolved in cold water, and upon addition of NaI to this solution orange-yellow crystals of the already known Mo(V) dimer [Mo₂-O₄L₂]I₂¹⁴ separated out.

Oxidation of ML(CO)₃ with Iodine. An experiment similar to that described above but using I₂ instead of Br₂ afforded presumably the analogous [MoL(CO)₃I]I₃, which was identified by its infrared spectrum. Because of the high instability of [LMo(CO)₃]I₃, no reasonable elemental analyses were obtained. This brown compound could be used to prepare the stable orange perchlorate salt [MoL(CO)₃I]ClO₄ (very explosive), characterized by its IR spectrum. Elemental analyses of the perchlorate salt were not performed because of its very explosive nature.

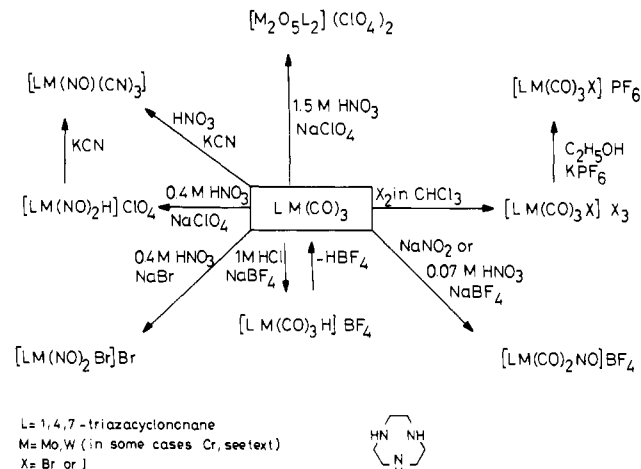
[WL(CO)₃I]PF₆. A 0.5-g sample of WL(CO)₃ was added to a solution of 0.65 g of iodine in 50 mL of chloroform. The suspension was stirred at room temperature for 90 min, and the resulting yellow-brown product, presumably [WL(CO)₃I]I₃, was filtered off, washed several times with chloroform, and air-dried; yield 0.94 g.

Gold-brown shining crystals of [WL(CO)₃I]PF₆ separated out on cooling an ethanol (80 mL) solution of the brown product, which was treated with a solution of NaPF₆ (1 g) in water (15 mL); yield 0.5 g.

X-ray Diffraction Study and Solution of the Structure

The crystal of [Mo([9]aneN₃)(CO)₃Br]ClO₄·H₂O selected for the structure analysis was of the approximate dimensions 0.02 × 0.02 × 0.03 mm. The unit cell parameters were obtained at 22 °C by a least-squares refinement of the angular settings of 25 reflections (Table III). Intensity data were collected on an Enraf-Nonius CAD4 diffractometer and were corrected for Lorentz and polarization effects. The function minimized during least-squares refinement was $\sum w_i(|F_o|$

Scheme I



$-|F_o|^2$ with final convergence to $R_1 = 0.043$ and $R_2 = 0.052$; $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_2 = [\sum w_i ||F_o| - |F_c||^2 / \sum w_i |F_o|^2]^{1/2}$ ($w_i = 1 / \sigma^2(F)$).

The structure was solved via a three-dimensional Patterson synthesis, which yielded the positions of the molybdenum, chlorine, and bromine atoms. Subsequent Fourier syntheses revealed the positions of all remaining non-hydrogen atoms. Idealized positions of H atoms bound to carbon atoms were calculated (on the basis of a $d(\text{C-H})$ of 0.97 Å and regular tetrahedral geometry about the C atoms). These were refined as a rigid moiety with fixed isotropic thermal parameters for the H atoms ($U = 0.050 \text{ \AA}^2$) and anisotropic thermal parameters for the C atoms. Refinements were carried out with anisotropic thermal parameters for all other atoms (supplementary material). At this stage a difference Fourier synthesis revealed the positions of the hydrogen atoms bound to the molecule of water of crystallization and those bound to nitrogen atoms (H1, H4, H7), which were included in the refinement ($U = 0.050 \text{ \AA}^2$). The final positional parameters are given in Table IV, and bond distances and angles in Table V. Listings of thermal parameters and of observed and calculated structure factors are available as supplementary material.

