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Syntheses and Properties of Anionic and Neutral Radical Complexes Containing $CpM(NO)_2$ Groups (M = Cr, Mo, or W)[1,2]

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The reduction behavior of a series of organometallic complexes containing $CpM(NO)_2$ groups (Cp = η^5-C_5H_5; M = Cr, Mo, or W) has been investigated by both cyclic voltammetry and chemical means. In general, neutral 18-electron $CpM(NO)_2Y$ compounds (Y = Me, Et, H, D, or Cl) undergo a single, essentially reversible, one-electron reduction in CH_2Cl_2/0.1 M $[n\text{-}Bu_4N]PF_6$. $E_{1/2}$ values range from −0.62 to −1.01 V vs SCE, varying linearly with the ν_{NO}'s of the $CpM(NO)_2Y$ reactant, and the ease of reduction increases with M as Cr < Mo $\simeq$ W. The exception is $CpCr(NO)_2Me$ which is the most difficult to reduce and exhibits two reduction waves in its cyclic voltammogram with peak potentials being dependent on scan rates. The electrochemically observed reductions can be effected on a preparative scale by employing Cp_2Co as the chemical reductant, and the $[Cp_2Co][CpM(NO)_2Y]$ (M $\neq$ Cr, Y $\neq$ Me) products are isolable in good yields as air- and temperature-sensitive solids. The stability of these products decreases in the order Y = Me $\simeq$ Et > H $\simeq$ D > Cl. IR and ESR spectra of the 19-electron $[CpM(NO)_2Y]^{\bullet-}$ radical anions are consistent with the anions possessing "three-legged piano-stool" molecular structures with linear, terminal nitrosyl ligands. Furthermore, they indicate considerable delocalization of the unpaired electron onto these nitrosyl ligands via M→NO back-bonding. The radical anions are cleanly reconverted to their neutral precursors by treatment with chemical oxidants such as $AgBF_4$ or $[Cp_2Fe]BF_4$. In a complementary manner, the 18-electron cations of $[CpM(NO)_2L]^+BF_4^-$ salts (M = Mo or W; L = PPh_3 or $P(OMe)_3$) undergo facile, one-electron reversible reductions in CH_2Cl_2, $E_{1/2}$ being ~0.1 V vs SCE. Consequently, treatment of the salts with Cp_2Co in CH_2Cl_2 affords isolable $[CpM(NO)_2L]^\bullet$ 19-electron, neutral radicals whose spectroscopic properties again reveal that their HOMO's are largely NO-based π^* molecular orbitals. This delocalization of electron density evidently stabilizes all the $CpM(NO)_2$-containing reduced species with respect to undergoing bond ruptures upon electron addition.

Introduction

In the preceding paper,[1] we describe the synthesis and characterization of the radical anion $[CpMo(NO)_2Et]^{\bullet-}$ as its cobalticinium salt. We also demonstrate that the presence of the nitrosyl ligands stabilizes the 19-electron anion by delocalizing the extra electron density via Mo→NO π-back-bonding. In this paper, we wish to report the results of an extension of this study to encompass the reduction behavior of a wide variety of organometallic complexes containing $CpM(NO)_2$ groups (Cp = η^5-C_5H_5; M = Cr, Mo, or W).

At the outset of this work, it was our hope that these investigations would provide some insight as to why some of these dinitrosyl complexes exhibit diverse reactivity patterns toward nucleophiles. Thus, for instance, while many organometallic carbonyl halide complexes can be converted to alkyl or aryl derivatives by using Grignard reagents,[3] similar reactions with $CpM(NO)_2X$ (M = Mo, W; X = halide) lead only to decomposition of the nitrosyl compounds into intractable materials.[4] Only for $CpCr(NO)_2X$ (X = halide) does this reaction yield the corresponding alkyl or aryl compounds.[3] The $CpM(NO)_2R$ (M = Mo, W; R = alkyl or aryl) compounds can be prepared from $CpM(NO)_2Cl$ (M = Mo, W) and $CpM(NO)_2BF_4$ precursors only by using relatively mild alkylating agents such as organoaluminum,[4] organotin,[5] or organoboron[5] compounds, as appropriate. Furthermore, the $CpM(NO)_2Cl$ (M = Mo, W) compounds decompose upon treatment with reducing metals such as Na or Zn[4] while $CpCr(NO)_2Cl$ can be converted cleanly to the dimer $[CpCr(NO)_2]_2$ under similar conditions.[4,6] The analogous dimers $[CpM(NO)_2]_2$ (M = Mo, W) have yet to be isolated even though they have been the object of much synthetic effort.[7] as a final example, reactions of the cationic complexes $[CpM(NO)_2L]PF_6$ [M = Mo, W; L = PPh_3, $P(OPh)_3$, or $P(OMe)_3$] with alkoxides have been recently reported.[8] The anticipated outcome of these reactions was the synthesis of alkyl nitrite complexes, i.e.

$$[CpM(NO)_2L]^+ + RO^- \rightarrow CpM(NO)(L)(N(O)OR) \quad (1)$$

Instead, the radicals $[CpM(NO)_2L]^\bullet$ are formed. This initially surprising transformation is now believed to be due to a very facile, reversible reduction of the cationic starting materials, a feature which was first revealed by cyclic voltammetry.[8]

In general, most carbonyl-containing halide, hydride, alkyl, and aryl complexes that have been investigated electrochemically undergo irreversible reduction upon the addition of electrons with concomitant scission of the metal–halide, –hydride, –alkyl, or –aryl bonds.[9] We find that such behavior is much less prevalent for the $CpM(NO)_2$-containing analogues. Indeed, our studies of the reduction properties of these complexes clearly demonstrate the profound role that the nitrosyl ligands play in establishing the physical and chemical properties of these compounds and their derivatives.

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.[10] The

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[1] Organometallic Nitrosyl Chemistry. 36. For part 35, see: Legzdins, P.; Wassink, B.; Einstein, F. W. B.; Jones, R. H. *Organometallics*, preceding paper in this issue.

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methodology employed during the cyclic voltammetry studies has also been outlined elsewhere.[1,11] The ESR spectra were obtained with either a Varian E3 spectrometer or a spectrometer and interfaced computer system operated by Dr. F. G. Herring.[12]

Preparation of CpMo(NO)$_2$Me.[4] A stirred solution of CpMo(NO)$_2$Cl[13] (5.20 g, 20.3 mmol) in CH_2Cl_2 (40 mL) was cooled to ~-65 °C with a dry ice/acetone bath and then treated with a 2 M solution of Me_3Al in toluene (11 mL, 22 mmol). The cold bath was then removed, and the green solution was allowed to warm to room temperature. Filtration of the mixture through an alumina (Woelm neutral, activity 1) column (3 × 7 cm) supported on a medium-porosity frit, followed by washing the column with a sufficient quantity of CH_2Cl_2 to remove all traces of green material, yielded a deep green solution. This was taken to dryness in vacuo, and the residue was sublimed (5×10^{-3} mm) at 40–60 °C onto a water-cooled probe to produce 2.21 g (46% yield) of CpMo(NO)$_2$Me as a green solid: IR (hexanes) ν_{NO} 1739 (s), 1650 (s) cm^{-1}.

Anal. Calcd for $C_6H_8N_2O_2Mo$: C, 30.53; H, 3.43; N, 11.87. Found: C, 30.82; H, 3.45; N, 11.77.

Preparation of CpW(NO)$_2$Me.[4] A solution of CpW(NO)$_2BF_4$ in CH_2Cl_2 (160 mL) was generated by the reaction of CpW(NO)$_2$Cl (5.00 g, 14.5 mmol) and $AgBF_4$ (2.82 g, 14.5 mmol).[5] A brilliant green solution formed with concomitant precipitation of AgCl. The mixture was cooled with a dry ice/acetone bath for ~10 min, and a roughly stoichiometric amount of a 2 M Me_3Al solution in toluene (8 mL, 16 mmol) was added by syringe. An instantaneous reaction occurred as evidenced by the formation of a large quantity of a very fine, brown precipitate. The supernatant solution remained green. The mixture was transferred by cannulation into tubes equipped with septa and centrifuged for several minutes until the brown solid had settled. The green solution was then cannulated onto a column (3 × 7 cm) of alumina (Woelm neutral, activity 1) supported on a medium-porosity frit and filtered into a flask. The column was washed with CH_2Cl_2 until the washings were colorless. (Direct filtration of the reaction mixture through alumina invariably rendered the column virtually impervious.) The solvent was removed in vacuo, and the solid residue was then sublimed (5×10^{-3} mm) onto a water-cooled probe at 40–60 °C to give 1.95 g (40% yield) of CpW(NO)$_2$Me as a bright green solid: IR (hexanes) ν_{NO} 1718 (s), 1638 (s) cm^{-1}; low-resolution mass spectrum (probe temperature 50 °C), *m/z* 324 (P$^+$, most intense parent ion).

Anal. Calcd for $C_6H_8N_2O_2W$: C, 22.24; H, 2.49; N, 8.65. Found: C, 22.25; H, 2.48; N, 8.55.

Preparation of [Cp$_2$Co][CpW(NO)$_2$Me]. A medium-porosity frit was charged with solid Cp$_2$Co[14] (0.465 g, 2.46 mmol), topped with a septum and attached to a three-necked flask. To this flask was added CpW(NO)$_2$Me (0.800 g, 2.47 mmol). Diethyl ether (~20 mL) was added to the flask by cannulation, and, likewise, ~50 mL of Et_2O was added to the frit. The cobaltocene solution was filtered into the rapidly stirred CpW(NO)$_2$Me solution. Immediately the reaction mixture became green-brown, and a dark, microcrystalline solid precipitated that was collected by filtration and washed with several portions of Et_2O (~100 mL in total) until the washings were colorless. The solid was dried in vacuo (5×10^{-3} mm) at room temperature for a few hours. This procedure gave 0.814 g (65% yield) of [Cp$_2$Co][CpW(NO)$_2$Me] as a purple-black, microcrystalline solid which was both air and thermally sensitive: IR (Nujol mull) ν_{NO} 1511 (s), 1427 (s) cm^{-1}, also 3100 (m), 3087 (m), 3069 (sh), 1414 (sh), 1361 (m), 1172 (w), 1112 (w), 1061 (w), 1013 (m), 946 (w), 906 (w), 865 (m), 847 (w), 816 (m), 803 (m) cm^{-1}.

