Table V. Bond Angles (Deg) in Compound **1**

Ta(1)–Cl(5)–Ta(2)	64.90 (6)	C(1)–S(1)–C(4)	94.9 (6)
–Cl(6)–Ta(2)	64.63 (6)	Ta(1)–S(2)–C(5)	110.6 (4)
–S(1)–Ta(2)	68.21 (7)	–C(8)	109.0 (4)
Cl(1)–Ta(2)–Cl(2)	100.5 (1)	C(5)–S(2)–C(8)	94.6 (6)
–Cl(5)	92.2 (1)	Ta(2)–S(3)–C(9)	108.1 (5)
–Cl(6)	165.6 (1)	–C(12)	112.1 (6)
–S(1)	89.19 (9)	C(9)–S(3)–C(12)	95.6 (6)
–S(2)	87.64 (9)	S(1)–C(1)–C(2)	106.4 (9)
Cl(2)–Ta(1)–Cl(5)	163.2 (1)	C(1)–C(2)–C(3)	112 (1)
–Cl(6)	90.1 (1)	C(1)–C(2)–C(33)	113 (2)
–S(1)	90.9 (1)	C(2)–C(3)–C(4)	108 (2)
–S(2)	86.20 (9)	C(2)–C(33)–C(4)	112 (3)
Cl(5)–Ta(1)–Cl(6)	75.69 (8)	S(1)–C(4)–C(3)	107 (1)
–S(1)	100.38 (8)	S(1)–C(4)–C(33)	106 (2)
–S(2)	83.25 (8)	S(2)–C(5)–C(6)	105.9 (8)
Cl(6)–Ta(1)–S(1)	100.44 (9)	C(5)–C(6)–C(7)	109 (1)
–S(2)	83.33 (9)	C(6)–C(7)–C(8)	105.7 (9)
S(1)–Ta(1)–S(2)	175.28 (9)	S(2)–C(8)–C(7)	102.2 (7)
Cl(3)–Ta(2)–Cl(4)	102.1 (1)	S(3)–C(9)–C(10)	102 (1)
–Cl(5)	90.47 (9)	S(3)–C(9)–C(20)	106 (1)
–Cl(6)	163.7 (1)	C(9)–C(10)–C(11)	113 (3)
–S(1)	89.7 (1)	C(9)–C(20)–C(11)	102 (2)
–S(3)	83.6 (1)	C(9)–C(10)–C(22)	110 (3)
Cl(4)–Ta(2)–Cl(5)	164.3 (1)	C(9)–C(20)–C(22)	113 (2)
–Cl(6)	90.5 (1)	C(10)–C(11)–C(12)	119 (3)
–S(1)	89.6 (1)	C(10)–C(22)–C(12)	108 (3)
–S(3)	89.8 (1)	C(12)–C(11)–C(20)	110 (3)
Cl(5)–Ta(2)–Cl(6)	75.52 (8)	C(12)–C(22)–C(20)	115 (3)
–S(1)	99.95 (9)	S(3)–C(12)–C(11)	107 (2)
–S(3)	82.17 (9)	S(3)–C(12)–C(22)	109 (2)
Cl(6)–Ta(2)–S(1)	100.73 (9)	C(3)–C(2)–C(33)	35 (2)
–S(3)	86.25 (9)	C(3)–C(4)–C(33)	35 (2)
S(1)–Ta(2)–S(3)	173.00 (9)	C(10)–C(9)–C(20)	26 (1)
Ta(1)–S(1)–C(1)	123.9 (4)	C(10)–C(11)–C(20)	25 (2)
–C(4)	124.0 (4)	C(10)–C(22)–C(20)	28 (2)
Ta(2)–S(1)–C(1)	123.6 (4)	C(11)–C(10)–C(22)	23 (2)
–C(4)	125.2 (5)	C(11)–C(20)–C(22)	20 (2)
		C(11)–C(12)–C(22)	22 (2)

Table VI. Bond Distances (Å) in Compound **2**[a]