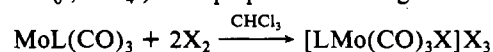
Results and Discussion

1,4,7-Triazacyclononane (L) reacts readily with $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) to produce in good yields $\text{M}(\text{CO})_3\text{L}$. The ligand, [9]aneN₃, is capable of facial coordination only, so that three carbonyl groups must also be in cis positions. This is confirmed by the infrared spectra (Table II), which consist of two strong bands^{15,16} assigned to the C-O stretch; the low-frequency band in each compound is very broad. These results are compatible with the formation of *fac*- $\text{M}(\text{CO})_3\text{L}$ derivatives (C_{3v} local symmetry; $A_1 + E$) where all three donor nitrogens are equivalent. These new tricarbonyl derivatives are stable to air and moisture and show no sign of decomposition, at least within 24 h.

The reactivity of $\text{M}(\text{CO})_3\text{L}$ is summarized in Scheme I.

Halogen Oxidation of $\text{M}(\text{CO})_3\text{L}$ ($\text{M} = \text{Mo}$ or W). There is considerable precedent in the literature^{17,18} that many metal carbonyls and their derivatives act as bases and form addition complexes with a wide variety of Lewis acids. Oxidative addition of halogens to zerovalent hexacoordinate group 6B transition metals affords divalent heptacoordinate complexes.¹⁹

The seven-coordinate compounds [MoL(CO)₃X]Y ($\text{X} = \text{I}, \text{Br}$; $\text{Y} = \text{PF}_6^-, \text{ClO}_4^-$) were prepared according to the equation



- (15) Orgel, L. E. *Inorg. Chem.* **1962**, *1*, 25.
 (16) Houk, L. W.; Dobson, G. R. *J. Chem. Soc. A* **1966**, 317.
 (17) Shriver, D. F. *Acc. Chem. Res.* **1970**, *2*, 231.
 (18) Kotz, T. C.; Pedrotty, D. G. *Organomet. Chem. Rev., Sect. A* **1969**, *4*, 479.
 (19) (a) Cotton, R. *Coord. Chem. Rev.* **1971**, *6*, 269. (b) Umland, P.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 3565 and references cited therein.

(14) Wiegardt, K.; Hahn, M.; Swiridoff, W.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 491.

Table IV. Final Positional Parameters for $[\text{Mo}(\text{9}]\text{aneN}_3)(\text{CO})_3\text{Br}]\text{ClO}_4 \cdot \text{H}_2\text{O}$

atom	x	y	z	atom	x	y	z
Mo	0.1681 (1)	0.3076 (1)	0.1717 (1)	C11	0.3208 (8)	0.5524 (8)	0.1229 (4)
Br	0.1053 (1)	0.2931 (1)	-0.0295 (1)	C12	0.2883 (7)	0.1698 (7)	0.1187 (4)
Cl	0.3294 (2)	0.8836 (2)	0.3504 (1)	C13	0.4074 (8)	0.4146 (8)	0.2412 (4)
O	0.375 (1)	0.3046 (8)	0.4956 (5)	H1	0.0041 (1)	0.5260 (1)	0.1974 (1)
O1	0.4030 (7)	0.6913 (6)	0.0918 (4)	H2	-0.1770 (1)	0.3228 (1)	0.0751 (1)
O2	0.3534 (6)	0.0911 (6)	0.0855 (3)	H2A	-0.3047 (1)	0.3106 (1)	0.1706 (1)
O3	0.5498 (5)	0.4746 (6)	0.2789 (3)	H3	-0.3181 (1)	0.0417 (1)	0.2327 (1)
O4	0.4169 (8)	1.0699 (6)	0.3331 (4)	H3A	-0.3319 (1)	0.0320 (1)	0.1123 (1)
O5	0.2085 (8)	0.7982 (7)	0.2664 (5)	H4	-0.1220 (1)	0.0000 (1)	0.1022 (1)
O6	0.4596 (7)	0.8207 (8)	0.3496 (5)	H5	-0.2248 (1)	-0.1781 (1)	0.2570 (1)
O7	0.233 (1)	0.8429 (9)	0.4402 (5)	H5A	-0.0001 (1)	-0.0862 (1)	0.2450 (1)
N1	-0.0360 (6)	0.4023 (5)	0.2096 (3)	H6	-0.0321 (1)	0.0060 (1)	0.4145 (1)
N4	-0.0978 (5)	0.0596 (5)	0.1669 (3)	H6A	-0.1441 (1)	0.0725 (1)	0.3789 (1)
N7	0.1015 (6)	0.2426 (5)	0.3370 (3)	H7	0.1991 (1)	0.2503 (1)	0.3670 (1)
C2	-0.2026 (7)	0.2867 (8)	0.1484 (5)	H8	0.0299 (1)	0.3675 (1)	0.4437 (1)
C3	-0.2578 (7)	0.0933 (7)	0.1661 (5)	H8A	0.1753 (1)	0.4821 (1)	0.3919 (1)
C5	-0.1005 (8)	-0.0504 (7)	0.2542 (4)	H9	-0.1806 (1)	0.3024 (1)	0.3265 (1)
C6	-0.0519 (8)	0.0598 (8)	0.3510 (4)	H9A	-0.0946 (1)	0.4948 (1)	0.3506 (1)
C8	0.0682 (8)	0.3836 (8)	0.3823 (4)	HW1	0.4358 (1)	0.3961 (1)	0.5430 (1)
C9	-0.0735 (8)	0.4027 (8)	0.3207 (5)	HW2	0.3997 (1)	0.2005 (1)	0.4955 (1)