Anal. Calcd for $C_{16}H_{18}N_2O_2CoW$: C, 37.45; H, 3.54; N, 5.46. Found: C, 37.15; H, 3.46; N, 5.25.

The ESR spectra of this and the following compounds displayed basic five-line patterns having the approximate intensity ratios 1:2:3:2:1. (These are discussed in the Results and Discussion.)

Preparation of [Cp$_2$Co][CpMo(NO)$_2$Me]. This reaction was carried out by using CpMo(NO)$_2$Me (0.450 g, 1.91 mmol) and Cp$_2$Co (0.360 g, 1.90 mmol) in a manner identical with that described above for the tungsten-containing analogue. Dark microcrystals precipitated from a green-brown reaction mixture and were collected by filtration, washed with Et_2O (~200 mL) until the washings were colorless, and dried in vacuo (5×10^{-3} mm). This produced 0.510 g (63% yield) of [Cp$_2$Co][CpMo(NO)$_2$Me] as a green-black, microcrystalline solid which exhibited thermal and air sensitivity: IR (Nujol mull) ν_{NO} 1526 (s), 1445 (s, br) [1443 (s, br) with Nujol spectrum subtracted] cm^{-1}, also 3101 (m), 3094 (sh), 1415 (m), 1363 (m), 1141 (w), 1112 (w), 1059 (w), 1011 (m), 945 (w), 904 (w), 866 (m), 847 (w), 807 (m), 794 (m) cm^{-1}.

Anal. Calcd for $C_{16}H_{18}N_2O_2CoMo$: C, 45.20; H, 4.27; N, 6.59. Found: C, 45.22; H, 4.33; N, 6.71.

Attempted Reaction of CpCr(NO)$_2$Me with Cp$_2$Co. The same procedure as that used to prepare [Cp$_2$Co][CpW(NO)$_2$Me] was employed in this experiment, using CpCr(NO)$_2$Me[4] (0.192 g, 1.00 mmol) and Cp$_2$Co (0.189 g, 1.00 mmol). A brown-green solution formed upon mixing Et_2O solutions (~40 mL total) of these two reagents, but no solid precipitated. An IR spectrum of the solution displayed nitrosyl absorptions only for CpCr(NO)$_2$Me (1777, 1669 cm^{-1}). The mixture was stirred overnight with no further change.

Reaction of CpCr(NO)$_2$Me with CpFe(η^6-C$_6$Me$_6$). In the same way as described above, an Et_2O (~50 mL) solution of CpFe(η^6-C$_6$Me$_6$)[15] (0.280 g, 0.989 mmol) was filtered into a rapidly stirred solution of CpCr(NO)$_2$Me (0.190 g, 0.990 mmol) in Et_2O (~20 mL). An instantaneous reaction occurred as a gray, flocculent precipitate formed, leaving a light green solution. The solid was collected by filtration, washed in several portions with Et_2O (~150 mL), and dried in vacuo (5×10^{-3} mm) for a few hours to yield 0.27 g of a gray powder, which was extremely pyrophoric in air: IR (Nujol mull) ν_{NO} 1555 (vs), 1509 (s) cm^{-1}, also 3084 (m), 3074 (sh), 1416 (m), 1162 (w), 1121 (w), 1110 (w), 1072 (m), 1010 (m), 969 (m), 857 (m), 785 (m) cm^{-1}.

Elemental analyses of this powder, prepared on two separate occasions, showed it to be quite variable in nitrogen content: C, 56.74; H, 6.73; N, 3.42 and C, 56.57; H, 6.44; N, 4.70.

Preparation of [Cp$_2$Co][CpW(NO)$_2$H]. A solution of Cp$_2$Co (0.095 g, 0.503 mmol) in hexanes (~40 mL) was filtered into a stirred solution of CpW(NO)$_2$H[5,16] (0.155 g, 0.500 mmol), also in hexanes (~30 mL). A fine, dark brown solid precipitated from solution immediately. This was collected by filtration, washed with hexanes (~100 mL) until the washings were only faintly colored, and dried in vacuo (5×10^{-3} mm) to give 0.163 g (65% yield) of [Cp$_2$Co][CpW(NO)$_2$H] as a dark brown, thermally sensitive powder: IR (Nujol mull) ν_{NO} 1521 (s), 1445 (s, br) [1438 (s) with Nujol spectrum subtracted] cm^{-1}, also 3073 (m, br), 1848 (m), 1411 (m), 1354 (w), 1110 (w), 1057 (w), 1009 (m), 863 (w), 851 (m), 812 (m) cm^{-1}.

Anal. Calcd for $C_{15}H_{16}N_2O_2CoW$: C, 36.10; H, 3.23; N, 5.61. Found: C, 35.20; H, 3.17; N, 5.50.

If Et_2O was used as the solvent instead of hexanes, the reaction appeared to proceed similarly, a dark brown, microcrystalline solid precipitating from solution as before. When this solid was washed with Et_2O though, the washings retained a more intense coloration than when hexanes were used, and the C, H, and N analyses of the product revealed a much lower nitrogen content.

Preparation of [Cp$_2$Co][CpW(NO)$_2$D]. This compound was prepared in the same manner as the hydrido analogue from CpW(NO)$_2$D[16] (0.150 g, 0.482 mmol) and Cp$_2$Co (0.091 g, 0.481 mmol), and was isolated as a slightly impure, dark brown powder (0.165 g, ~69% yield): IR (Nujol mull) ν_{NO} 1513 (s), 1447 (s, br) [1439 (s) with Nujol spectrum subtracted] cm^{-1}, also 3086 (m), 3075 (m), 1525 (m), 1411 (m), 1337 (w), 1316 (w), 1112 (w), 1060 (w), 1008 (m), 862 (m), 811 (m) cm^{-1}.

Anal. Calcd for $C_{15}H_{15}DN_2O_2CoW$: C, 36.03; H, 3.43; N, 5.60. Found: C, 35.29; H, 3.18; N, 5.09.

Preparation of [Cp$_2$Co][CpW(NO)$_2$Cl]. A solution of CpW(NO)$_2$Cl[13] (0.344 g, 0.999 mmol) in Et_2O (~40 mL) was

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treated with a filtered solution of Cp_2Co (0.189 g, 1.00 mmol) in Et_2O (~50 mL). Instantly a gray, flocculent precipitate formed that was collected by filtration, washed with Et_2O (3 × 20 mL), and dried in vacuo for ~2 h. This produced 0.471 g (88% yield) of $[Cp_2Co][CpW(NO)_2Cl]$ as a gray, highly pyrophoric and quite thermally sensitive powder: IR (Nujol mull) ν_{NO} 1708 (w), 1585 (sh), 1534 (s), 1456 (s) cm^{-1}, also 3090 (m, br), 1413 (s), 1112 (w), 1059 (w), 1009 (m), 863 (m), 814 (m) cm^{-1}.

Anal. Calcd for $C_{15}H_{15}N_2O_2ClCoW$: C, 33.77; H, 2.83; N, 5.25. Found: C, 33.45; H, 2.80; N, 4.97.

Preparation of $[Cp_2Co][CpMo(NO)_2Cl]$. The same procedure as described above to prepare the tungsten analogue was employed in this reaction starting from Cp_2Co (0.189 g, 1.00 mmol) and $CpMo(NO)_2Cl$[13] (0.256 g, 0.998 mmol). This generated 0.347 g (78% yield) of gray-green, pyrophoric, and thermally sensitive $[Cp_2Co][CpMo(NO)_2Cl]$: IR (Nujol mull) ν_{NO} 1558 (s, br), 1485 (s, br) [1490 (s, br) with Nujol spectrum subtracted] cm^{-1}, also 3092 (m, br), 1413 (m), 1355 (sh), 1112 (w), 1059 (m), 1012 (m), 863 (m), 807 (m) cm^{-1}.

Anal. Calcd for $C_{15}H_{15}N_2O_2ClCoMo$: C, 40.43; H, 3.39; N, 6.29. Found: C, 40.61; H, 3.50; N, 6.08.

Preparation of $CpW(NO)_2P(OMe)_3$. A solution of $[CpW(NO)_2P(OMe)_3]BF_4$ (0.541 g, 1.04 mmol) [this compound was prepared from $CpW(NO)_2BF_4$ and $P(OMe)_3$][5] in CH_2Cl_2 (~10 mL) was treated with solid Cp_2Co (0.197 g, 1.04 mmol) and stirred. The solution instantly became an intense red-purple color. An IR spectrum of this solution displayed nitrosyl absorptions at 1608 (s) and 1542 (s) cm^{-1}. Addition of Et_2O (~80 mL) to the reaction mixture resulted in the precipitation of a pale yellow solid. The mixture was filtered through a medium-porosity frit, and the filtrate was taken to dryness under reduced pressure. The solid, purple residue was dissolved in CH_2Cl_2 (~5 mL), and Et_2O (~100 mL) was added. The mixture was cooled to -78 °C with a dry ice/acetone bath whereupon a purple, microcrystalline solid precipitated over the course of 1.5 h. The supernatant solution was removed by cannulation, the solid was washed with hexanes (~10 mL), and the washings were similarly removed. The solid was dried in vacuo (5×10^{-3} mm) for a few hours at 20 °C to obtain 0.211 g (47% yield) of $CpW(NO)_2P(OMe)_3$ as a purple, microcrystalline solid: IR (CH_2Cl_2) ν_{NO} 1608 (s), 1542 (s) cm^{-1}; IR (Nujol mull) ν_{NO} 1593 (s), 1533 (s) cm^{-1}, also 3105 (m), 1353 (w), 1177 (m), 1049 (m), 1021 (s), 931 (w), 844 (m), 808 (m), 794 (m), 759 (m) cm^{-1}.