Ta(1)–Ta(1)′	2.691 (1)	Ta(1)–Cl(24)	2.865 (4)
–Cl(1)	2.478 (5)	S(1)–C(1)	1.91 (3)
–Cl(2)	2.519 (5)	–C(4)	1.88 (3)
–S(1)	2.378 (5)	S(2)–C(2)	1.85 (2)
–Cl(14)	2.378 (5)	–C(3)	1.84 (2)
–S(2)	2.618 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Table VII. Bond Angles (Deg) in Compound **2**

Cl(1)–Ta(1)–Cl(2)	76.0 (2)	Cl(14)–Ta(1)–Cl(24)	102.4 (2)
Cl(1)–Ta(1)–Cl(14)	163.5 (2)	–S(1)	89.1 (2)
–Cl(24)	91.6 (2)	–S(2)	87.8 (2)
–S(1)	99.7 (2)	Cl(24)–Ta(1)–S(1)	89.2 (2)
–S(2)	85.1 (2)	–S(2)	84.3 (2)
Cl(2)–Ta(1)–Cl(14)	88.9 (2)	S(1)–Ta(1)–S(2)	172.1 (2)
–Cl(24)	165.7 (2)	Ta(1)–Cl(1)–Ta(1)	65.8 (2)
–S(1)	99.8 (2)	–Cl(2)–Ta(1)	64.6 (1)
–S(2)	87.4 (2)	Ta(1)–S(1)–Ta(1)	68.9 (2)
		C(1)–S(1)–C(4)	101 (2)
		C(2)–S(2)–C(3)	97 (1)

Br atoms would be even smaller. Presumably, this is energetically unfavorable and beyond a certain point Ta–Ta bond stretching becomes energetically as feasible as further compression of the Ta–X–Ta angle.

Compound **1** is of particular interest for comparison with $Ta_2Cl_6(THF)_2(\mu$-*t*-BuCC-*t*-Bu)] (**3**) whose structure has recently been reported.[6] The Ta–Ta bond length in **3**, 2.677 (1) Å, is shorter than that reported for any other Ta–Ta bond (or Nb–Nb bond, for that matter). The results presented here for **1** suggest that this is at least partly due to the presence of bridging Cl atoms in place of bridging Br atoms, since the previously reported structures were of the $M_2Br_6(THT)_3$ (M = Nb, Ta) compounds. There are, however, two other features of **3** that may influence the bond length. One is the replacement of the bridging THT by a bridging alkyne, *t*-BuCC-*t*-Bu, and the other is replacement of the terminal THT's by THF's. It is not possible to say anything with certainty about the role played by these two features.

On comparison of the structures of **1** and **2**, it is clear that they are virtually identical, as would certainly be expected. Their Ta–Ta bonds do not differ in length to a statistically significant extent.

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Registry No. 1, 66758-43-8; **2**, 77827-59-9; Ta, 7440-25-7.

Supplementary Material Available: Tables of structure factors (19 pages) for both structures. Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Triiodo(η^5-methylcyclopentadienyl)dicarbonylmolybdenum(IV), (η^5-$CH_3C_5H_4$)$Mo(CO)_2I_3$

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Organometallic complexes in exceptionally high oxidation states are expected to have low-energy ligand-to-metal charge-transfer (LMCT) excited states.[1] The photochemical reactivity of these states is of considerable interest. We have therefore been studying the photochemical reactivity of the complexes $CpM(CO)_2X_3$ (Cp = η^5-C_5H_5; M = Mo, W; X = Cl, Br, I).[2,3] The metal atom formal oxidation state of IV is exceptionally high for metal carbonyl compounds. To facilitate interpretation of the photochemical behavior and electronic spectroscopic properties of this series of complexes, we investigated the molecular structure of a representative member. Attempts to prepare crystals of the $CpM(CO)_2X_3$ complexes suitable for an X-ray diffraction study were unsuccessful and invariably resulted in crystals that were twinned. Suitable single crystals of the methyl-substituted cyclopentadienyl complex $(MeCp)Mo(CO)_2I_3$ (MeCp = η^5-$CH_3C_5H_4$)[4] were obtained, however. This paper reports the results of an X-ray study of this derivative.

