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Cyclopentadienylethyldinitrosylmolybdate Anion, a Novel, Prototypal 19-Electron Nitrosyl Complex[1,2]

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The cyclic voltammogram of $CpMo(NO)_2Et$ ($Cp = \eta^5\text{-}C_5H_5$) in CH_2Cl_2/0.1 M $[n\text{-}Bu_4N]PF_6$ reveals that the nitrosyl compound undergoes essentially reversible reduction with $E_{1/2} = -0.86$ V vs SCE. On a preparative scale, this reduction is best effected in Et_2O with Cp_2Co as the reducing agent, the $[Cp_2Co][CpMo(NO)_2Et]$ product being isolable in moderate yields as a green-black microcrystalline solid. The IR (Nujol) and ESR (CH_3CN) spectra of the product indicate that the extra electron density of the $[CpMo(NO)_2Et]^{\bullet-}$ radical anion is delocalized primarily onto the nitrosyl ligands by strong Mo→NO π-back-bonding. A single-crystal X-ray crystallographic analysis of $[Cp_2Co][CpMo(NO)_2Et]$ substantiates this view, the anion being shown to possess a "three-legged piano-stool" molecular structure with long N–O bonds (average 1.232 Å) and a large N–Mo–N angle (average 100.5°). The $[Cp_2Co]^+$ cation in this lattice exhibits an eclipsed conformation. Crystal data for $[Cp_2Co][CpMo(NO)_2Et]$: $a = 8.715$ (4) Å, $b = 15.770$ (4) Å, $c = 12.876$ (3) Å, $\beta = 105.29$ (4)°, $Z = 4$, space group $P2_1/n$, unique reflections 3125, number of variables 200, $R = R_w = 0.034$.

Introduction

Anionic organo transition-metal complexes have attracted considerable attention,[3] particularly from the viewpoint of their reactions as nucleophiles with diverse organic, inorganic, or organometallic electrophiles.[4] The vast majority of such anions contain carbonyl ligands, the strong π-acidity of the CO groups effectively stabilizing these complexes by delocalizing the extra electron density.[5] On this basis, it would be anticipated that the presence of nitrosyl ligands (stronger π-acids than carbonyl ligands)[6] would particularly facilitate the formation of anionic complexes. This anticipation notwithstanding, there are relatively few examples of diamagnetic nitrosyl metalates presently known, and many of these known species also contain the ubiquitous CO groups attached to their metal centers. Some examples of these diamagnetic anions include $[Fe(CO)_3(NO)]^-$,[7] $[Fe(NO)(CN)_5]^{2-}$ (and related cyanonitrosyl complexes),[8] $[CpM(CO)(NO)(M'Ph_3)]^-$ ($Cp = \eta^5\text{-}C_5H_5$; M = Mo or W; M′ = Si, Ge or Sn),[9] $[V(CO)_4(NO)I]^-$,[10] $[CpV(CO)_2(NO)]^-$,[10] $[Mn(CO)_2(NO)_2]^-$,[11] $[M_3(CO)_{10}(NO)]^-$ (M = Ru or Os),[11] $[Co(CO)_2(NO)(NO_2)]^-$,[11] and $[CpCo(NO)]^-$.[12,13] On the other hand, reports of paramagnetic radical anion complexes containing NO ligands are becoming more frequently encountered. For instance, salts containing the anions $[Cp_2Cr_2(NO)_4]^{\bullet-}$,[14] $[Cp_2Fe_2(NO)_2]^{\bullet-}$,[15] $[Fe(NO)Cl_3]^{\bullet-}$,[16] and $[\{HB(Me_2pz)_3\}Mo(NO)I_2]^{\bullet-}$ (Me_2pz = 3,5-dimethylpyrazolyl)[17] have been recently isolated. In addition, the anionic complexes $[(R_2NCS_2)_2M(NO)_2]^{\bullet-}$ (M = Mo or W; R = alkyl)[18] and $[CpM(CO)_2(NO)]^{\bullet-}$ (M = Cr or Mo)[19] have been well-characterized by ESR spectroscopy, and reversible electron-transfer processes have been reported for a variety of other nitrosyl-containing compounds.[20] Nevertheless, isolable organometallic nitrosyl radical anions are still rare.