Anal. Calcd for $C_8H_{14}N_2O_5PW$: C, 22.19; H, 3.26; N, 6.47. Found: C, 21.89; H, 3.28; N, 6.32.

Preparation of $CpW(NO)_2PPh_3$. A mixture of Cp_2Co (0.178 g, 0.942 mmol) and $[CpW(NO)_2PPh_3]BF_4$[5] (0.620 g, 0.942 mmol) was stirred in CH_2Cl_2 (~25 mL) for ~10 min. An intense red-purple coloration developed rapidly in the solution. Hexanes (~10 mL) were carefully added until a pale yellow solid had precipitated, accompanied by a small amount of purple solid. The mixture was filtered through a medium porosity frit and the filtrate was taken to dryness in vacuo to give 0.290 g (54% yield) of $CpW(NO)_2PPh_3$ as a purple powder: IR (CH_2Cl_2) ν_{NO} 1598 (s), 1532 (s) cm^{-1}; IR (Nujol mull) ν_{NO} 1594 (s), 1527 (s) cm^{-1}, also 1583 (m), 1570 (w), 1479 (w), 1436 (m), 1185 (w), 1158 (w), 1095 (m), 1071 (w), 1028 (w), 1014 (w), 851 (w), 815 (m), 749 (m), 742 (w), 706 (w), 695 (m) cm^{-1}.

Anal. Calcd for $C_{23}H_{20}N_2O_2PW$: C, 48.35; H, 3.50; N, 4.90. Found: C, 48.64; H, 3.69; N, 5.00.

Reaction of $[Cp_2Co][CpMo(NO)_2Me]$ with $[Cp_2Fe]BF_4$. A mixture of $[Cp_2Co][CpMo(NO)_2Me]$ (0.190 g, 0.447 mmol) and $[Cp_2Fe]BF_4$ (0.120 g, 0.440 mmol) was stirred in CH_2Cl_2 (~25 mL) at -78 °C for ~5 min. The mixture was then allowed to warm to room temperature with stirring to produce a green solution, an IR spectrum of which exhibited nitrosyl absorptions at 1730 (s) and 1636 (s) cm^{-1}. The volume of the solution was reduced to ~10 mL in vacuo whereupon a yellow solid precipitated. Addition of Et_2O (~20 mL) precipitated more of the yellow powder which was collected by filtration to obtain 0.09 g (73% yield) of $[Cp_2Co]BF_4$ which was identified by comparison of its IR (Nujol mull) and ^1H NMR ($(CD_3)_2CO$) spectra with those of an authentic sample.

The filtrate from which $[Cp_2Co]BF_4$ had been collected was taken to dryness in vacuo. The solid residue was dissolved in Et_2O (~3 mL), and the resulting green solution was transferred by syringe onto an alumina column (Woelm neutral, activity 1) (2 × 10 cm) made up in Et_2O. A yellow band developed that was eluted from the column with Et_2O. The solvent was removed in vacuo from the eluate to obtain 0.03 g (36% yield) of Cp_2Fe which was identified by comparison of its ^1H NMR ($CDCl_3$) spectrum with that of an authentic sample and its characteristic low-resolution mass spectrum (probe temperature 120 °C), *m/z* 186 (P^+, most intense parent ion).

Finally, a green band was eluted from the column with Et_2O. The solvent was removed in vacuo, and the solid residue was sublimed (5×10^{-3} mm) at 40–60 °C onto a water-cooled probe to afford 0.05 g (47% yield) of $CpMo(NO)_2Me$: IR (hexanes) ν_{NO} 1739 (s), 1651 (s) cm^{-1}; low-resolution mass spectrum (probe temperature 120 °C), *m/z* 236 (P^+, most intenst parent ion).

Reaction of $[Cp_2Co][CpW(NO)_2Me]$ with $AgBF_4$. A mixture of $AgBF_4$ (0.048 g, 0.25 mmol) and purple-black $[Cp_2Co][CpW(NO)_2Me]$ (0.128 g, 0.250 mmol) was stirred in CH_3CN (~10 mL) at -25 °C for ~5 min. A black precipitate formed, and the mixture was warmed to room temperature. An IR spectrum of the green supernatant solution exhibited nitrosyl absorptions at 1706 (s) and 1620 (s) cm^{-1}. No other NO bands were apparent. The solvent was removed in vacuo, and 0.04 g (49% yield) of $CpW(NO)_2Me$ was sublimed (5×10^{-3} mm) from the residue at 40–60 °C: IR (hexanes) ν_{NO} 1720 (s), 1639 (s) cm^{-1}; low-resolution mass spectrum (probe temperature 120 °C), *m/z* 324 (P^+, most intense parent ion).

The solid residue was extracted with CH_2Cl_2, and the extracts were removed from the remaining solid material by filtration. The solvent was removed from the filtrate in vacuo, and the resulting yellow solid was identified as $[Cp_2Co]BF_4$ by its characteristic Nujol mull IR spectrum in comparison with that of an authentic sample.

Reaction of $[Cp_2Co][CpW(NO)_2H]$ with $AgBF_4$. This reaction was effected in the same manner as the reaction for the methyl analogue described above, with $AgBF_4$ (0.020 g, 0.10 mmol) and $[Cp_2Co][CpW(NO)_2H]$ (0.050 g, 0.10 mmol) in CH_2Cl_2 (~10 mL) initially at -78 °C. The mixture was allowed to warm to room temperature. An IR spectrum of the supernatant solution displayed ν_{NO} bands only at 1721 (s) and 1635 (s) cm^{-1}. The solvent was removed in vacuo, and $CpW(NO)_2H$ (yield inestimable due to small reaction scale) was sublimed (5×10^{-3} mm) from the residue at 40–60 °C onto a water-cooled probe, low-resolution mass spectrum (probe temperature 120 °C), *m/z* 310 (P^+, most intense parent ion).

Reaction of $[Cp_2Co][CpMo(NO)_2Cl]$ with $AgBF_4$. In a manner similar to the two previously described oxidations, $AgBF_4$ (0.146 g, 0.749 mmol) and $[Cp_2Co][CpMo(NO)_2Cl]$ (0.334 g, 0.748 mmol) were stirred together in CH_3CN (~10 mL) at -25 °C for ~5 min, and then the mixture was warmed to room temperature. Once again, only two NO absorptions at 1757 (s) and 1668 (s) cm^{-1} were evident in the IR spectrum of the supernatant solution. The green solution was taken to dryness in vacuo, and the solid residue was treated with CH_2Cl_2 (~20 mL). This solution was filtered through a Florisil column (1 × 3 cm) made up in CH_2Cl_2. The column was washed with CH_2Cl_2 until the washings were only faintly colored. The combined filtrates were taken to dryness in vacuo, and the residue was redissolved in CH_2Cl_2 (~5 mL). Hexanes (~5 mL) were added to induce precipitation of $[Cp_2Co]BF_4$ which was collected by filtration and identified by its characteristic IR spectrum. The filtrate was concentrated in vacuo whereupon a green, microcrystalline solid precipitated which was collected onto a sintered glass filter to obtain 0.09 g (47% yield) of $CpMo(NO)_2Cl$: IR (CH_2Cl_2) ν_{NO} 1760 (s), 1669 (s) cm^{-1}; low-resolution mass spectrum (probe temperature 120 °C), *m/z* 258 (P^+, most intense parent ion).

Reaction of $CpW(NO)_2P(OMe)_3$ with $AgBF_4$. A solution of $CpW(NO)_2P(OMe)_3$ (0.108 g, 0.249 mmol) in CH_2Cl_2 (~10 mL) was treated with solid $AgBF_4$ (0.049 g, 0.25 mmol). The initially red-purple solution rapidly became bright green, and a dark precipitate formed. The mixture was filtered through a medium-porosity frit, and the filtrate was concentrated to ~5 mL under reduced pressure. This solution was treated with Et_2O (~20 mL) which resulted in the precipitation of a green solid. The solid was collected by filtration, washed with Et_2O (2 × ~10 mL), and dried in vacuo (5×10^{-3} mm) for a few hours at 20 °C to obtain bright green $[CpW(NO)_2P(OMe)_3]BF_4$: IR (Nujol mull) ν_{NO} 1767

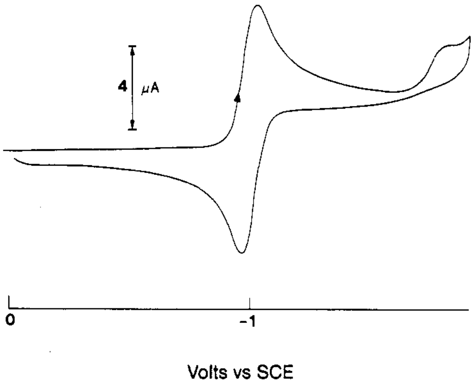

Figure 1. Ambient temperature cyclic voltammogram of 5×10^{-4} M $CpCr(NO)_2Me$ in CH_2Cl_2 containing 0.1 M $[n\text{-}Bu_4N]PF_6$ measured at a platinum-bead electrode at a scan rate of 0.12 V s^{-1}.