Table V. Bond Distances (Å) and Angles (deg)

Mo-Br	2.676 (1)	N1-C2	1.492 (9)
Mo-N1	2.273 (5)	N1-C9	1.495 (9)
Mo-N4	2.240 (5)	N4-C3	1.500 (8)
Mo-N7	2.257 (5)	N4-C5	1.489 (8)
Mo-C11	1.998 (7)	N7-C6	1.504 (9)
Mo-C12	2.008 (6)	N7-C8	1.488 (9)
Mo-C13	1.972 (7)	C2-C3	1.53 (1)
H7-O _w		C5-C6	1.508 (9)
		C8-C9	1.50 (1)
N1-Mo-N7	74.5 (2)	O1-C11-Mo	177.1 (6)
N1-Mo-C11	85.0 (2)	O2-C12-Mo	177.6 (5)
N1-Mo-C12	164.1 (2)	O3-C13-Mo	177.4 (6)
N1-Mo-C13	120.3 (2)	C2-N1-C9	112.3 (5)
N1-Mo-Br	94.1 (1)	C2-N1-Mo	105.6 (4)
N1-Mo-N4	76.5 (2)	C9-N1-Mo	114.4 (4)
N7-Mo-C11	123.4 (2)	C3-N4-Mo	113.1 (4)
N7-Mo-C12	108.8 (2)	C3-N4-C5	112.1 (5)
N7-Mo-C13	76.3 (2)	C5-N4-Mo	108.1 (4)
N7-Mo-Br	156.9 (1)	C6-N7-C8	113.6 (5)
N7-Mo-N4	75.6 (2)	C6-N7-Mo	112.8 (4)
C11-Mo-C12	104.9 (3)	C8-N7-Mo	107.3 (4)
C11-Mo-C13	69.9 (3)	N1-C2-C3	110.2 (5)
C11-Mo-Br	74.2 (2)	C2-C3-N4	112.0 (5)
C11-Mo-N4	148.8 (2)	N4-C5-C6	109.2 (5)
C12-Mo-C13	75.3 (3)	C5-C6-N7	112.4 (5)
C12-Mo-Br	77.0 (2)	N7-C8-C9	110.2 (5)
C12-Mo-N4	89.1 (2)	C8-C9-N1	109.9 (6)
C13-Mo-Br	126.4 (2)		
C13-Mo-N4	141.3 (2)		
Br-Mo-N4	82.3 (1)		

followed by metathesis in water-ethanol to obtain the X-ray-quality crystals of perchlorate or hexafluorophosphate salts.

When treated with iodine in chloroform, the tungsten complex $\text{W}(\text{CO})_3\text{L}$ yielded an unstable brown product analyzing nearly to $[\text{WL}(\text{CO})_3]\text{I}_3$. Recrystallization from warm ethanol and NaPF_6 gave red-brown air-stable crystals of $[\text{WL}(\text{C}-\text{O})_3]\text{PF}_6$.

The cation $[\text{ML}(\text{CO})_3\text{X}]^+$ is stable in the absence of halide as a counterion and may be stored as air-stable hexafluorophosphate or perchlorate (*Danger!* explosive) salts. The complexes are sparingly soluble in hot water, but easily soluble in alcohols. They are diamagnetic in the solid state and obey noble-gas formalism. The IR spectra of all these compounds contain three characteristic $\nu(\text{C}-\text{O})$ stretching modes, which are shifted to higher frequencies compared with those of the tricarbonyl complexes in the zero oxidation state. This shift reflects the increase in the positive charge on the metal.