In this paper we wish to report the synthesis, isolation, and characterization of the $[CpMo(NO)_2Et]^{\bullet-}$ radical anion as its cobalticinium salt. This complex is a prototype of a whole host of radical species containing the $CpM(NO)_2$ group (M = Cr, Mo, or W).[21] The spectroscopic properties and a single-crystal X-ray crystallographic analysis of $[Cp_2Co][CpMo(NO)_2Et]$ indicate substantial delocalization of the anion's extra electron density onto the nitrosyl ligands.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and anhydrous conditions. General procedures routinely employed in these laboratories have been described in detail previously.[22] The methodology employed during the cyclic voltammetry studies has also been outlined elsewhere.[14] The triangular waveform potential

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Table I. Crystal Data and Experimental Parameters

formula	$[C_{10}H_{10}Co]^+[C_7H_{10}N_2O_2Mo]^-$
fw	441.25
cryst system	monoclinic
space group	$P2_1/n$[a]
a, Å	8.715 (4)
b, Å	15.770 (4)
c, Å	12.876 (3)
β, deg	105.29 (4)
V, Å^3	1707.0
Z	4
D_{calcd}, g cm^{-3}	1.717
$F(000)$	892
λ, Å	0.7093
μ(Mo Kα), cm^{-1}	16.98
cryst dimens, mm	0.28 × 0.34 × 0.06
transmissn factors	0.589–0.897
ω_0, deg	$0.70 + 0.35 \tan \theta$
ω scan speed range, deg min^{-1}	4.12–0.57
$2\theta_{max}$, deg	50
data collected	$+h,+k,\pm l$
cryst decay	4%
unique reflctns	3125
obsd reflctns, $I > 3\sigma(I)$	1828
no. of restraints	12
no. of variables	200
R	0.034
R_w	0.034
goodness of fit	1.049

[a] Nonstandard setting of $P2_1/c$, equivalent positions are as follows: x, y, z; $-x, +y, -z$; $-x, -y, -z$; $+x, -y, +z$.

required during these studies was obtained with a Wavetek Model 143 function generator in conjunction with a unity-gain inverter (±15 V, 50 mA) constructed in the Electronics Shop of the Department of Chemistry at UBC under the direction of Mr. Joe Sallos. The ESR spectrum was recorded at X-band by using a Varian E3 spectrometer. Elemental analyses were performed by Mr. P. Borda at UBC.

Preparation of [Cp$_2$Co][CpMo(NO)$_2$Et]. A medium-porosity glass frit was charged with solid Cp$_2$Co[23] (0.163 g, 0.862 mmol), capped with a septum, and attached to a three-necked, 200-mL flask containing liquid CpMo(NO)$_2$Et[24] (0.216 g, 0.864 mmol). Diethyl ether was then added by cannula, ~20 mL to the flask and ~50 mL onto the frit. The resulting dark purple solution of Cp$_2$Co was filtered into the bright green solution in the flask, and the green-brown solution thus formed was stirred for a few minutes at ambient temperature to ensure homogeneity. The flask containing this solution was then cooled with a dry ice/acetone bath for ~10 min to induce the precipitation of a dark green microcrystalline solid. After this solid had settled, the supernatant solution was carefully removed by cannulation. The solid was washed with Et$_2$O (2 × 15 mL) that had been previously cooled with a dry ice/acetone bath, and the washings were again removed by cannulation. Most of the residual Et$_2$O was removed under reduced pressure at −60 °C before the solid was permitted to warm gradually to room temperature. Ultimate drying of the solid in vacuo (5×10^{-3} mm) at 20 °C for 5 h afforded 0.195 g (52% yield) of [Cp$_2$Co][CpMo(NO)$_2$Et] as analytically pure, dark green microcrystals: IR (Nujol mull) ν_{NO} 1527 (s), 1458 (s) cm^{-1}, also 3104 (m, br), 1415 (m), 1361 (w), 1262 (w), 1145 (w), 1113 (w), 1059 (w), 1013 (m), 893 (w), 874 (w), 861 (m), 847 (w), 801 (m), 788 (m) cm^{-1}. Anal. Calcd for $C_{17}H_{20}N_2O_2CoMo$: C, 46.49: H, 4.59; N, 6.38. Found: C, 46.40; H, 4.57; N, 6.47.

If the reaction was effected by using more concentrated solutions of the reactants (e.g. 0.42 mmol of each reagent in a total of 20 mL of Et$_2$O), a dark green precipitate of [Cp$_2$Co][CpMo(NO)$_2$Et] formed upon mixing of the reactant solutions at room temperature.