(s), 1689 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.40 (d, 5 H, $^3J_{^{31}P-^1H} = 0.9$ Hz, C_5H_5), 3.88 (d, 9 H, $^3J_{^{31}P-^1H} = 12.0$ Hz, $P(OCH_3)_3$).

Results and Discussion

Cyclic Voltammetry Studies. (a) $CpCr(NO)_2Me$. A cyclic voltammogram of $CpCr(NO)_2Me$ in CH_2Cl_2 is shown in Figure 1. (Data for the reductions of all the compounds investigated are summarized in Table I.) Under the specified conditions,[17] this compound exhibits a largely reversible one-electron reduction at $E_{1/2} = -1.01$ V vs SCE. The peak potentials do separate somewhat with increasing scan rate, being 70 mV at 0.06 V s^{-1} and 90 mV at 0.28 V s^{-1}. In addition $i_{p,a}/i_{p,c}$[19] increases with a rise in scan rate from 0.87 at 0.06 V s^{-1} to 0.99 at 0.28 V s^{-1}. As shown in Figure 1, if the scan is extended to the solvent limit, a second, low-current wave is evident at $E_{p,c} = -1.87$ V (0.12 V s^{-1}). This latter feature may result from a product derived from the initially formed radical anion, i.e.

$$CpCr(NO)_2Me \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [CpCr(NO)_2Me]^{\bullet -} \rightarrow \text{other products} \quad (2)$$

It seems unlikely that the second wave is due to reduction of the radical anion since its peak current is so low.

Of the compounds investigated in this study, $CpCr(NO)_2Me$ is the most difficult to reduce. It also contrasts sharply with $CpCr(NO)_2Cl$ in that the reduction of the latter is chemically irreversible at the maximum accessible scan rate.[11] The methyl compound is also the only neutral $CpM(NO)_2$-containing complex to complex to exhibit a second reduction peak and the only alkyl compound investigated with scan-rate-dependent peak potentials. For comparison, many carbonyl-containing alkyl compounds [e.g. $CpM(CO)_3R$ (M = Cr, Mo, W; R = Me, Et), $CpFe(CO)_2Me$] do not exhibit cathodic waves in CH_2Cl_2 under these conditions. In CH_3CN or DMF, however, $CpFe(CO)_{2-x}(PPh_3)_xR$ ($x = 0$,[20a] 1;[20b] R = Me, Ph, and other alkyl or aryl groups) each exhibit a two-electron, irreversible reduction, e.g.

$$CpFe(CO)_2Me + 2e^- \rightarrow [CpFe(CO)_2]^- + Me^- \quad (3)$$

or, as in the case of some of the phosphine-substituted compounds, two one-electron, irreversible reductions. In any event, reduction of these carbonyl compounds results in scission of the Fe–R bonds.

Table I. Data for the Reductions of Several Dinitrosyl Complexes

compd[a]	$E_{1/2}$[b]	ΔE_p[c]	$i_{p,a}/i_{p,c}$	comments
$[CpCr(NO)_2(CH_3CN)]PF_6$				$E_{p,a}{}^b = -0.27$ (0.10 V s^{-1})
$CpCr(NO)_2Cl$				$E_{p,a} = -0.68$ (0.07 V s^{-1})
$CpCr(NO)_2Me$	-1.01	70	0.87	at 0.06 V s^{-1}
	-1.01	90	0.99	at 0.28 V s^{-1}
				second weak wave at $E_{p,c} = -1.87$ (0.12 V s^{-1})
$CpCr(NO)_2Me$	-0.99[d]	60	0.99	at 0.21 V s^{-1}
$[CpMo(NO)_2PPh_3]BF_4$	-0.12	65	0.81	at 0.02 V s^{-1}
		65	0.96	at 0.09 V s^{-1}
				also $E_{1/2} = -1.65$ with $\Delta E_p = 420$ mV and $E_{p,a} = -0.58$ (0.21 V s^{-1})
$CpMo(NO)_2Cl$	-0.59	75	0.92	at 0.03 V s^{-1}
		75	0.97	at 0.23 V s^{-1}
$CpMo(NO)_2Me$	-0.83	65	0.96	at 0.04 V s^{-1}
		65	0.97	at 0.22 V s^{-1}
$CpMo(NO)_2Et$	-0.86	65	1.00	at ≥0.05 V s^{-1}
$[CpW(NO)_2PPh_3]BF_4$	-0.14	65	0.90	at 0.02 V s^{-1}
		65	0.95	at 0.11 V s^{-1}
				also $E_{1/2} = -1.53$ with $\Delta E_p = 190$ mV and $E_{p,a} = -0.61$ (0.16 V s^{-1})
$[CpW(NO)_2P(OMe)_3]BF_4$	-0.10	60	0.85	at 0.01 V s^{-1}
		60	0.99	at 0.21 V s^{-1}
				also $E_{1/2} = -1.49$ with $\Delta E_p = 200$ mV and $E_{p,a} = -0.61$ (0.17 V s^{-1})
$CpW(NO)_2Cl$	-0.62	60	0.85	at 0.02 V s^{-1}
		60	0.95	at 0.16 V s^{-1}
$CpW(NO)_2H$	-0.79	60	0.85	at 0.02 V s^{-1}
		90	0.95	at 0.18 V s^{-1}
$CpW(NO)_2Me$	-0.83	60	0.96	at 0.05 V s^{-1}
		60	0.98	at 0.18 V s^{-1}
$CpW(NO)_2Me$	-0.85[d]	60	0.83	at 0.02 V s^{-1}
		60	0.97	at 0.22 V s^{-1}
$CpW(NO)_2Et$	-0.86	65	0.95	at 0.04 V s^{-1}
		65	0.96	at 0.18 V s^{-1}

[a] In CH_2Cl_2/0.1 M $[n\text{-}Bu_4N]PF_6$ unless otherwise noted. [b] V vs. SCE. [c] mV. [d] In CH_3CN/0.1 M $[n\text{-}Bu_4N]PF_6$.

(b) $CpM(NO)_2R$ (M = Mo, W; R = Me, Et). These four compounds are very similar in their reduction behavior. The two methyl compounds reduce reversibly at $E_{1/2} = -0.83$ V, and, not surprisingly, the two ethyl compounds undergo reduction at a slightly more negative potential of $E_{1/2} = -0.86$ V. In all four cases, the peak potentials are independent of scan rate up to ~0.2 V s^{-1}, the maximum scan-rate region accessible. The peak separations are 60–65 mV under these conditions. The extent of chemical reversibility is substantial in these systems, the lowest $i_{p,a}/i_{p,c}$ ratio being 0.95 for $CpW(NO)_2Et$ at 0.04

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(17) Ferrocene was used as an internal standard during the cyclic voltammetry studies.[18] 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 (<1 V s^{-1}). In CH_3CN/0.1 M $[n\text{-}Bu_4N]PF_6$, $E_{1/2} = +0.37$ V vs SCE, $i_{p,c}/i_{p,a} = 1$, $E_{p,a}$ does not vary with scan rate, and $\Delta E_p = 60$ mV.

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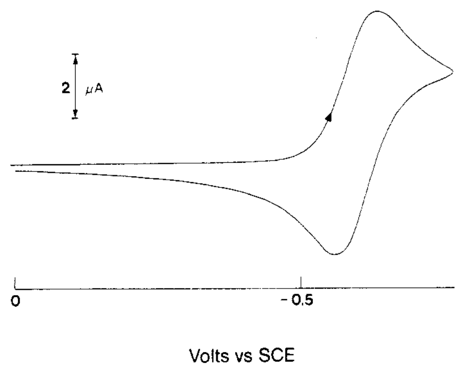

Figure 2. Cyclic voltammogram of $CpMo(NO)_2Cl$ in CH_2Cl_2 at a scan rate of 0.08 V s^{-1}.

V s^{-1}; for $CpMo(NO)_2Et$, $i_{p,a}/i_{p,c}$ is unity at even 0.05 V s^{-1}. These facts indicate considerable stability for the $[CpM(NO)_2R]^{\bullet -}$ radical anions.[1] In CH_3CN, $CpW(NO)_2Me$ exhibits only one reduction wave at $E_{1/2} = -0.85$ V with $\Delta E_p = 60$ mV even up to 0.22 V s^{-1}. The couple is quite chemically reversible, $i_{p,a}/i_{p,c}$ ranging from 0.83 at 0.02 V s^{-1} to 0.97 at 0.22 V s^{-1}. No other cathodic wave is present in CH_3CN out to -2.35 V.

The polarographic reduction of the related complex $CpW(CO)_3Me$ in CH_3CN reportedly proceeds via a single, irreversible two-electron step,[21] i.e.

$$CpW(CO)_3Me + 2e^- \rightarrow [CpW(CO)_3]^- + Me^- \quad (4)$$

as the reduction results in cleavage of the metal–alkyl bond. Such cleavage does not appear to be happening with the nitrosyl alkyl compounds. Evidently, as previously observed for $[\{CpCr(NO)_2\}_2]^{\bullet -}$,[11] the nitrosyl ligands stabilize the initially formed radical anions against bond ruptures.

(c) $CpW(NO)_2H$. This compound is slightly easier to reduce than the alkyl complexes described above. A cyclic voltammogram of $CpW(NO)_2H$ in CH_2Cl_2 displays a single, quite reversible one-electron reduction at $E_{1/2} = -0.79$ V. The peak separation increases with increasing scan rate over a range of 60 mV at 0.02 V s^{-1} to 90 mV at 0.18 V s^{-1}, similar to the reduction wave of $CpCr(NO)_2Me$. The extent of chemical reversibility increases with increased scan rate also, the $i_{p,a}/i_{p,c}$ ratio being 0.85 at 0.02 V s^{-1} and 0.95 at 0.16 V s^{-1}. No other cathodic waves are evident in CH_2Cl_2. In contrast, the polarographic reduction of $CpW(CO)_3H$ in CH_3CN also is reported to occur in a one-electron, but irreversible, step and results in cleavage of the W–H bond.[21] The scan rate dependence of ΔE_p for $CpW(NO)_2H$ reduction and the somewhat lowered chemical reversibility of this process suggest a diminished stability for $[CpW(NO)_2H]^{\bullet -}$ relative to the molybdenum- and tungsten-containing alkyl compounds (vide supra), although the anion would appear to be chemically accessible nonetheless.