Reactions with Nitric Acid. Since the publication of Piper et al.,¹² there have been no reports concerning the employment

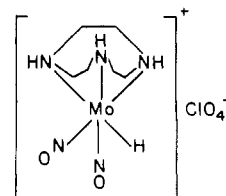
of nitric acid as a nitrosating agent for a zerovalent metal center.

fac- $\text{M}(\text{CO})_3\text{L}$ ($\text{M} = \text{Mo}, \text{W}$) dissolved in 0.4 M HNO_3 yielded green solutions. Upon addition of NaBr to these solutions, diamagnetic bright green crystals with the chemical composition $\text{ML}(\text{NO})_2\text{Br}_2$ separated out. The solid compound showed no sign of decomposition on storage in air at room temperature; but the aqueous solutions decomposed slowly on standing. Their UV-vis spectra in water show bands (Experimental Section) that are typical for dinitrosyl complexes of molybdenum and tungsten.

The IR spectra of the complexes exhibited two strong bands separated by about 100 cm^{-1} in the terminal nitrosyl stretching region, as is expected for two nonbridging NO groups on the same metal atom. It is expected that with increasing principal quantum number n , the strength of $\text{M}-\text{NO}$ back-bonding should increase, resulting in the decrease in $\nu(\text{NO})$ stretching modes. The observed $\nu(\text{NO})$ value decreases (Table II) on going from molybdenum to tungsten.

A complete X-ray structure determination of $\text{LMo}(\text{NO})_2\text{Br}_2$ was not possible, because of crystal disorder; but a qualitative investigation showed that only one of the two bromine atoms is directly attached to the molybdenum center, yielding a six-coordinate octahedral compound that should be formulated as $[\text{MoL}(\text{NO})_2\text{Br}]^+\text{Br}^-$.

If solid NaClO_4 , instead of NaBr , is added to the above-mentioned green solution of the Mo complex, a yellow-green diamagnetic solid separates out. This complex can also be handled in air without any noticeable decomposition, but the green aqueous solution becomes slowly ($\sim 30 \text{ h}$) colorless, yielding presumably the $\text{Mo}(\text{VI})$ compound, $[\text{Mo}_2\text{O}_5\text{L}_2]^{2+}$ (vide infra). Its IR spectrum is identical with that of the corresponding bromo derivative, $[\text{LMo}(\text{NO})_2\text{Br}]\text{Br}$, with two additional bands at ~ 1100 (vs, br) and $\sim 620 \text{ cm}^{-1}$ (s) characteristic of the ClO_4^- anion. Chemical analyses showed the composition to be $\text{Mo}(\text{C}_6\text{H}_{15}\text{N}_3)(\text{NO})_2\text{ClO}_4$, which does not obey 18-valence-electron formalism. In conformity with its diamagnetism and by analogy with the corresponding bromodinitrosylmolybdenum complex, the yellow-green solid must have the following structure:



Accordingly, a pK_H value of 4.9 at 20° could be determined by potentiometric titration of an aqueous solution of the complex with sodium hydroxide. Attempts to isolate a neutral complex from such solutions have failed. Accordingly, deprotonation of the amine or attack of OH⁻ at a coordinated NO cannot be ruled out completely. But the acidity of amine protons in low-valent and low-charged cations is very low, and dinitrosyl complexes of molybdenum are not known to be susceptible to nucleophilic attack of OH⁻.

These dinitrosyl compounds of Mo and W differ from their cyclopentadienyl analogues²⁰⁻²² in being stable to storage and may be exposed to air, but they have properties similar to those of the corresponding tris(1-pyrazolyl)borate complexes.²¹ It is noted that the reported instability of $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{NO})_2\text{X}$ has been contradicted.²²

Interestingly, the $[\text{LMo}(\text{NO})_2\text{H}]^+$ cation reacts with KCN in aqueous solution to yield the colorless diamagnetic compound $[\text{LMo}(\text{NO})(\text{CN})_3]$.