Larger diamond-shaped plates of [Cp$_2$Co][CpMo(NO)$_2$Et] used for X-ray crystallographic analysis were grown by slow cooling of a saturated Et$_2$O solution of the salt to −25 °C for 6 h.

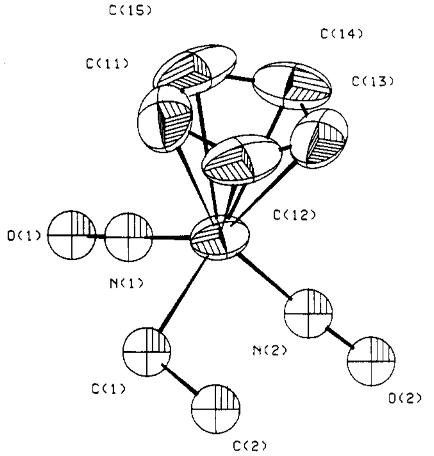

Figure 1. View of the molecular structure of the [CpMo(NO)$_2$Et]$^{\bullet-}$ anion showing non-hydrogen atoms. Only the major orientation of the disordered Mo(NO)$_2$Et fragment is shown.

Crystal Structure Analysis. A dark green, plate-shaped crystal of [Cp$_2$Co][CpMo(NO)$_2$Et] was selected and sealed in a thin-walled glass capillary under dry N$_2$. After a preliminary photographic investigation, the crystal was transferred to an Enraf-Nonius CAD4-F diffractometer where accurate cell dimensions and an orientation matrix were obtained from the least-squares refinement on the setting angles of 25 reflections with $23° \leq 2\theta \leq 31°$. The intensities of a unique data set were then collected by using the conventional $\theta/2\theta$ scan technique; experimental parameters and crystal data are given in Table I.

The diffraction data were corrected for Lorentz and polarization effects, and an analytical absorption correction was applied.[25] The structure was solved by conventional heavy-atom methods, refinement being by full-matrix least squares. Hydrogen atoms were geometrically placed (C–H = 0.95 Å) and allowed to ride on their respective carbon atoms. The initial geometry of the ethyl group was unreasonable, there were several residual peaks of electron density in the vicinity of this group, and the nitrosyl environments were deformed. This evidence indicated that the ethyl and nitrosyl groups were disordered, and so an appropriate model with restraints was applied to each of the individual fragments. The final model has two orientations for the three ligands involved in the base of the piano stool, the sites involving the NO groups having atoms less than 0.5-Å apart. Extensive use was made of restraints[26,27] which were gradually removed so that during the final cycles of refinement the only restraints applied to the geometry of the anion were that the Mo–N bonds, the N–O bonds, and the Mo–C–C bond angles were restricted to their mean values and the C–C bonds of the ethyl groups were restrained to a value of 1.54 Å. All non-hydrogen atoms were refined anisotropically except that each disordered fragment was given the same isotropic temperature factor for each atom of the nitrosyl and ethyl groups, common isotropic temperature factors were assigned to each H atom on each Cp ring, and one occupancy factor was given to each group of 11 atoms in the disordered portion of the anion. These occupancy factors refined to values of 0.559 (8) and 0.441 (8), their sum being constrained to unity. Finally, the temperature factors of the H atoms in the C$_2$H$_5$ group were set 0.02 Å^2 higher than those of the C atoms to which they were bonded. The final difference Fourier map showed no abnormal features, the highest peak of 0.51 e Å^{-3} being close (1.122 Å) to the molybdenum atom. During the final stages of refinement, the weight for each reflection was calculated from a three-term Chebyshev series so that the weight assigned to each reflection was $w = [24.30t_0(X) + 30.84t_2(X) + 13.32t_3(X)]^{-1}$ where $X = F_o/F_{max}$.[28]