(d) $CpM(NO)_2Cl$ (M = Mo, W). A cyclic voltammogram of $CpMo(NO)_2Cl$ in CH_2Cl_2 recorded under the customary conditions is shown in Figure 2. Both $CpMo(NO)_2Cl$ and $CpW(NO)_2Cl$ exhibit one-electron reduction waves ($E_{1/2} = -0.59$ and -0.62 V, respectively) with high degrees of chemical reversibility. For $CpMo(NO)_2Cl$, $i_{p,a}/i_{p,c}$ ranges from 0.92 at 0.03 V s^{-1} to 0.97 at 0.23 V s^{-1}, and for $CpW(NO)_2Cl$ this ratio is 0.85 at 0.02 V s^{-1} and 0.95 at 0.16 V s^{-1}. In both cases, ΔE_p is independent of scan rate over the ranges investigated. On these time scales, both compounds are relatively stable toward subsequent chemical reactions upon electron transfer, no other reduction processes being apparent in CH_2Cl_2, i.e.

$$CpM(NO)_2Cl + e^- \rightleftharpoons [CpM(NO)_2Cl]^{\bullet -} \quad (5)$$
$$M = Mo, W$$

The transient stability of $[CpM(NO)_2Cl]^{\bullet -}$ (M = Mo, W) in solution is particularly novel in light of the cathodic processes in which various carbonyl-containing halide complexes participate. In general, a complex L_nMX undergoes reduction with involvement of the M–X bond in one of two types of processes, i.e.

$$L_nM\text{–}X + e^- \rightarrow [L_nM]^\bullet + X^-$$

or

$$L_nM\text{–}X + 2e^- \rightarrow [L_nM]^- + X^-$$

while π and dative bonds are electrochemically inactive.[9] Thus, for example

$$CpW(CO)_3X + e^- \xrightarrow{CH_3CN} [CpW(CO)_3]^\bullet + X^- \quad (6)^{21,22}$$
$$X = Cl, Br, I$$

$$CpFe(CO)_2X + e^- \xrightarrow[\text{or THF}]{DMF} [CpFe(CO)_2]^\bullet + X^- \quad (7)^{20b,23}$$
$$X = Cl, Br, I$$

$$CpMo(CO)_2(PPh_3)I + 2e^- \xrightarrow{DMF} [CpMo(CO)_2(PPh_3)]^- + I^- \quad (8)^{20b}$$

$$M(CO)_5X + 2e^- \xrightarrow[\text{or DME}]{CH_3CN} [M(CO)_5]^- + X^- \quad (9)^{22,24}$$
$$M = Mn, X = Cl, Br; M = Re, X = Cl, Br, I$$

The dinitrosyl complex $[Fe(NO)_2Cl]_2$ also undergoes chloride loss upon electron addition in THF in a complicated series of reductions and chemical reactions.[25] The first steps believed to be occurring are depicted in reactions 10 and 11.

$$[Fe(NO)_2Cl]_2 \xrightarrow{THF} 2Fe(NO)_2Cl(THF)_n \quad (10)$$

$$Fe(NO)_2Cl(THF)_n + e^- \rightarrow Fe(NO)_2(THF)_n + Cl^- \quad (11)$$

Clearly, however, the NO ligands of $CpM(NO)_2Cl$ (M = Mo, W) exert considerable influence on their reductions, rendering them reversible. The LUMO of $CpW(NO)_2Cl$ is known to be an orbital possessing a large degree of NO 2π character[26,27] and is antibonding between the N and O atoms of each NO group.[8] Thus, the initially formed radical anions $[CpM(NO)_2Cl]^{\bullet -}$ (M = Mo, W) are stabilized by delocalization of the extra electron density onto the NO ligands. This effect, no doubt, is at the heart of the reversibility of the reductions displayed by $CpM(NO)_2R$ (M = Cr, R = Me; M = Mo, R = Me, Et;[1] M = W, R = H, Me, Et) as well. This same acceptor ability of the NO ligands has been used to explain the reversible reduction of *cis*-

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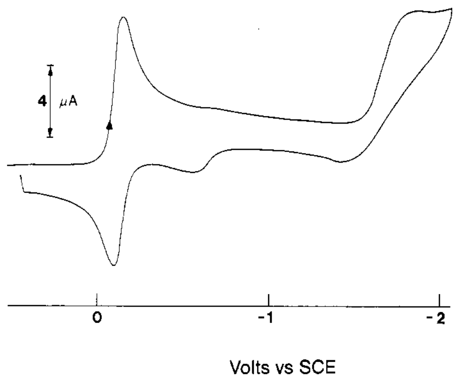

Figure 3. Cyclic voltammogram of $[CpMo(NO)_2PPh_3]BF_4$ in CH_2Cl_2 at a scan rate of 0.21 V s^{-1}.

$M(R_2NCS_2)_2(NO)_2$ (M = Mo, W; R = alkyl groups) as well as the solution and frozen-solution ESR spectra of the resultant $[cis\text{-}M(R_2NCS_2)_2(NO)_2]^{\bullet -}$ radical anions.[28]

The occurrence of the facile reductions of $CpM(NO)_2Cl$ (M = Mo or W) may also explain why the corresponding alkyl compounds, $CpM(NO)_2R$, can only be synthesized from the chloro complexes if gentle alkylating agents such as R_3Al are used.[4] More nucleophilic reagents such as RMgX may simply attack the nitrosyl ligands of the $CpM(NO)_2Cl$ reactants (probably via initial reduction followed by $R^\bullet$ attack on the electron-rich NO groups of $[CpM(NO)_2Cl]^{\bullet -}$) rather than effect the desired R for Cl metatheses. Certainly, the reversible reductions of $CpM(NO)_2Cl$ (M = Mo or W) are significantly different from the behavior of $CpCr(NO)_2Cl$ which undergoes irreversible reduction under identical experimental conditions.[11] As a consequence, treatment of $CpMo(NO)_2Cl$ or $CpW(NO)_2Cl$ with reducing metals such as Na or Zn probably results in the formation of the reactive $[CpM(NO)_2Cl]^{\bullet -}$ (M = Mo or W) radical anions which subsequently decompose in solution.[7] In contrast, $CpCr(NO)_2Cl$ is converted to $[CpCr(NO)_2]_2$ by these metals, the formation of the dimer being facilitated by metal-assisted chloride removal.[11] The analogous dimers containing molybdenum or tungsten remain unknown.[7]

(e) $[CpM(NO)_2L]BF_4$ [M = Mo, L = PPh_3; M = W, L = PPh_3, $P(OMe)_3$]. The first, reversible, reductions of these cationic complexes are very facile as exemplified by a cyclic voltammogram of $[CpMo(NO)_2PPh_3]BF_4$ (Figure 3), and as first noted by Angelici and co-workers.[8] The reduction potentials are presented in Table I; in all three cases, the peak potentials are scan-rate independent with ΔE_p being 60–65 mV, depending on L. The peak current ratio, $i_{p,a}/i_{p,c}$, is lowest for $[CpMo(NO)_2PPh_3]BF_4$ (0.81 at 0.02 V s^{-1} to 0.96 at 0.09 V s^{-1}). Again, the LUMOs of the cations are believed to be largely of NO 2π character.[8] A weak rise around $E_{p,c} \simeq -0.65$ V (Figure 3) after the first wave is passed is apparent in the CVs of all three compounds and may be due in part to a minor product derived from the $[CpM(NO)_2L]^\bullet$ radicals. One possibility could involve a slow phosphine or phosphite loss, i.e.

$$[CpM(NO)_2L]^+ + e^- \rightleftharpoons [CpM(NO)_2L]^\bullet \rightleftharpoons [CpM(NO)_2]^\bullet + L \quad (12)$$

A second cathodic wave occurs in the CVs of all three compounds at quite negative potentials as shown in Figure 3 and tabulated in Table I.

Table II. Infrared Stretching Frequencies and Reduction Potentials of Various Dinitrosyl Complexes

compd	ν_{NO}[a] (cm^{-1})		$E_{1/2}$[b]
$[CpCr(NO)_2(CH_3CN)]PF_6$	1844	1744	∼−0.23[c]
$CpCr(NO)_2Cl$	1817	1711	∼−0.64[c]
$CpCr(NO)_2Me$	1777	1669	−1.01
$[CpMo(NO)_2(PPh)_3]BF_4$	1792	1710	−0.12
$CpMo(NO)_2Cl$	1759	1665	−0.59
$CpMo(NO)_2Me$	1730	1635	−0.83
$CpMo(NO)_2Et$	1727	1633	−0.86
$[CpW(NO)_2PPh_3]BF_4$	1770	1694	−0.14
$[CpW(NO)_2P(OMe)_3]BF_4$	1767	1689	−0.10
$CpW(NO)_2Cl$	1733	1650	−0.62
$CpW(NO)_2H$	1718	1632	−0.79
$CpW(NO)_2Me$	1720	1609	−0.83
$CpW(NO)_2Et$[5]	1707	1619	−0.86

[a] CH_2Cl_2 solution. [b] V vs SCE. [c] Estimated from $E_{p,c}$ +0.04 at slow scan rates.