LM(CO)₃ reacts with 1.5 M HNO₃, yielding first a yellow-green solution that slowly becomes pale yellow. Upon addition of NaClO₄ to this solution, a pale yellow (Mo) or colorless (W) binuclear M(VI) species with the chemical composition $[(\text{C}_6\text{H}_{15}\text{N}_3)_2\text{M}_2\text{O}_5](\text{ClO}_4)_2$ separates out. This perchlorate salt shows a strong infrared band at 750–780 cm⁻¹ indicative of μ -oxo bridging and most probably contains the μ -oxo-bridged M₂O₅ core, which is well-known in molybdenum(VI) chemistry but to our knowledge has not been observed previously for tungsten(VI). A cyclopentadienyl-molybdenum complex formulated as $[\text{Mo}_2\text{O}_5(\eta^5\text{-C}_5\text{H}_5)]$ is reported.²⁴ This again stresses the structural relationship of the neutral six-electron donor 1,4,7-triazacyclononane and the six-electron donor cyclopentadienyl anion.

Reactions with Nitrosyl Acid. Nitrosyl groups could be readily attached to a metal center by treating ML(CO)₃ with a source of NO⁺, e.g. nitric acid or nitrous acid. In this fashion the stable derivatives $[\text{ML}(\text{CO})_2(\text{NO})]\text{ClO}_4$ or $[\text{ML}(\text{CO})_2(\text{NO})]\text{BF}_4$ (M = Cr, Mo, W) were obtained by treating ML(CO)₃ with NaNO₂/HCl or dilute (~0.07 M) HNO₃. The yellow-orange mononitrosyl compounds readily react further with a nitrosating agent to yield the green dinitrosyl derivative (vide infra). These mononitrosyl complexes are diamagnetic and show no sign of decomposition on exposure to air for several weeks. The corresponding cyclopentadienyl compounds $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ are stable in air only for short periods of time.²⁵

IR spectra (Table II) of these compounds show one $\nu(\text{NO})$ and two $\nu(\text{CO})$ stretching modes as is also found in $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{NO})$ complexes.^{20,26} $\nu(\text{CO})$ and $\nu(\text{NO})$ decrease in the order Cr > Mo > W, showing the strengthening of M–NO and M–CO back-bonding on going from chromium to tungsten (vide infra).

Reactions of ML(CO)₃ with HCl (M = Mo, W). A yellow-brown solution is obtained on stirring a suspension of M(CO)₃L in 1 M HCl at room temperature. Pale yellow-brown or yellow-green crystals of tetrafluoroborate salts $[\text{ML}(\text{CO})_3\text{H}]\text{BF}_4$ have been obtained by adding the BF₄⁻ anion to the above-mentioned solution. Corresponding per-

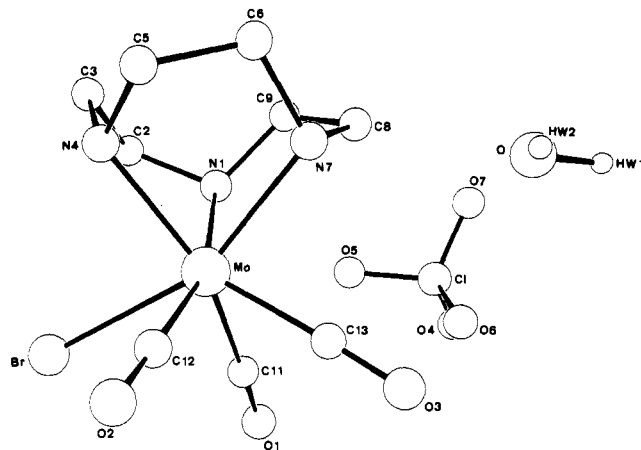


Figure 1. Ball and stick representation of the complex cation $[(9)\text{aneN}_3]\text{Mo}(\text{CO})_3\text{Br}]^+$ and atomic labeling scheme.

chlorate salts have also been obtained; but it is recommended not to synthesize the perchlorate salt because of its very explosive nature. Like the hydridonitrosyl derivatives, these new carbonyl hydrides are very stable to air, light, and ordinary laboratory moisture. The hydrido complexes are diamagnetic in the solid state, and this is consistent with a spin-paired d^4 configuration, the number of valence electrons thereby being in agreement with the noble-gas formalism. The shifts of 150–100 cm⁻¹ to higher $\nu(\text{CO})$ frequencies compared with those of the $\text{M}(\text{CO})_3\text{L}$ compounds can again be attributed to an increase in positive charge carried by the metal in these formally divalent seven-coordinate species.