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Table II. Final Positional (Fractional × 10^4) and Isotropic Thermal Parameters ($U \times 10^4$ Å^2) of the Non-Hydrogen Atoms of $[Cp_2Co][CpMo(NO)_2Et]^a$

atom	x/a	y/b	z/c	U_{eq}/U_{iso}
Mo(1)*	1566.3 (7)	250.7 (4)	2074.2 (5)	509
Co(1)	7791.3 (9)	−2521.8 (5)	2405.4 (6)	420
N(1)*	1444 (18)	1348 (5)	1613 (10)	498 (19)
N(2)*	−385 (10)	74 (10)	2224 (11)	526 (20)
N(101)*	1430 (23)	1367 (5)	1866 (13)	498 (19)
N(102)*	−505 (11)	25 (12)	1987 (14)	526 (20)
O(1)*	1254 (12)	2078 (5)	1235 (7)	587 (17)
O(2)*	−1748 (9)	−66 (6)	2268 (7)	579 (17)
O(101)*	1476 (15)	2115 (6)	1626 (10)	587 (17)
O(102)*	−1943 (11)	−103 (8)	1873 (10)	579 (17)
C(1)*	2656 (17)	630 (8)	3785 (10)	626 (27)
C(2)*	2332 (16)	−19 (8)	4575 (11)	836 (34)
C(101)*	2185 (17)	293 (12)	3860 (12)	626 (27)
C(102)*	3658 (19)	848 (11)	4279 (14)	836 (34)
C(11)	4105 (9)	−210 (6)	1897 (9)	785
C(12)	3562 (11)	−857 (6)	2401 (7)	700
C(13)	2267 (11)	−1187 (5)	1707 (9)	729
C(14)	1930 (11)	−741 (7)	761 (7)	766
C(15)	3117 (14)	−130 (6)	867 (8)	775
C(21)	7483 (8)	−2554 (6)	3901 (5)	628
C(22)	8531 (9)	−3193 (5)	3773 (5)	621
C(23)	9818 (8)	−2801 (5)	3523 (5)	606
C(24)	9555 (10)	−1920 (5)	3487 (5)	638
C(25)	8127 (10)	−1784 (5)	3717 (5)	659
C(31)	5641 (9)	−2683 (7)	1378 (6)	720
C(32)	6658 (14)	−3321 (5)	1248 (6)	741
C(33)	7928 (10)	−2923 (6)	948 (6)	681
C(34)	7642 (9)	−2061 (5)	916 (5)	635
C(35)	6249 (10)	−1916 (6)	1184 (5)	659

[a] The asterisk denotes that a restraint was applied involving this atom.

Table III. Bond Lengths (Å) of the Non-Hydrogen Atoms of $[Cp_2Co][CpMo(NO)_2Et]^a$

Mo(1)–N(1)	1.824*	N(1)–O(1)	1.244*
Mo(1)–N(2)	1.784*	N(2)–O(2)	1.224*
Mo(1)–N(101)	1.780*	N(101)–O(101)	1.222*
Mo(1)–N(102)	1.814*	N(102)–O(102)	1.239*
Mo(1)–C(1)	2.238*	C(1)–C(2)	1.522*
Mo(1)–C(101)	2.220*	C(101)–C(102)	1.530*
Mo(1)–C(11)	2.396 (7)	C(11)–C(12)	1.360 (11)
Mo(1)–C(12)	2.422 (7)	C(11)–C(15)	1.383 (11)
Mo(1)–C(13)	2.427 (7)	C(12)–C(13)	1.345 (11)
Mo(1)–C(14)	2.385 (7)	C(13)–C(14)	1.369 (11)
Mo(1)–C(15)	2.389 (8)	C(14)–C(15)	1.394 (12)
Co(1)–C(21)	2.014 (6)	C(21)–C(22)	1.399 (10)
Co(1)–C(22)	2.010 (7)	C(21)–C(25)	1.385 (10)
Co(1)–C(23)	2.011 (6)	C(22)–C(23)	1.391 (9)
Co(1)–C(24)	2.019 (7)	C(23)–C(24)	1.407 (11)
Co(1)–C(25)	2.008 (7)	C(24)–C(25)	1.370 (11)
Co(1)–C(31)	2.004 (7)	C(31)–C(32)	1.381 (11)
Co(1)–C(32)	2.002 (7)	C(31)–C(35)	1.370 (11)
Co(1)–C(33)	2.013 (7)	C(32)–C(33)	1.412 (11)
Co(1)–C(34)	2.023 (7)	C(33)–C(34)	1.381 (10)
Co(1)–C(35)	2.022 (7)	C(34)–C(35)	1.367 (10)

[a] The asterisk denotes a restraint was applied involving this bond.