Experimental Section

Synthesis of $(MeCp)Mo(CO)_2I_3$. Preparative work was carried out under an atmosphere of nitrogen with use of Schlenk techniques or in a Vacuum Atmospheres drybox. A solution of iodine (0.2 g, 0.79 mmol) in degassed benzene (30 mL) was added dropwise to a stirred solution of 0.1 g (0.19 mmol) of $[(MeCp)Mo(CO)_3]_2$ (Strem Chemical Co.) in degassed benzene (50 mL). The mixture was then irradiated (λ > 320 nm) for 15 min with use of a 200-W high-pressure

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Table I. Experimental Details of the X-ray Diffraction Study of $(MeCp)Mo(CO)_2I_3$

(A) Crystal Parameters[a] at 26 °C

$a = 26.244$ (2) Å
$b = 7.554$ (2) Å
$c = 13.390$ (2) Å
$\beta = 90.159$ (8)°
$V = 2654.5$ Å^3
mol wt 611.8
space group $C2/c$
$Z = 8$
ρ(calcd) = 3.061 g cm^{-3}
ρ(obsd)[b] = 3.05 (1) g cm^{-3}

(B) Measurement of Intensity Data

instrument: Enraf-Nonius CAD-4F κ-geometry diffractometer
radiation: Mo Kα ($\lambda_{\alpha_1} = 0.709\,30$ Å, $\lambda_{\bar{\alpha}} = 0.710\,73$ Å) graphite monochromated
takeoff angle: 2.0°
detector aperture: vertical, 4.0 mm; horizontal, variable (3.0 + tan θ) mm
cryst–detector dist: 173 mm
scan technique: coupled ω(crystal)–2θ(counter)
scan width: variable, $\Delta\omega = (0.80 + 0.35 \tan\theta)°$
scan rate: variable from 1.26 to 6.71° min^{-1} in ω
prescan rejection limit: 1σ
prescan acceptance limit: 100σ
maximum counting time: 60 s
bkgd measurements: moving cryst–moving detector, 25% added to scan width at both ends of each scan
stds: three reflctns (020), (004), and $(0\bar{2}0)$, measured every 3600 s of X-ray exposure time showed no decay
no. of reflctns collected: [$3° \leqslant 2\theta \leqslant 60°$ ($\pm h, +k, +l$)] 3880 unique, non space group extinguished
reorientation control: the 3 stds were recentered every 100 data and if the position of any scattering vector deviated by more than 0.10° from its calculated position a new orientation matrix was calcd on the basis of the recentering of a further 22 reflctns

(C) Treatment of Intensity Data

reduction to F_o and $\sigma(F_o)$: cor for bkgd, attenuator, and Lorentz–polarization of monochromatized X radiation as described previously[c]
abs cor:[d] $\mu = 78.53$ cm^{-1}; transmission factors ranged from 0.205 to 0.698
obsd data: 2730 reflctns, with $F_o > 6\sigma(F_o)$, used in the structure refinement

[a] From a least-squares fit to the setting angles of 25 reflections with $2\theta > 40°$. [b] By suspension in a mixture of diiodomethane and bromoform. [c] Reference 6. [d] Performed with the Wehe–Busing–Levy ORABS program.

Hg arc. The reaction solution was continually flushed with nitrogen during this period. After standing for 48 h, the deep red crystals (yield 50%) that deposited were collected by filtration. The infrared spectrum of the product is identical with the spectrum reported for $CpMo(CO)_2I_3$.[2]

Collection and Reduction of X-ray Data. The crystal used in the diffraction study was mounted in a capillary to minimize decomposition. It was bounded by the six faces (100) and $(\bar{1}00)$ (0.216 mm apart), (010) and $(0\bar{1}0)$ (0.566 mm apart), and (001) and $(00\bar{1})$ (0.046 mm apart). Preliminary oscillation and Weissenberg photographs showed the lattice to have Laue symmetry $2/m$. The systematic absences hkl when $h + k \neq 2n$ and $h0l$ when $l \neq 2n$ were consistent with either space group $C2/c$ (C_{2h}^6, No. 15) or Cc (C_s^4, No. 9),[5] the former being confirmed by the successful solution and refinement of the structure. The quality of the data crystal was checked by taking open–counter ω scans of several strong low-angle reflections and was judged to be acceptable ($\Delta\bar{\omega}_{1/2} \approx 0.10°$). Further details of the data collection and reduction appear in Table I and ref 6.