The acid–base behavior of these carbonyl hydrides and dinitrosyl hydrides is strikingly different. The carbonyl hydrides are relatively strong acids, and pK_H values of the Mo and W complexes are estimated by pH measurements to be 2.40 and 2.90, respectively. In contrast, the nitrosylhydrido complex of Mo, $[\text{MoL}(\text{NO})_2\text{H}]\text{ClO}_4$, is a very weak acid; the pK_H is found to be 4.90. This weak acidic character of M–H bonds in dinitrosyl hydrides has also been observed in $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ ²⁷ and shows weak π -acid character of nitrosyl ligands in removing electron density from the metal center.

These carbonyl hydride complexes function as a source of H⁺ in aqueous solution and slowly yield the starting compound ML(CO)₃, which is consistent with the view of $\text{M}(\delta^-)\text{—H}(\delta^+)$ bond polarity in $[\text{ML}(\text{CO})_3\text{H}]^+$ complexes. In this regard, they also do not differ from their cyclopentadienyl counterparts, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{H}$, which have been shown to be rather strong acids.^{25b} The ¹H NMR spectrum (Bruker WP-80) of $[\text{LW}(\text{CO})_3\text{H}]\text{BF}_4$ in dimethyl-*d*₆ sulfoxide consists of resonances at δ 2.81 (s, 12 H) and 6.52 (s, 3 H) and a broader resonance at δ 8.20 (s, 1 H). The latter we assign to a hydrogen atom bonded directly to the tungsten center, since it does not appear in the ¹H NMR spectrum of $[\text{LW}(\text{CO})_3\text{I}]\text{PF}_6$ recorded under identical conditions. The spectrum of $[\text{LMo}(\text{CO})_3\text{H}]\text{BF}_4$ could not be measured because of its decomposition in Me₂SO.

$[\text{LMo}(\text{NO})_2\text{H}]\text{ClO}_4$ exhibits a broad low-field hydride resonance at δ 7.10 in the ¹H NMR spectrum measured in D₂O. For $(\eta^5\text{-C}_5\text{H}_5)\text{W}(\text{NO})_2\text{H}$ this signal has been found at δ 2.77.²⁷

Structure of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Br}]\text{ClO}_4 \cdot \text{H}_2\text{O}$. The crystal structure of $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Br}]\text{ClO}_4 \cdot \text{H}_2\text{O}$ consists of the distinct complex cation $[\text{Mo}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_3\text{Br}]^+$, the perchlorate anion, and one molecule of water of crystallization per formula unit. Bond distances and angles are listed in Table

- (20) (a) King, R. B. *Inorg. Chem.* **1968**, *7*, 90. (b) Green, M. L. H.; Sanders, T. R.; Whiteley, R. N. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1968**, *23*, 106. (c) Stewart, R. P.; Moore, G. T. *Inorg. Chem.* **1975**, *14*, 2699.
- (21) Trofimenko, S. *Inorg. Chem.* **1969**, *8*, 2675.
- (22) Legzdins, P.; Malito, T. T. *Inorg. Chem.* **1975**, *14*, 1875.
- (23) (a) Stiefel, E. *Prog. Inorg. Chem.* **1977**, *22*, 1. (b) Dori, Z. *Ibid.* **1981**, *28*, 239.
- (24) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1964**, 1567.
- (25) (a) Hoyano, T. K.; Legzdins, P.; Malito, T. T. *Inorg. Synth.* **1978**, *18*, 126. (b) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255.
- (26) Brunner, H. *J. Organomet. Chem.* **1969**, *16*, 119.

- (27) Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1979**, *18*, 1250.

V. The molecular geometry and the atomic labeling scheme for $[\text{Mo}([\text{9]aneN}_3)(\text{CO})_3\text{Br}]^+$ are shown in Figure 1. The molybdenum atom is seven-coordinate; it is surrounded by three nitrogen atoms of the cyclic amine, three carbonyl groups, and one bromide ion. The geometry can be described as a 4:3 piano stool as has been found for diiododicarbonyl-tris(*tert*-butyl isocyanide)tungsten(II).²⁸ Features of the coordinated carbonyl and 1,4,7-triazacyclononane are unexceptional. The Mo-Br and Mo-C bond lengths agree well with values reported for related seven-coordinate compounds.¹⁰

The single crystals form with a water of crystallization that is bound via a relatively short hydrogen bond to one amine proton ($\text{N7-O}_w = 2.927(3) \text{ \AA}$). Carbonyl oxygens are not involved in hydrogen bonding. The oxygen atoms O4 and O3 of the perchlorate ion form rather long hydrogen bonds to O_w ($3.056(3)$ and $3.247(3) \text{ \AA}$, respectively).