Table IV. Bond Angles (deg) of the Non-Hydrogen Atoms of $[Cp_2Co][CpMo(NO)_2Et]^a$

N(2)–Mo(1)–N(1)	102.0 (7)	C(14)–C(13)–C(12)	109.7 (9)
N(102)–Mo(1)–N(101)	99.1 (9)	C(15)–C(14)–C(13)	106.8 (8)
C(1)–Mo(1)–N(1)	92.3 (5)	C(14)–C(15)–C(11)	106.8 (8)
C(1)–Mo(1)–N(2)	96.0 (5)	C(25)–C(21)–C(22)	107.8 (6)
C(101)–Mo(1)–N(101)	96.6 (7)	C(23)–C(22)–C(21)	107.4 (7)
C(101)–Mo(1)–N(102)	92.0 (7)	C(24)–C(23)–C(22)	108.2 (7)
O(1)–N(1)–Mo(1)	174.9 (12)	C(25)–C(24)–C(23)	107.2 (7)
O(2)–N(2)–Mo(1)	176.3 (11)	C(24)–C(25)–C(21)	109.4 (7)
O(101)–N(101)–Mo(1)	170.7 (15)	C(35)–C(31)–C(32)	109.3 (8)
O(102)–N(102)–Mo(1)	176.4 (16)	C(33)–C(32)–C(31)	106.4 (7)
C(2)–C(1)–Mo(1)	111.9*	C(34)–C(33)–C(32)	107.4 (7)
C(102)–C(101)–Mo(1)	109.5*	C(35)–C(34)–C(33)	108.8 (8)
C(15)–C(11)–C(12)	108.6 (8)	C(34)–C(35)–C(31)	108.1 (8)
C(13)–C(12)–C(11)	108.0 (8)		

[a] The asterisk denotes restraints were applied to this bond angle.

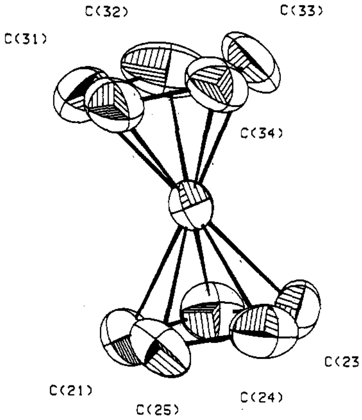

Figure 2. Solid-state molecular structure of the cobalticinium cation as it occurs in $[Cp_2Co][CpMo(NO)_2Et]$. Hydrogen atoms have been omitted.

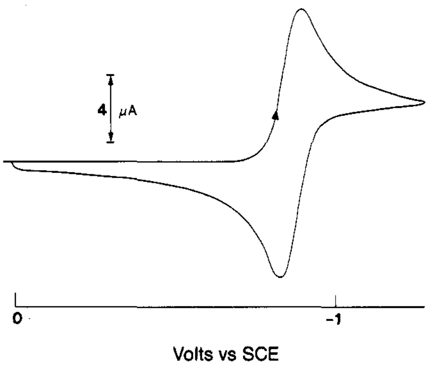

Figure 3. Ambient-temperature cyclic voltammogram of 5×10^{-4} M $CpMo(NO)_2Et$ in CH_2Cl_2 containing 0.1 M $[n\text{-}Bu_4N]PF_6$ measured at a platinum-bead electrode.

The computations were performed on a VAX 11/750 computer using the N.R.C. VAX crystal structure package[29] and the CRYSTALS suite of programs.[30] Complex neutral-atom scattering factors were taken from ref 31. Final positional and isotropic (or equivalent isotropic, $U_{eq} = (\text{ax1} \times \text{ax2} \times \text{ax3})^{1/3}$) thermal parameters are presented in Table II, and bond lengths and angles are tabulated in Tables III and IV, respectively. Calculated hydrogen atom positions (Table V), anisotropic thermal parameters (Table VI), mean plane calculations (Table VII), torsion angles (Table VIII), and calculated and measured structure factors (Table IX) are deposited as supplementary material. Thermal ellipsoid plots of the solid-state molecular structures of the anion and cation are shown in Figures 1 and 2, respectively.[32]

Results and Discussion

The presence of the nitrosyl ligands has a profound effect on the reduction behavior of $CpMo(NO)_2Et$. Figure 3 shows the ambient-temperature cyclic voltammogram of this compound in CH_2Cl_2 containing 0.1 M $[n\text{-}Bu_4N]PF_6$ measured at a platinum-bead electrode. Under these ex-