Determination and Refinement of the Structure. The structure was solved by the $\sum_2$ sign expansion direct methods program of SHELX-76 which revealed the positions of the molybdenum and three iodine atoms. A difference Fourier map, phased with use of these four atoms, revealed the positions of the remaining nonhydrogen atoms. All hydrogen atoms were located on a difference Fourier map, calculated toward the final stages of refinement, and their positional and isotropic thermal parameters were successfully refined. All nonhydrogen atoms were refined anisotropically. Neutral-atom scattering factors and anomalous dispersion corrections, for the nonhydrogen atoms, were obtained from ref 7. Scattering factors for the hydrogen atoms were those of Stewart et al.[8]

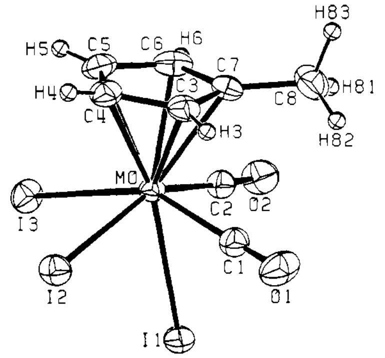

Figure 1. Geometry of $(MeCp)Mo(CO)_2I_3$ showing the atom labeling scheme. Thermal ellipsoids are depicted at the 40% probability level for all atoms except hydrogen which are assigned as arbitrary spheres having $B = 1.0$ Å^2.

Full-matrix least-squares refinement of 155 variables, using their converged to final residual indices[10] of $R_1 = 0.029$ and $R_2 = 0.038$. The function minimized in the least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 1.1684/[\sigma^2(F_o) + 0.00770F_o^2]$. In the final cycle of refinement, no parameter shifted by more than 0.005 of its estimated standard deviation. The nine largest peaks on a final difference Fourier map ranged from 0.63–1.24 e Å^{-3} and were all located 0.76–0.94 Å from the Mo or I atoms. The average $w\Delta^2$ for groups of data sectioned according to parity group, $|F_o|$, $(\sin\theta)/\lambda$, $|h|$, $|k|$, or $|l|$ showed good consistency, and the weighting scheme was considered satisfactory.

Final positional and thermal parameters, together with their estimated standard deviations, appear in Table II. Interatomic distances and angles, with standard deviations, are given in Table III. A list of final observed and calculated structure factor amplitudes is available as Table S1, and least-squares planes are given in Table S2.[11] Figure 1 depicts the geometry of the $(MeCp)Mo(CO)_2I_3$ molecule along with the atom labeling scheme.

Discussion

The structure of the title compound consists of discrete molecules of $(MeCp)Mo(CO)_2I_3$ wherein each formally Mo(IV) atom is coordinated to three iodine atoms, two carbonyl ligands, and a η^5-methylcyclopentadienyl ligand. If the MeCp ligand, normally thought to occupy three coordination sites, is considered to occupy only one position, the geometry around the Mo atom (Figure 1) can be described as distorted octahedral with I(1) being trans to MeCp [Mo–I(1) = 2.881 (1) Å]. The "equatorial" plane then consists of two iodine atoms [Mo–I(2) = 2.842 (1), Mo–I(3) = 2.859 (1) Å] and two carbonyl ligands [Mo–C(1) = 2.045 (6), Mo–C(2) = 2.041 (6) Å]. As expected, the two carbonyl ligands are cis to each other.[12] The molecule possesses approximate C_s symmetry where the pseudo mirror plane passes through atoms Mo, C(7), and C(8). Structural distortions of the $(MeCp)Mo(CO)_2I_3$ complex arise from intramolecular steric crowding. The iodide ligand trans to the MeCp ring is bent away from the two cis iodide ligands [Ω–Mo–I(1) = 167°] in order to minimize nonbonded I···I contacts. Similarly, steric factors may account

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(10) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

(11) Supplementary material.