Conclusion

In light of the presently available data, it can be concluded that there are strong analogies between the synthesis and chemistry of these 1,4,7-triazacyclononane complexes and those of the corresponding η^5 -cyclopentadienyl species and the

tris(1-pyrazolyl)borate complexes although the cyclopentadienide ion and the tris(1-pyrazolyl)borate anion are negatively charged. However, a great advantage of working with 1,4,7-triazacyclononane complexes is that the intermediate and the final products are usually more air, moisture, and light stable than their cyclopentadienyl counterparts.

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Registry No. $\text{Cr}(\text{CO})_3\text{L}$, 88253-23-0; $\text{Mo}(\text{CO})_3\text{L}$, 88253-24-1; $\text{W}(\text{CO})_3\text{L}$, 88253-25-2; $[\text{Mo}_2\text{O}_5\text{L}_2](\text{ClO}_4)_2$, 88253-27-4; $[\text{W}_2\text{O}_5\text{L}_2](\text{ClO}_4)_2$, 88253-29-6; $[\text{LMo}(\text{CO})_3\text{Br}]\text{Br}_3$, 88253-31-0; $[\text{LMo}(\text{CO})_3\text{Br}]\text{PF}_6$, 88253-32-1; $[\text{LMo}(\text{CO})_3\text{Br}]\text{ClO}_4 \cdot \text{H}_2\text{O}$, 88253-34-3; $[\text{LMo}(\text{CO})_3\text{I}]\text{ClO}_4$, 88253-36-5; $[\text{LW}(\text{CO})_3\text{I}]\text{PF}_6$, 88253-38-7; $[\text{LMo}(\text{CO})_3\text{H}]\text{BF}_4$, 88253-40-1; $[\text{LW}(\text{CO})_3\text{H}]\text{BF}_4$, 88253-42-3; $[\text{LW}(\text{CO})_3\text{H}]\text{ClO}_4$, 88253-43-4; $[\text{LCr}(\text{CO})_2(\text{NO})]\text{ClO}_4$, 88253-45-6; $[\text{LMo}(\text{CO})_2(\text{NO})]\text{ClO}_4$, 88253-47-8; $[\text{LW}(\text{CO})_2(\text{NO})]\text{BF}_4$, 88253-49-0; $[\text{LMo}(\text{NO})_2\text{Br}]\text{Br}$, 88253-50-3; $[\text{LW}(\text{NO})_2\text{Br}]\text{Br}$, 88253-51-4; $[\text{LMo}(\text{NO})_2\text{H}]\text{ClO}_4$, 88253-53-6; $[\text{LMo}(\text{NO})(\text{CN})_3]$, 88253-54-7; $\text{Cr}(\text{CO})_6$, 13007-92-6; $\text{Mo}(\text{CO})_6$, 13939-06-5; $\text{W}(\text{CO})_6$, 14040-11-0; HNO_3 , 7697-37-2; nitrous acid, 7782-77-6.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes, elemental analyses (Table I), and anisotropic temperature parameters (Table VI) (15 pages). Ordering information is given on any current masthead page.

(28) Dreyer, E. B.; Lam, C. T.; Lippard, S. J. *Inorg. Chem.* 1979, 18, 1904.

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Bis(pentamethylcyclopentadienyl)ytterbium(II) as a Lewis Acid and Electron-Transfer Ligand. Preparation and Crystal Structures of $[\text{Yb}(\text{Me}_5\text{C}_5)_2(\mu\text{-CO})_x\text{Mn}(\text{CO})_{5-x}]_y$ ($x, y = 2$; $x = 3, y = \infty$)