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perimental conditions, $E_{1/2} = -0.86$ V (vs SCE)[33] for the reduction wave shown, and no other waves occur out to the solvent limit of −1.9 V. Furthermore, the observed peak potential ($E_{p,c}$) does not vary with scan rates ranging from 0.04 to 0.21 V s^{-1}, the peak current ratio ($i_{p,a}/i_{p,c}$)[35] is unity even at a scan rate of 0.05 V s^{-1}, and $\Delta E_p = 65$ mV. All these features are indicative of chemical reversibility being associated with this particular reduction process, i.e.

$$\mathrm{CpMo(NO)_2Et} + e^- \rightleftharpoons [\mathrm{CpMo(NO)_2Et}]^{\bullet -} \qquad (1)$$

This behavior of $\mathrm{CpMo(NO)_2Et}$ upon reduction contrasts with that exhibited by related alkyl carbonyl complexes. Upon the addition of electrons, the carbonyl compounds either undergo irreversible metal–alkyl bond scission in CH_3CN or DMF, e.g.[36]

$$\mathrm{CpFe(CO)_2Me} + 2e^- \rightarrow [\mathrm{CpFe(CO)_2}]^- + \mathrm{Me}^- \qquad (2)$$

and

$$\mathrm{CpW(CO)_3Me} + 2e^- \rightarrow [\mathrm{CpW(CO)_3}]^- + \mathrm{Me}^- \qquad (3)$$

or do not exhibit any reduction behavior in CH_2Cl_2 out to −1.9 V vs SCE,[33] e.g. $\mathrm{CpCr(CO)_3Me}$ and $\mathrm{CpMo(CO)_3Et}$. In other words, the nitrosyl ligands make $\mathrm{CpMo(NO)_2Et}$ much easier to reduce than its carbonyl analogues and ensure that its Mo–Et linkage remains intact upon reversible reduction.

Not surprisingly, bulk electrolytic methods cannot be employed successfully to effect conversion 1 on a preparative scale,[14] but chemical means for doing so can be readily found. Thus, treatment of $\mathrm{CpMo(NO)_2Et}$ with an equimolar amount of cobaltocene (a moderately potent one-electron reducing agent)[37] in Et_2O affords $[\mathrm{Cp_2Co}][\mathrm{CpMo(NO)_2Et}]$ which can be isolated in reasonable yields as a dark green microcrystalline solid. This transformation may well proceed via an initial equilibrium involving a solvated adduct, i.e.

$$\begin{aligned} &\mathrm{Cp_2Co} + \\ &\mathrm{CpMo(NO)_2Et} \overset{\mathrm{Et_2O}}{\rightleftharpoons} \underset{\text{(solvated adduct)}}{[(\mathrm{Cp_2Co})(\mathrm{CpMo(NO)_2Et})]} \overset{\mathrm{Et_2O}}{\rightleftharpoons} \\ &\qquad\qquad \underset{\text{(precipitated salt)}}{[\mathrm{Cp_2Co}]^+[\mathrm{CpMo(NO)_2Et}]^{\bullet -}} \qquad (4) \end{aligned}$$

since the mixture of reactants must be quite concentrated or be cooled to −60 °C in order to induce the precipitation of the salt product from Et_2O, not a particularly strong solvating solvent.[38] In any event, cobaltocene (having oxidation potentials of −0.94 V in CH_3CN and −0.80 V in DME vs SCE)[39] is the reducing agent of choice for effecting this conversion, and the slight solubility of the $[\mathrm{Cp_2Co}][\mathrm{CpMo(NO)_2Et}]$ product in Et_2O facilitates its isolation as a crystalline material. These crystals are remarkably stable in air, remaining unchanged after several hours in the atmosphere at room temperature. They are, however, best stored under N_2 at −20 °C. In addition, the crystals are moderately soluble in CH_2Cl_2 and CH_3CN and quite soluble in DMF, but the resulting solutions are stable only well below ambient temperature (i.e. −10 to −25 °C).