For the complex $[CpW(NO)_2P(OMe)_3]BF_4$ in particular, the peak separation for this wave varies from 180 mV at 0.09 V s^{-1} to 250 mV at 0.35 V s^{-1}, while $E_{1/2}$ is invariant with scan rate. These waves thus appear to be quasi-reversible reductions. The extent of chemical reversibility seems to increase with scan rate, but the trend is difficult to quantify. It has been previously suggested by Angelici and co-workers that this process may involve reduction of the 19-electron $[CpW(NO)_2L]^\bullet$ radicals to the corresponding 20-electron anions,[8] i.e.

$$[CpW(NO)_2L]^\bullet + e^- \rightleftharpoons [CpW(NO)_2L]^- \quad (13)$$

(Presumably this process, if applicable, would be operative for $[CpMo(NO)_2PPh_3]^\bullet$ as well.) An anodic wave also occurs at $E_{p,a} = -0.58$ V for the molybdenum complex and at $E_{p,a} = -0.61$ V for the two tungsten complexes. For $[CpW(NO)_2P(OMe)_3]BF_4$ this anodic peak potential does not shift with scan rate. Furthermore, the peak current of this wave does not increase with increased scan rate. One possible rationale to explain these observations involves loss of phosphine or phosphite ligands after reduction, followed by oxidation of the resulting anion, i.e.

$$[CpM(NO)_2L]^- \rightleftharpoons [CpM(NO)_2]^- + L \quad (14)$$

$$[CpM(NO)_2]^- - e^- \rightleftharpoons [CpM(NO)_2]^\bullet \quad (15)$$

The fate of the putative $[CpM(NO)_2]^\bullet$ radicals is not known.

Overview of the Electrochemical Results. Table I summarizes the reduction behavior of the various dinitrosyl complexes examined in this study. From the previous discussion, it seems reasonable to implicate the strong π-acid nature of the NO ligands as being largely responsible for the reversible character of the reductions described. Only some $CpCr(NO)_2$-containing compounds exhibit irreversible reduction, perhaps reflecting the existence of weaker metal–ligand linkages involving the first-row transition metal.[29] It would be expected that if the nitrosyl ligands dominate the reversible reduction behavior observed for the many and varied dinitrosyl compounds of the group 6 metals,[30] then there should be a correlation between $E_{1/2}$ and physical properties associated with the NO ligands in these complexes. The infrared stretching frequency of the nitrosyl group is one such property. A

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(30) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA became groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

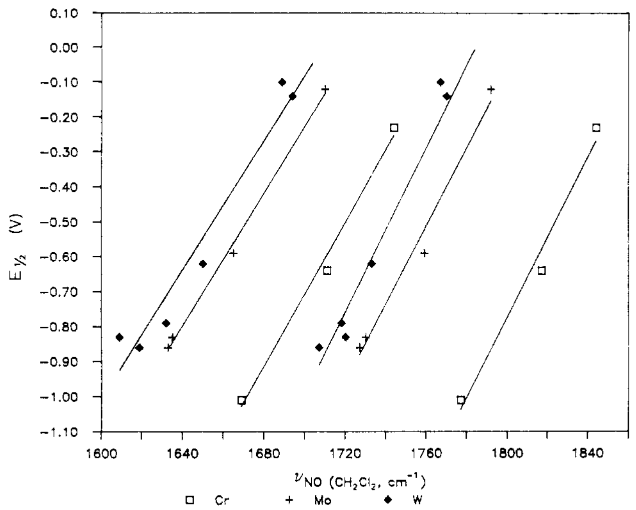

Figure 4. Plots of $E_{1/2}$ vs ν_{NO} for various $CpM(NO)_2$-containing (M = Cr, Mo, W) complexes in CH_2Cl_2.

lower ν_{NO} frequency is indicative of greater back-bonding to the NO ligand as compared with a higher ν_{NO} (all other factors being equal).[31] The greater the extent of this delocalization onto the NO ligands is, the more difficult it should be for the nitrosyl groups to accept more electron density. Thus, the lower the ν_{NO}'s, the more negative $E_{1/2}$ should be. Table II lists the two nitrosyl-stretching frequencies of each of the various $CpM(NO)_2$-containing compounds in CH_2Cl_2 used in this study and their $E_{1/2}$ values, also in CH_2Cl_2. Plots of $E_{1/2}$ vs each ν_{NO} are shown in Figure 4 and illustrate that for a given metal, $|E_{1/2}|$ does indeed increase roughly linearly with decreasing ν_{NO}. Furthermore, a given chromium complex is somewhat harder to reduce than its molybdenum analogue, which differs little in its reduction potential compared to the tungsten analogue. These results are consistent with (a) the π-acceptor effect of the NO ligand and the LUMO of the $[CpM(NO)_2Y]^{n+}$ (M = Cr, Mo, W; Y = halides, H, alkyl groups, n = 0; Y = phosphines, phosphites, amines, n = 1) complexes involving a largely NO 2π orbital and (b) the strength of the M–NO interaction increasing in the order M = Cr < Mo $\lesssim$ W.

At the beginning of this work, the electrochemical reduction behavior of organometallic nitrosyl complexes had been little studied. A report on the electrochemistry of CpNi(NO) in DMF at a mercury electrode indicates that this compound reduces with concomitant rapid reaction to form Cp_2Ni and other products.[32] The reduction electrochemistry of $CpW(CO)_2(NO)$ has been briefly examined by Dessy and co-workers, and a short-lived radical anion (presumably $[CpW(CO)_2(NO)]^{\bullet -}$) reportedly is formed.[22] A detailed investigation of $(\eta^5\text{-}C_5H_4R)M(CO)_2(NO)$ (M = Cr, R = H, C(O)CH$_3$; M = Mo, R = H) has shown that these compounds undergo quasi-reversible reduction in CH_3CN, DMF, or THF to give the corresponding radical anions.[33] An ESR study of frozen solutions of these anionic radicals suggests that the extra electron density is localized in the MNO group and that the nitrosyl ligand becomes substantially bent upon reduction to accommodate this. This does not appear to be the case for the dinitrosyl complexes considered in this study[1] (vide infra).

Preparative Work. (a) $[Cp_2Co][CpM(NO)_2R]$ (M = Mo, R = Me, Et; M = W, R = Me). All the new radical anion complexes $[Cp_2Co][CpM(NO)_2Y]$ (M = Mo, Y = Me, Et, Cl; M = W, Y = Me, H, D, Cl) may be readily synthesized in moderate to high yields from their neutral precursors and cobaltocene, a moderately potent, one-electron reductant,[34] i.e.

$$CpM(NO)_2Y + Cp_2Co \rightarrow [Cp_2Co][CpM(NO)_2Y] \quad (16)$$

All but the hydrido and deuterio derivatives are best prepared by using Et_2O as the solvent. The two methyl compounds $[Cp_2Co][CpM(NO)_2Me]$ (M = Mo, W) precipitate instantly when solutions of the two reagents are mixed and are obtained as analytically pure, purple-black (M = W) and green-black (M = Mo) microcrystalline solids in moderate yields. The molybdenum compound, in particular, must be prepared with rapid addition of the two reactants and efficient stirring. If the reaction mixture is not stirred, or is stirred slowly, a brown, amorphous and insoluble material accompanies the formation of the desired product. On occasion, traces of this brown solid can be detected even when rapid stirring is employed. This may possibly hinder the preparation of $[Cp_2Co][CpMo(NO)_2Me]$ on a large scale. Simply adding Et_2O to an equimolar mixture of the two solid reagents also results in formation of the desired complex, but the resultant solid is of poor quality, being contaminated with other insoluble byproducts. Not surprisingly, attempts to grow single crystals of this molybdenum complex by allowing two separate solutions of Cp_2Co and $CpMo(NO)_2Me$ to slowly diffuse together fail, resulting only in the formation of a brown amorphous solid. It may be that the initially formed radical anion is susceptible to further attack by the 19-electron cobaltocene. This kind of problem does not appear to be as severe for the tungsten complex. By analogy to the reaction between Cp_2Co and $CpMo(NO)_2Et$,[1] it is probable that the particular cases of reactions 16 when Y = alkyl proceed via an initial equilibrium involving a solvated adduct, i.e.

$$Cp_2Co + CpM(NO)_2R \xrightleftharpoons{Et_2O} \underset{\text{(solvated adduct)}}{[(Cp_2Co)(CpM(NO)_2R)]} \xrightleftharpoons{Et_2O} \underset{\text{(precipitated salt)}}{[Cp_2Co]^+[CpM(NO)_2R]^{\bullet -}} \quad (17)$$

where M = Mo or W and R = Me or Et. Certainly, the 30-mV difference in reduction potentials between the methyl and ethyl complexes will not drastically influence the magnitudes of the equilibrium constants for reactions 17. However, the ethyl-containing solvated adduct should be more soluble in Et_2O than its methyl analogues.

The methyl-containing salts are somewhat air- and temperature-sensitive. The molybdenum complex, for example, decomposes slowly in air overnight into an amorphous solid of unknown composition. Under N_2 at ambient temperatures it also gradually decomposes over the course of several days. At −25 °C, however, these complexes appear to be stable under N_2 for at least several months. These radical anion compounds are soluble in good solvating solvents[35] such as CH_3CN and DMF at ~−25 °C but only slightly soluble in CH_2Cl_2 at ~−78 °C. The molybdenum complex gives green solutions while the tungsten complex forms red-purple solutions. They very rapidly decompose in all solvents at room temperature to

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give brown solutions. The tungsten complex is stable in CH_3CN for a few hours at −25 °C after which it starts to show signs of decomposition.