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Received June 2, 1983

The divalent ytterbium metallocene $(\text{Me}_5\text{C}_5)_2\text{Yb}(\text{OEt}_2)$ reacts with $\text{Mn}_2(\text{CO})_{10}$ to give a compound of composition $(\text{Me}_5\text{C}_5)_2\text{YbMn}(\text{CO})_5 \cdot 1/4\text{PhMe}$, which was shown by an X-ray crystallographic study to be composed of a polymeric chain of $[(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-OC})_3\text{Mn}(\text{CO})_2]$ units with dimeric units $[(\text{Me}_5\text{C}_5)_2\text{Yb}(\mu\text{-OC})_2\text{Mn}(\text{CO})_3]$ packed between the polymeric sheets. The toluene of solvation fills regularly spaced voids in the network of dimer and polymer sheets. The space group is $C2/m$ with $a = 18.942(5) \text{ \AA}$, $b = 32.592(5) \text{ \AA}$, $c = 19.029(5) \text{ \AA}$, $\beta = 109.92(2)^\circ$, $V = 11045(18) \text{ \AA}^3$, and $Z = 16$. The contact-ion-pair complex results from $(\text{Me}_5\text{C}_5)_2\text{Yb}$ acting as an electron-transfer reagent, $(\text{Me}_5\text{C}_5)_2\text{Yb} \rightarrow (\text{Me}_5\text{C}_5)_2\text{Yb}^+ + 1e^-$, and as a Lewis acid by way of $\text{Yb}(\mu\text{-OC})\text{Mn}$ interactions. The solution and solid-state infrared spectra are discussed relative to the alkali-metal analogues. The rhenium carbonyl $\text{Re}_2(\text{CO})_{10}$ behaves similarly.

The concept of transition-metal carbonyl basicity, the ability of the lone pair of electrons on the oxygen atom to act as a Lewis base, is well-known.¹ In particular, group 3B compounds form acid-base complexes with the bridging carbonyl groups in, for example, $\text{Cp}_2\text{Fe}_2(\mu\text{-CO})_2(\text{CO})_2$ or $\text{Cp}_4\text{Fe}_4(\mu_3\text{-CO})_4$.² The acid-base interaction leads to a reduction in the C-O stretching frequency; e.g., the bridging CO stretching frequency in $\text{Cp}_2\text{Fe}_2[(\mu\text{-CO})\text{AlEt}_3]_2(\text{CO})_2$ is lowered 113 cm^{-1} relative to that found in the acid-free complex.^{2a,b} Carbonyl complexes whose solid-state structures do not contain bridging carbonyl groups and whose solution behavior is stereochemically rigid, e.g., $\text{Mn}_2(\text{CO})_{10}$,³ do not form complexes with aluminum compounds.^{2b,d}

Early-transition-metal complexes also can act as Lewis acids toward metal carbonyls, giving complexes with M-CO-M' interactions.⁴ In these complexes the C-O stretching frequency also is lowered relative to that in the uncoordinated

complex. In addition, it is generally observed that the M-C-O angle is essentially linear and the C-O-M' angle is less than 180° . In particular, the Mo-C-O bond angle is $178.8(4)^\circ$ and the O-C-Ti angle is $144.3(3)^\circ$ in $\text{CpMo}(\text{CO})_2[(\mu\text{-$

- (1) Shriver, D. F. *J. Organomet. Chem.* 1975, 94, 159; *Acc. Chem. Res.* 1970, 3, 231.
- (2) (a) Nelson, N. J.; Kime, N. E.; Shriver, D. F. *J. Am. Chem. Soc.* 1969, 91, 5173. (b) Alich, A.; Nelson, N. J.; Strope, D.; Shriver, D. F. *Inorg. Chem.* 1972, 11, 2976. (c) Shriver, D. F.; Alich, A. *Ibid.* 1972, 11, 2984. (d) Kristoff, J. S.; Shriver, D. F. *Ibid.* 1974, 13, 499.
- (3) (a) Dahl, L. F.; Rundle, R. E. *Acta Crystallogr.* 1963, 16, 419. (b) Martin, M.; Rees, B.; Mitschler, A. *Acta Crystallogr., Sect. B* 1982, B38, 6. (c) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* 1981, 20, 1609. (d) Todd, L. J.; Wilkinson, J. R. *J. Organomet. Chem.* 1974, 77, 1.
- (4) (a) Schneider, M.; Weiss, E. *J. Organomet. Chem.* 1976, 121, 365. (b) Renault, P.; Tainturier, G.; Gautheron, B. *Ibid.* 1978, 150, 9. (c) Longato, B.; Norton, J. R.; Huffman, J. C.; Marsella, J. H.; Caulton, K. G. *J. Am. Chem. Soc.* 1981, 103, 209. (d) Hamilton, D. M.; Willis, W. S.; Stucky, G. D. *Ibid.* 1981, 103, 4255. (e) Barger, P. T.; Bercaw, J. E. *J. Organomet. Chem.* 1980, 201, C39. (f) Pasynskii, A. A.; Skripkin, Y. V.; Eremanko, I. L.; Kalinnikov, V. T.; Alexandrov, G. G.; Andrianov, V. G.; Struchkov, Yu. T. *Ibid.* 1979, 165, 49.

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