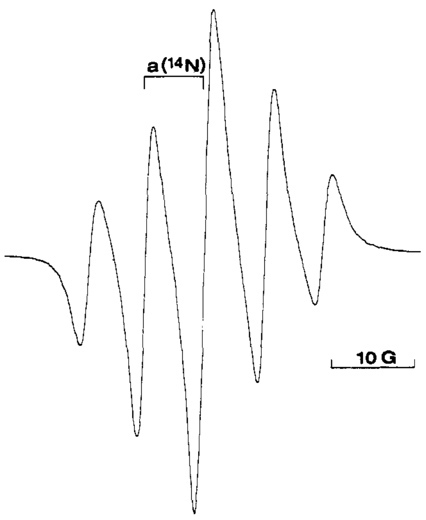

Figure 4. X-band ESR spectrum of $[\mathrm{Cp_2Co}][\mathrm{CpMo(NO)_2Et}]$ in CH_3CN at −20 °C; $a_N = 7$ G.

The proclivity of room-temperature solutions of $[\mathrm{Cp_2Co}][\mathrm{CpMo(NO)_2Et}]$ to decompose hampers the acquisition of reliable solution IR spectra of the complex. As a Nujol mull, it exhibits strong nitrosyl absorptions at 1527 and 1458 cm^{-1}, the pattern being typical of a dinitrosyl.[40] These absorption bands are 208 and 185 cm^{-1} lower in energy than those exhibited by neutral $\mathrm{CpMo(NO)_2Et}$ in hexanes[24] and lie well below the generally accepted range of ν_{NO} values for linear, terminal nitrosyl groups.[41] This large shift of the nitrosyl absorptions to lower energies upon the reduction of $\mathrm{CpMo(NO)_2Et}$ is indicative of substantially increased Mo→NO back-donation of electron density in the anionic product.

The isotropic ESR spectrum of $[\mathrm{Cp_2Co}][\mathrm{CpMo(NO)_2Et}]$ in CH_3CN at −20 °C (Figure 4) is also consistent with the existence of increased π-back-donation to the NO ligands. The spectrum consists of a simple five-line pattern having an approximately 1:2:3:2:1 intensity ratio and $a_N = 7$ G. It thus indicates strong coupling of the extra electron to the two equivalent ^{14}N ($I = 1$) nuclei of the nitrosyl ligands but no interaction with $^{95,97}Mo$. A similar pattern has been previously observed for the related neutral radical complexes, $[\mathrm{CpW(NO)_2L}]^{\bullet}$ (L = PPh_3 or $P(OPh)_3$),[42] and also for $[cis\text{-}(\mathrm{R_2NCS_2})_2\mathrm{M(NO)_2}]^{\bullet -}$ (M = Mo or W; R = alkyl).[18]

The crystal structure of $[\mathrm{Cp_2Co}][\mathrm{CpMo(NO)_2Et}]$ has been established by a single-crystal X-ray crystallographic analysis. It consists of discrete $[\mathrm{CpMo(NO)_2Et}]^{\bullet -}$ radical anions and $[\mathrm{Cp_2Co}]^+$ cations in a "CsCl-type" of arrangement since each ion is surrounded by eight counterions disposed at the corners of an irregular cube. Consistent with its spectroscopic properties, the anion has a "three-legged piano-stool" molecular geometry, albeit disordered, in the solid state (Figure 1), the distance of the Mo atom from the plane of the cyclopentadienyl ring (2.102 Å) being normal.[44,45] The nitrosyl ligands are essentially linear, and

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[33] Ferrocene was used as an internal standard during the cyclic voltammetry studies.[34] Under the experimental conditions employed throughout this work, the oxidation of Cp_2Fe occurs at $E_{1/2} = +0.47$ V vs SCE in CH_2Cl_2/0.1 M $[n\text{-}Bu_4N]PF_6$ at a Pt-bead electrode. The peak current ratio, $i_{p,c}/i_{p,a}$, is 1, $\Delta E_p = 70$ mV, and the peak potential, $E_{p,a}$, does not vary within the scan rate range available (0.04–0.21 V s^{-1}).