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Table II. Final Positional and Thermal Parameters for (MeCp)Mo(CO)$_2$I$_3$[a,b]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo	0.38048 (2)	0.19346 (6)	0.96612 (3)	0.02747 (19)	0.0280 (2)	0.0234 (2)	−0.00247 (15)	0.00200 (15)	−0.00024 (16)
I(1)	0.30736 (1)	0.13847 (6)	1.12314 (3)	0.03498 (17)	0.0523 (2)	0.03264 (19)	0.00213 (15)	0.00820 (14)	0.00691 (17)
I(2)	0.41480 (1)	−0.14693 (5)	1.02663 (3)	0.04341 (19)	0.03009 (19)	0.0439 (2)	0.00372 (14)	0.00339 (15)	0.00131 (16)
I(3)	0.44016 (1)	0.32323 (6)	1.12940 (3)	0.04050 (19)	0.0465 (2)	0.0364 (2)	−0.00583 (15)	−0.00369 (15)	−0.00996 (16)
O(1)	0.28901 (18)	−0.0316 (7)	0.8781 (4)	0.054 (2)	0.068 (3)	0.049 (3)	−0.024 (2)	0.003 (2)	−0.013 (2)
O(2)	0.31226 (16)	0.5381 (6)	0.9873 (4)	0.052 (2)	0.036 (2)	0.065 (3)	0.0053 (19)	0.008 (2)	0.003 (2)
C(1)	0.3208 (2)	0.0481 (8)	0.9118 (4)	0.036 (3)	0.041 (3)	0.035 (3)	−0.002 (2)	0.001 (2)	0.000 (2)
C(2)	0.3360 (2)	0.4130 (8)	0.9833 (4)	0.034 (2)	0.042 (3)	0.033 (3)	−0.003 (2)	0.000 (2)	0.003 (2)
C(3)	0.3995 (2)	0.1247 (9)	0.8030 (4)	0.043 (3)	0.042 (3)	0.023 (2)	−0.003 (2)	0.006 (2)	−0.002 (2)
C(4)	0.4474 (2)	0.1343 (9)	0.8525 (5)	0.035 (3)	0.047 (3)	0.036 (3)	0.004 (2)	0.012 (2)	0.004 (3)
C(5)	0.4545 (2)	0.3060 (10)	0.8867 (5)	0.039 (3)	0.062 (4)	0.037 (3)	−0.019 (3)	0.007 (2)	0.005 (3)
C(6)	0.4114 (2)	0.4069 (9)	0.8587 (5)	0.056 (3)	0.033 (3)	0.038 (3)	−0.012 (3)	0.014 (3)	−0.001 (3)
C(7)	0.3769 (2)	0.2968 (8)	0.8034 (4)	0.043 (3)	0.045 (3)	0.023 (2)	−0.001 (2)	0.006 (2)	0.005 (2)
C(8)	0.3307 (3)	0.3583 (12)	0.7477 (5)	0.057 (4)	0.063 (5)	0.036 (3)	0.014 (4)	0.002 (3)	0.008 (3)

atom	x	y	z	U, Å^2	atom	x	y	z	U, Å^2
H(3)	0.3813 (20)	0.030 (8)	0.779 (4)	0.029 (15)	H(81)	0.315 (3)	0.443 (12)	0.769 (7)	0.08 (3)
H(4)	0.471 (2)	0.065 (10)	0.856 (5)	0.047 (19)	H(82)	0.306 (3)	0.236 (12)	0.731 (6)	0.07 (2)
H(5)	0.481 (2)	0.353 (9)	0.913 (5)	0.041 (18)	H(83)	0.340 (3)	0.360 (12)	0.661 (7)	0.08 (3)
H(6)	0.406 (2)	0.512 (8)	0.882 (4)	0.029 (15)					

[a] Atoms are labeled as indicated in Figure 1. Estimated standard deviations, in parentheses, occur in the last significant figure(s) for each parameter. [b] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)]$. Hydrogen atoms are labeled according to the carbon atom to which they are bound.