The crystal structure of $[Cp_2Co][CpMo(NO)_2Et]$ consists of discrete cations and anions arranged in a "CsCl-type" of lattice, the radical anion maintaining a monomeric "three-legged piano-stool" molecular geometry with terminal, linear nitrosyl ligands.[1] The spectroscopic properties of each of the isolated $[CpM(NO)_2R]^{\bullet-}$ radical anions are indicative of their possessing the same type of molecular structures. Thus, their Nujol mull IR spectra are consistent with substantially increased back-bonding to the nitrosyl ligands. The ν_{NO} absorptions of these complexes are among the lowest yet observed for terminal nitrosyl groups and lie well below the range generally expected for terminal nitrosyl ligands,[36,37] thereby indicating that the mode of attachment of a nitrosyl ligand to a transition metal is best not inferred solely from the nitrosyl-stretching frequency. The ν_{NO}'s of the radical anion complexes occur at lower energies by ~190–210 cm^{-1} than those of their neutral precursors. A similar effect is observed for ν_{NO} absorptions of $[CpFe(\eta^6\text{-}C_6Me_6)][\{CpCr(NO)_2\}_2]$ which drop by ~175 cm^{-1} for the bridging NO ligands.[11] The neutral radicals $[CpW(NO_2)L]^{\bullet}$ [L = PPh_3, $P(OPh)_3$, $P(OMe)_3$] also display ν_{NO}'s ~160–175 cm^{-1} lower than their precursor cations, $[CpW(NO)_2L]BF_4$.[8] For some of the new alkyl complexes the lower energy nitrosyl absorption overlaps with the strong 1462 cm^{-1} band of Nujol. Utilizing a computer-assisted subtraction process, the Nujol spectrum can be removed from the experimental spectrum. The subtraction is deemed to be complete for these spectra when the more well-resolved 1377 cm^{-1} band of Nujol is just removed. For the three $[CpM(NO)_2R]^{\bullet-}$ anions considered here, however, the effect is quite small (see Experimental Section). Each of the radical anion complexes also show medium-intensity absorptions between 3069 and 3104 cm^{-1} attributable to C–H stretches of the cyclopentadienyl rings. For $[Cp_2Co][CpW(NO)_2Me]$ these are moderately well-resolved into two sharp bands (3100, 3087 cm^{-1}) and a shoulder (3069 cm^{-1}). (For $[Cp_2Co]BF_4$ this band occurs at 3119 cm^{-1}.) Medium-intensity bands around 1415 and 1360 cm^{-1}, seen for all three compounds, are likely due to C–H vibrations of the C_5H_5 ring and C–H symmetric deformations[38] of the Me or Et groups, respectively.

The ESR spectra of the three radical anion alkyl complexes in CH_3CN or DMF at ~−20 to −40 °C exhibit five-line patterns of approximate intensity ratios 1:2:3:2:1, characteristic of coupling of the unpaired electron to two equivalent ^{14}N nuclei. (In all three cases a_N is of the order of 7 G.) While g values have not been determined, the point of greatest interest is that these patterns are consistent with delocalization of the extra electron density onto the terminal, linear nitrosyl ligands.[1] Hence, the IR and ESR spectra of the $[CpM(NO)_2R]^{\bullet-}$ anions are in accord with the view that their HOMO's are largely NO-based π^* molecular orbitals.[1]

The anions $[CpMo(NO)_2Me]^{\bullet-}$ and $[CpW(NO)_2Me]^{\bullet-}$ can be oxidized readily to the neutral alkyl complexes by $[Cp_2Fe]BF_4$ and $AgBF_4$, respectively, e.g.

$$[Cp_2Co][CpMo(NO)_2Me] + [Cp_2Fe]BF_4 \xrightarrow{CH_2Cl_2} CpMo(NO)_2Me + [Cp_2Co]BF_4 + Cp_2Fe \quad (18)$$

These reactions appear to be quite clean as indicated by IR monitoring of their progress which shows nitrosyl absorptions only for the appropriate $CpM(NO)_2Me$ species (M = Mo, W) in each reaction. Recovery of the neutral alkyl complexes lends further support to the formulation of the nitrosyl-containing reactants as $[Cp_2Co][CpM(NO)_2Me]$ (M = Mo, W), i.e., cobalticinium salts of radical anion nitrosyl complexes.

Radical anion complexes such as these would appear to have little precedent in transition-metal carbonyl chemistry. As mentioned earlier, most alkyl complexes of the type $CpM(CO)_nR$ and $M(CO)_nR$ (M = transition metal, R = alkyl group) reduce with concomitant expulsion of the alkyl group.[9] The ability of the NO ligands to accept and stabilize excess electron density is no doubt key to the isolation of these new complexes. (Their solution and thermal sensitivity could, however, involve alkyl loss.) Alkyl-containing transition-metal radical complexes are not unknown though. For example,[39] $Cp_2TiCH_2CMe_3$, Cp_2NbMe_2, $V(CH_2Ph)_4$, and $ReMe_6$ are all fairly well-characterized, paramagnetic compounds (although each of these possess a less than 18-electron valence shell).

(b) Reactions of $CpCr(NO)_2Me$ with Reducing Agents. Unlike the alkyl complexes just described, $CpCr(NO)_2Me$ does not react with Cp_2Co to any appreciable extent. This does not appear to be a function of the solubility of an initially formed low concentration of the reduced species as in the case of $[CpMo(NO)_2Et]^{\bullet-}$.[1] The reduction potential of the chromium complex is 180 mV more negative of $CpMo(NO)_2Me$ (in CH_2Cl_2; see Table I), and this probably renders $CpCr(NO)_2Me$ too difficult to reduce by cobaltocene in Et_2O. This view is supported by an IR spectrum of the reaction mixture which displays ν_{NO} bands only due to $CpCr(NO)_2Me$.

On the other hand, when a filtered Et_2O solution of $CpFe(\eta^6\text{-}C_6Me_6)$ is mixed with $CpCr(NO)_2Me$ in Et_2O, an instantaneous reaction occurs and a gray precipitate forms. This solid is very pyrophoric, bursting into flame upon contact with air. On the basis of the CVs of $CpCr(NO)_2Me$ and its molybdenum and tungsten analogues and the previously described radical anion complexes, it seems likely that a radical anion is formed, but it is too unstable to be isolated pure in this manner. This difficulty is not surprising when one considers the CV of $CpCr(NO)_2Me$ (Figure 1). The lower $i_{p,a}/i_{p,c}$ ratios compared with the Mo and W analogues (Table I), the second reduction at $E_{p,c} \simeq -1.87$ V, and the variation of peak potentials with scan rate are all consistent with the complex behavior of this compound toward the chemical reductant, $CpFe(\eta^6\text{-}C_6Me_6)$. Elemental analyses of the gray solid are quite variable and low in nitrogen content. The Nujol mull IR spectrum of this material exhibits a strong NO absorption at 1555 cm^{-1} and a weaker (but still quite strong) band at 1509 cm^{-1}. This intensity pattern does not correspond to a $\{M(NO)_2\}$ group with linear nitrosyl ligands. All the same, the radical anion $[CpCr(NO)_2Me]^{\bullet-}$ may perhaps yet prove to be obtainable at low temperature.

(c) $[Cp_2Co][CpW(NO)_2Y]$ (Y = H, D). These two compounds are best prepared by utilizing hexanes as the solvent. The reactions can be carried out in the same manner as for the alkyl analogues described above (eq 16) and generate the radical anion complexes in moderate yields as brown solids that are soluble in CH_3CN and DMF to give red-violet solutions at ~−25 °C. They rapidly decompose in these solvents at room temperature. Unfortunately, these complexes could not be obtained as

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analytically pure materials. The carbon analyses were generally slightly low, and in the case of the deuterio analogue, the nitrogen content was low also. A combustion additive did not improve the analyses.

The IR and ESR spectra of these compounds provide good evidence for their formulations as radical anion species analogous to the alkyl-containing radical anions. The Nujol mull IR spectrum of $[Cp_2Co][CpW(NO)_2H]$ displays two strong NO absorptions at 1521 and 1445 cm^{-1}, consistent with a highly electron-rich dinitrosyl complex. The lower band overlaps with the strong 1462 cm^{-1} absorption of Nujol. The Nujol spectrum can be subtracted from the experimental spectrum (as described above) leaving the lower energy NO band at $\sim$1438 cm^{-1}. The W–H stretch appears as a medium intensity band at 1848 cm^{-1}, somewhat lower than that found for $CpW(NO)_2H$ (1897 cm^{-1}).[16] A broad, medium intensity band at 3073 cm^{-1} is attributable to C–H stretching of the cyclopentadienyl rings. Likewise, a medium-intensity band at 1411 cm^{-1} can be assigned to C–H vibrations of the C_5H_5 rings. The ν_{NO} absorptions of the deuterio analogue occur at 1513 and 1447 cm^{-1}, similar to, but not identical with, the NO bands of the hydrido complex. Again, the lower ν_{NO} appears at $\sim$1439 cm^{-1} if the Nujol spectrum is subtracted. The W–D stretch of $[Cp_2Co][CpW(NO)_2D]$ may give rise to one of the weak bands at 1337 or 1316 cm^{-1}, neither of which is seen in the IR spectrum of the hydrido complex. The band at 1337 cm^{-1} is shifted down from the W–H band of the hydrido analogue (1848 cm^{-1}) by a factor of 1.38 which is nearly identical with the shift observed for the W–H and W–D stretches of the neutral complexes $CpW(NO)_2H$ and $CpW(NO)_2D$.[16] The band at 1316 cm^{-1} is shifted down from the W–H stretch of the radical anion by a factor of 1.40. In any event, the band at 1848 cm^{-1} observed in the IR spectrum of the hydrido-containing anion is not present in the IR spectrum of the deuterio analogue, further supporting its assignment to the W–H stretch.