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[42] The ESR spectra of these complexes also exhibit coupling of the extra electron to ^{31}P nuclei.[43]

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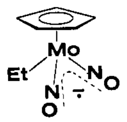
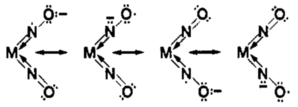
the average values of the Mo–N (1.801 Å) and N–O (1.232 Å) bonds are also in reasonable agreement with previously determined structures,[44,46–48] the average lengths of both bonds being closer to the larger observed values. The values for the N–Mo–N bond angles are 102.0 (7) and 99.1 (9)° which are similar to that found in the related, 19-electron $CpW(NO)_2[P(OPh)_3]$ radical (102.7°).[43] They are, however, larger than those determined for the related 18-electron $CpM(NO)_2Cl$ complexes which exhibit N–M–N angles of 93.9° and 92.0° for M = Cr and W, respectively.[45,49] Hence, despite the disorder in the anion and the fact that the partially occupied N and O sites are the most imprecisely refined atoms (see Experimental Section), the intramolecular dimensions of the O–N–Mo–N–O groups in the anion are consistent with the extra electron density residing in the largely NO-based π^* molecular orbital. Such an orbital is the LUMO of $CpCr(NO)_2Cl$,[50] and its population by electrons is expected to both widen the N–M–N angle and to lengthen the N–O bonds, concepts previously invoked by Angelici and co-workers to rationalize the molecular structure of $CpW(NO)_2[P(OPh)_3]$.[43] In a similar manner, careful analyses of the ESR spectra of the $[cis\text{-}(R_2NCS_2)_2M(NO)_2]^{\bullet-}$ radical anions (M = Mo or W; R = alkyl) have led to the conclusion that their unpaired electrons are housed in dinitrosyl-based molecular orbitals that have virtually no metal character.[18]

The solid-state molecular structure of the cobalticinium cation as it occurs in $[Cp_2Co][CpMo(NO)_2Et]$ (Figure 2) merits some comment. While disorder or other problems have so far prevented precise structural studies of $[Cp_2Co]^+$ salts per se,[51–53] the structures of several related derivatives have been accurately determined.[54–56] The molecular dimensions of the cobalticinium cation in $[Cp_2Co][CpMo(NO)_2Et]$ are, gratifyingly, in good agreement with the latter studies. The significant shortening of the Co–C distance (average 2.013 (7) Å) as compared to the value found in cobaltocene (2.096 (8) Å)[57] is a manifestation of the removal of an electron from the e_{1g} antibonding molecular orbital of Cp_2Co.[55,58] The most notable difference between the structure of the cation determined in this study and those established accurately by others[54–56] is that in $[Cp_2Co][CpMo(NO)_2Et]$ the two cyclopentadienyl rings of the cation are almost perfectly eclipsed, the torsion angle $C(21 + n)$–centroid(1)–centroid(2)–$C(31 + n)$ $(0 < n < 5)$[59] ranging between −0.8° and +0.4°. In the other structures, a staggered conformation for the cobalt-containing entities was observed.

In summary, the spectroscopic and crystallographic data all indicate that the prototypal anion $[CpMo(NO)_2Et]^{\bullet-}$ is stabilized by strong Mo→NO π-back-bonding. Hence, the anion may be viewed in a simplified form as



the $Mo(NO)_2$ bonding being representable in valence-bond terms by the four resonance forms shown below (M = CpMoEt).



The most interesting feature of this representation is that, in the extreme, the central Mo atom can be considered to maintain its favored 18-valence-electron configuration as the extra electron is delocalized onto the two nitrosyl ligands, a view completely in accord with the ESR spectrum and the molecular orbital rationale of the bonding in the anion (vide supra). Such a view also suggests that the sites of reactivity of the $[CpMo(NO)_2Et]^{\bullet-}$ anion with nonoxidizing electrophiles or radicals may well be its nitrosyl ligands. This hypothesis remains to be tested experimentally.

A variety of other organometallic dinitrosyl complexes of Cr, Mo, and W also undergo facile reversible reductions. The results of cyclic voltammetric studies of these compounds and their reactions with reducing agents are presented in the following paper.

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Registry No. $[Cp_2Co][CpMo(NO)_2Et]$, 111409-66-6; Cp_2Co, 1277-43-6; $CpMo(NO)_2Et$, 57034-47-6.

Supplementary Material Available: Tables of calculated hydrogen atom positions, anisotropic thermal parameters, mean plane calculations, and torsion angles for $[Cp_2Co][CpMo(NO)_2Et]$ (4 pages); a listing of observed and calculated structure factors for $[Cp_2Co][CpMo(NO)_2Et]$ (17 pages). Ordering information is given on any current masthead page.

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[45] The solid-state molecular structure of the neutral $CpMo(NO)_2Et$ precursor, a liquid at room temperature, has not been determined.

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