Table III. Interatomic Distances (Å) and Angles (Deg) for (MeCp)Mo(CO)$_2$I$_3$[a]

Distances

Mo-I(1)	2.881 (1)	C(3)-H(3)	0.92 (6)
Mo-I(2)	2.842 (1)	C(4)-C(5)	1.387 (9)
Mo-I(3)	2.859 (1)	C(4)-H(4)	0.81 (7)
Mo-C(1)	2.045 (6)	C(5)-C(6)	1.413 (10)
Mo-C(2)	2.041 (6)	C(5)-H(5)	0.85 (6)
Mo-C(3)	2.301 (5)	C(6)-C(7)	1.434 (9)
Mo-C(4)	2.369 (5)	C(6)-H(6)	0.87 (6)
Mo-C(5)	2.375 (6)	C(7)-C(8)	1.496 (9)
Mo-C(6)	2.310 (6)	C(8)-H(81)	0.81 (9)
Mo-C(7)	2.316 (5)	C(8)-H(82)	1.14 (8)
Mo-Ω[b]	2.000	C(8)-H(83)	1.18 (10)
C(1)-O(1)	1.123 (7)	O(1)···O(2)[c]	3.215 (7)
C(2)-O(2)	1.133 (7)	O(2)···C(8)[d]	3.604 (9)
C(3)-C(4)	1.423 (8)	O(2)···H(83)[d]	2.56 (10)
C(3)-C(7)	1.429 (9)		

Angles

I(1)-Mo-I(2)	82.7 (2)	C(1)-Mo-C(7)	79.5 (2)
I(1)-Mo-I(3)	81.7 (2)	C(1)-Mo-Ω	102
I(1)-Mo-C(1)	70.8 (2)	C(2)-Mo-C(3)	114.6 (2)
I(1)-Mo-C(2)	69.7 (2)	C(2)-Mo-C(4)	130.6 (2)
I(1)-Mo-C(3)	143.8 (1)	C(2)-Mo-C(5)	103.2 (2)
I(1)-Mo-C(4)	159.7 (2)	C(2)-Mo-C(6)	72.9 (2)
I(1)-Mo-C(5)	157.8 (2)	C(2)-Mo-C(7)	79.0 (2)
I(1)-Mo-C(6)	142.3 (2)	C(2)-Mo-Ω	101
I(1)-Mo-C(7)	135.2 (1)	Mo-C(1)-O(1)	177.1 (5)
I(1)-Mo-Ω	167	Mo-C(2)-O(2)	175.9 (5)
I(2)-Mo-I(3)	85.4 (2)	C(4)-C(3)-C(7)	108.6 (5)
I(2)-Mo-C(1)	81.8 (2)	C(4)-C(3)-H(3)	132 (4)
I(2)-Mo-C(2)	152.1 (2)	C(7)-C(3)-H(3)	120 (4)
I(2)-Mo-C(3)	89.8 (2)	C(3)-C(4)-C(5)	108.6 (6)
I(2)-Mo-C(4)	77.1 (2)	C(3)-C(4)-H(4)	132 (5)
I(2)-Mo-C(5)	101.1 (2)	C(5)-C(4)-H(4)	119 (5)
I(2)-Mo-C(6)	134.2 (2)	C(4)-C(5)-C(6)	108.1 (6)
I(2)-Mo-C(7)	125.8 (2)	C(4)-C(5)-H(5)	129 (4)
I(2)-Mo-Ω	107	C(6)-C(5)-H(5)	122 (4)
I(3)-Mo-C(1)	150.9 (2)	C(5)-C(6)-C(7)	109.2 (6)
I(3)-Mo-C(2)	87.0 (2)	C(5)-C(6)-H(6)	123 (4)
I(3)-Mo-C(3)	133.1 (1)	C(7)-C(6)-H(6)	127 (4)
I(3)-Mo-C(4)	98.6 (2)	C(3)-C(7)-C(6)	105.5 (5)
I(3)-Mo-C(5)	76.9 (2)	C(3)-C(7)-C(8)	128.0 (6)
I(3)-Mo-C(6)	92.5 (2)	C(6)-C(7)-C(8)	126.0 (6)
I(3)-Mo-C(7)	128.6 (1)	C(7)-C(8)-H(81)	118 (6)
I(3)-Mo-Ω	107	C(7)-C(8)-H(82)	107 (4)
C(1)-Mo-C(2)	92.2 (2)	C(7)-C(8)-H(83)	109 (4)
C(1)-Mo-C(3)	73.1 (2)	H(81)-C(8)-H(82)	115 (7)
C(1)-Mo-C(4)	103.8 (2)	H(81)-C(8)-H(83)	117 (8)
C(1)-Mo-C(5)	131.3 (2)	H(82)-C(8)-H(83)	87 (6)
C(1)-Mo-C(6)	115.1 (2)	O(2)···H(83)[d]-C(8)[d]	146 (6)

[a] See footnote *a* of Table II. Values reported have not been corrected for thermal motion. [b] Ω is the center of the cyclopentadienyl ring. [c] Atom is at ($^1/_2 - x$, $^1/_2 - y$, $2 - z$). [d] Atom is at (x, $1 - y$, $^1/_2 + z$).

for the slight elongation of the Mo–C(4) and Mo–C(5) bonds relative to the Mo–C(3), Mo–C(6), and Mo–C(7) bonds (Table III). In addition, the two C(4)–H and C(5)–H units of the MeCp ring interact with the I(2) and I(3) iodide ligands to induce a slight bend in the cyclopentadienyl ring across the line joining atoms C(3) and C(6).

The elongation of the Mo–C(4) and Mo–C(5) bonds and the bending of the ring may also be indicative of a tendency for the MeCp ring to be coordinated in a η^3 (allylic) + η^2 (ene) rather than a η^5 fashion.[13-16] Consistent with this proposal is the short C(4)–C(5) bond length (1.387 Å) in comparison to the other C(ring)–C(ring) distances. Complexes for which an "allyl-ene" coordination of a cyclopentadienyl ligand has

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Table IV. Mo-C and C-O Bond Lengths in Selected Molybdenum Carbonyl Complexes[a]

complex	av Mo-C (carbonyl) bond length, Å	av C-O bond length, Å	ref
$(MeCp)Mo(CO)_2I_3$	2.043 (2)	1.128 (5)	this work
$(\eta^5\text{-}C_9H_7)Mo(CO)_3I$	1.93 (4)	1.187 (13)	17
$(\eta^5\text{-}C_5H_5)Mo(CO)_3Cl$	1.990 (7)	1.163 (22)	18
$(\eta^5\text{-}C_5H_5)Mo(CO)_3(C_2H_5)$	1.96 (1)	1.16 (1)	19
$(\eta^5\text{-}C_5H_5)Mo(CO)_3(C_3F_7)$	2.012 (6)	1.167 (11)	20
$(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$	1.960 (17)	1.16 (13)	21
$(\eta^5\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$	1.983 (1)	1.124 (14)	22
$[(C_4H_9)_4N][(\eta^5\text{-}C_5H_5)Mo(CO)_3]$	1.909 (6)	1.176 (5)	23

[a] Standard deviations (in parentheses) on mean values ($\bar{p}$) of n equivalent distances (p_i) were calculated by the formula $[\Sigma_i(p_i - \bar{p})^2/n(n-1)]^{1/2}$.

been proposed generally have bond lengths of about 1.388 Å for the "ene" bond in the Cp ring.[16]

The methyl substituent on the Cp ring is directed between the two CO ligands. This orientation minimizes steric repulsions between the "equatorial" iodide ligands and the methyl group. Noteworthy is the fact that the methyl carbon atom C(8) is displaced by 0.214 (7) Å out of the mean plane through the C_5 ring away from the coordination sphere. Similar results have been found for other methyl-substituted cyclopentadienyl rings.[16]

The structure of the $(MeCp)Mo(CO)_2I_3$ complex is consistent with spectroscopic data previously reported for the $CpM(CO)_2X_3$ complexes.[2,3] In particular, the high $\nu(C{\equiv}O)$ frequencies reported reflect the short C-O bond lengths [C(1)-O(1) = 1.123 (7), C(2)-O(2) = 1.133 (7) Å]. These short distances indicate that there is little π back-bonding from the metal to the carbonyl groups, as expected in a Mo(IV) complex. That the C-O bonds are short can be seen by comparison to the C-O bond lengths reported for other molybdenum carbonyl complexes (Table IV). The low degree of π back-bonding is also reflected in the long Mo-CO bond distances [Mo-C(1) = 2.045 (6) Å, Mo-C(2) = 2.041 (6) Å]. Table IV shows that the Mo-CO bonds in $(MeCp)Mo(CO)_2I_3$ are longer than the Mo-CO bonds in other molybdenum carbonyl complexes. The high coordination number of the $(MeCp)Mo(CO)_2I_3$ complex is also expected to lengthen the M-CO bonds in comparison to less sterically crowded molecules.[24]

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Supplementary Material Available: Table S1, listing observed and calculated structure factor amplitudes, and Table S2, listing least-squares planes (14 pages). Ordering information is given on any current masthead page.

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Bonding Mode and Trans Influence of the Nitromethyl Ligand. Structure of *trans*-Bis(dimethylglyoximato)(nitromethyl)(pyridine)cobalt(III)

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We are interested in developing new methods of forming Co-C bonds as part of a program aimed at elucidating the effects of alkyl groups with differing electronic properties on the structure,[1-5] reactions,[5-8] and spectral properties[1,2,5-7,9-12] of cobalt complexes. We describe here a synthetic procedure for preparing cobaloxime complexes which contain the nitromethyl substituent, $LCo(DH)_2CH_2NO_2$, where DH = monoanion of dimethylglyoximme. A study of the interrelationship between the Co-C bond and systematic variations in the L ligand and the substituent on carbon may provide insight into the factors which promote cleavage of the Co-C bond in vitamin B_{12} coenzyme.[1,2]

We have previously investigated in detail cobaloximes containing good electron-donor alkyl ligands. The nitromethyl substituent is a relatively poor electron-donating ligand. Since there was a small possibility that bonding was via O rather than C,[13] we have elucidated the structure of the complex with L = pyridine. This complex serves as a "bridge" between organocobaloximes and acidocobaloximes. In addition, it can be argued that the chemistry of cobaloximes and of Pt(II) compounds has many analogies,[9,10] and we wanted to explore the application to cobaloximes of preparative procedures used in Pt(II) chemistry.[14]

Experimental Section

(a) Preparation of $pyCo(DH)_2CH_2NO_2$. A solution of 3.0 g (7.43 mmol) of $pyCo(DH)_2Cl$[9] in 40 mL of nitromethane was treated with 1.73 g (7.46 mmol) of silver oxide and heated with stirring at 60-65 °C for 1.5 h. At the end of this time, the hot reaction mixture was filtered through Celite to remove precipitated silver chloride. The filtrate was allowed to evaporate to dryness overnight in a fume hood. The residue, either a dry solid or an oil, was taken up in about 50 mL of warm acetone. Then, 20 mL of water was added and the acetone was allowed to evaporate slowly, giving product which is ~95% pure, as evidenced by ^1H NMR spectra. Two recrystallizations from acetone/H_2O yielded pure product in about 40-50% yield. The contaminant which was removed in the recrystallizations was $pyCo(DH)_2NO_2$ (determined by ^{13}C NMR spectral comparison with the authentic complex), although no study was made to determine the mechanism of formation of the NO_2 complex. This procedure has proved useful in preparing analogous complexes with substituted pyridines.

(b) Crystal Data. Crystals of $pyCo(DH)_2CH_2NO_2$ were obtained by slow crystallization from acetone/H_2O. Cell dimensions were determined from Weissenberg and precession photographs and refined on a Siemens AED single-crystal diffractometer. The results are given in Table I. One check reflection intensity was measured every 100 reflections. There was no systematic variation throughout the data collection. The intensities for which $I > 3\sigma(I)$ were corrected for Lorentz and polarization effects but not for absorption.

(c) Solution and Refinement of Structure. The structure was solved by conventional Patterson and Fourier methods and refined by the block-diagonal anisotropic least-squares method to a final R value of 0.035. This approach probably underestimates the esd's. Only the oxime bridge hydrogen atoms were refined anisotropically; the remainder were held constant at $B = 5$ Å^2.

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