The ESR spectra of both of these complexes are qualitatively similar (Figure 5) and supportive of their formulation as radical anions analogous to the alkyl complexes discussed previously (vide supra). The familiar 1:2:3:2:1 five-line pattern is obvious for these species, but no coupling to either the ^1H or ^2H ligand nuclei is resolvable in these spectra. The line widths of the spectrum arising from the hydrido complex are somewhat broader, perhaps reflecting a larger, though unresolved, coupling to a ^1H nucleus as compared to a ^2H nucleus.

Unlike for the syntheses of the alkyl radical complexes, Et_2O is not a suitable solvent for preparing the hydrido analogue. Although a more attractive microcrystalline solid is isolated when the reaction is carried out in Et_2O, satisfactory C, H, and N analyses cannot be obtained, the nitrogen content being especially low and variable. An IR spectrum (Nujol mull) of this solid reveals that it does largely contain $[Cp_2Co][CpW(NO)_2H]$ as evidenced by ν_{NO}, ν_{W-H}, and C_5H_5 absorptions identical with those of the complex prepared in hexanes. In Et_2O, however, the hydrido radical anion may more readily decompose, perhaps due to its slight solubility in this solvent.

In accord with the previous discussion on the electrochemistry of $CpW(NO)_2H$, the isolation and characterization of $[Cp_2Co][CpW(NO)_2H]$ appear to be quite distinct from the chemistry of transition-metal carbonyl hydrides, which generally undergo metal–hydride bond scission upon reduction.[9] The long-term thermal instability and the solution instability (at room temperature) of this radical anion may perhaps involve W–H bond cleavage as one pathway of decomposition. Other examples of hydride-containing radical complexes include Cp_2NbH_2 and $[Cp_2TiH_2]^-$ (also a radical anion).[39]

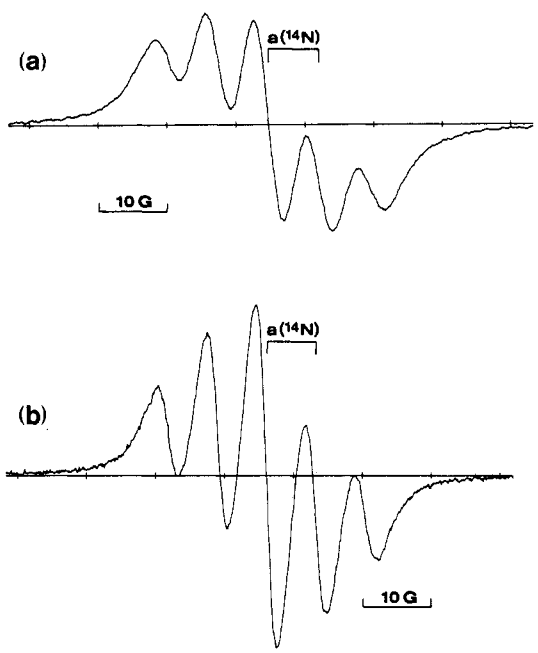

Figure 5. X-band ESR spectra of (a) $[Cp_2Co][CpW(NO)_2H]$ in CH_3CN at -22 °C (g = 2.011 86; $a_N \simeq$ 7.3 G) and (b) $[Cp_2Co][CpW(NO)_2D]$ in DMF at -22 °C (g = 2.000 25; $a_N \simeq$ 7.2 G).

The oxidation of $[CpW(NO)_2H]^{\bullet -}$ is readily accomplished by $AgBF_4$ in CH_2Cl_2. The reaction is quite rapid and regenerates $CpW(NO)_2H$ which is easily identified by its characteristic IR and mass spectra. The chemical reversibility of the reduction of $CpW(NO)_2H$ is thus established.

(d) $[Cp_2Co][CpM(NO)_2Cl]$ (M = Mo, W). The syntheses of these compounds are also readily accomplished in good yields by mixing Et_2O solutions of cobaltocene and the appropriate halide complex (eq 16). The solids thus obtained are highly pyrophoric, amorphous, pale gray-green (M = Mo) and gray (M = W) powders. Both solids are quite thermally sensitive, the tungsten complex especially so, taking on a brown coloration overnight under N_2. Both salts are soluble in CH_3CN and DMF to give greenish solutions which are stable only at low temperatures ($\sim$-25 °C). Satisfactory elemental analyses are obtainable for these complexes if they are kept cold ($\sim$-20 °C) until a few minutes prior to the analysis being carried out.

The fact that these complexes are acquired as amorphous powders, while the alkyl-containing radical anions are crystalline materials may be reflective of two differences. First, the reduction potentials of $CpM(NO)_2Cl$ (M = Mo, W) are $\sim$230 mV less negative than the alkyl complexes, thereby making them more susceptible to reduction by cobaltocene. Secondly, the initially formed $[CpM(NO)_2Cl]^{\bullet -}$ anion may be much less soluble in Et_2O than an alkyl-containing analogue. These factors may also be behind the greater isolated yields of the chloro-containing radical anion complexes.

The Nujol mull IR spectrum of the molybdenum complex displays ν_{NO} bands at very low frequencies (1558, 1485 cm^{-1}; 1490 cm^{-1} with the Nujol spectrum subtracted out as described previously), as would be expected for $[CpMo(NO)_2Cl]^{\bullet -}$. These absorptions are 198 and $\sim$165 cm^{-1}, respectively, lower than those of $CpMo(NO)_2Cl$ (1756, 1655 cm^{-1}) in a Nujol mull. A broad, medium-intensity absorption at 3092 cm^{-1} can be attributed to C–H stretching of the cyclopentadienyl rings, and a band at 1413 cm^{-1} can also be assigned to C–H vibrations arising from the C_5H_5 rings. For $[Cp_2Co][CpW(NO)_2Cl]$ the IR spectrum is somewhat more complex. Two strong NO bands are observed at 1534 and 1456 cm^{-1}. The latter absorption overlaps nearly coincidentally with the 1462 cm^{-1} band of Nujol. The Nujol spectrum could not be satisfactorily subtracted from the experimental spectrum due to other bands also overlapping with the 1377 cm^{-1} band of Nujol. The band at 1456 cm^{-1}, however, obtained from a concentrated sample, is likely a good estimate of the lower ν_{NO} frequency since bands that overlap this closely with the Nujol absorption at 1462 cm^{-1} do not shift much upon subtraction of the Nujol spectrum. (Compare with, for example, $[Cp_2Co][CpMo(NO)_2Et]$: ν_{NO} (Nujol mull) 1458 cm^{-1}, with or without the Nujol spectrum subtracted.[1]) These bands are 192 and ~174 cm^{-1}, respectively, lower in frequency than those of neutral $CpW(NO)_2Cl$ (1726, 1630 cm^{-1}) under the same conditions. Two other broad bands, both substantially weaker, also appear in the IR spectrum of $[Cp_2Co][CpW(NO)_2Cl]$, at 1705 and 1588 cm^{-1}. Similar absorptions are not apparent in the IR spectrum of the molybdenum analogue. It may be that these new bands result from thermal decomposition of the $[CpW(NO)_2Cl]^{\bullet-}$ radical anion in the solid state, perhaps even via slow Cl^- loss, i.e.

$$[CpW(NO)_2Cl]^{\bullet-} \rightarrow [CpW(NO)_2]^{\bullet} + Cl^- \qquad (19)$$

The fate of the putative $[CpW(NO)_2]^{\bullet}$ radical is not clear, other than it is proposed to generate the species responsible for the IR bands at 1708 and 1585 cm^{-1}. This possibility is suggested on the basis of a preliminary investigation of the reaction of $CpW(NO)_2BF_4$ with Cp_2Co which in CH_2Cl_2 produces a brown, insoluble, amorphous solid of as yet undeteremined composition with ν_{NO}'s at 1708 and 1585 cm^{-1} in its Nujol mull IR spectrum. This material probably results from a reaction of the initially formed $[CpW(NO)_2]^{\bullet}$, i.e.

$$CpW(NO)_2BF_4 + Cp_2Co \xrightarrow{CH_2Cl_2} [CpW(NO)_2]^{\bullet} + [Cp_2Co]BF_4 \qquad (20)$$

$$[CpW(NO)_2]^{\bullet} \rightarrow \text{brown solid} \qquad (21)$$

The proposed loss of Cl^- from $[CpW(NO)_2Cl]^{\bullet-}$ would appear to be slow on the CV time scale in CH_2Cl_2 (Table I) since the electrochemical reduction of $CpW(NO)_2Cl$ is quite reversible. Just when this proposed loss of Cl^- occurs from the tungsten radical anion is not known at present.

Both $[CpM(NO)_2Cl]^{\bullet-}$ (M = Mo, W) complexes exhibit ESR spectra (Figure 6) in CH_3CN or DMF similar to those previously discussed. Interestingly, however, the ESR spectrum of $[Cp_2Co][CpMo(NO)_2Cl]$ exhibits more hyperfine structure than just the expected five-line pattern (Figure 6a). Indeed, it appears that a second, more highly coupled spectrum is superimposed onto the familiar 1:2:3:2:1 five-line pattern. It therefore seems unlikely that the spectrum in Figure 6a can be interpreted as arising from coupling of the electron to two equivalent ^{14}N atoms and to the ^{35}Cl (75.53%; $I = ^3/_2$) and ^{37}Cl (24.47%; $I = ^3/_2$) nuclei. A more satisfactory interpretation involves coupling to the ^{95}Mo (15.72%; $I = ^5/_2$) and ^{97}Mo (9.46%; $I = ^5/_2$) nuclei. If $a_{^{95}Mo} \simeq a_{^{97}Mo}$ and $a_{Mo} \simeq ^1/_3 a_N$, an 18-line pattern (accounting for ~25% of the total intensity) superimposed onto a five-line pattern (accounting for the remaining 75% of the total intensity) would result, in good agreement with the observed spectrum. Unfortunately, the resolution of this spectrum is not high enough to evaluate unambiguously the coupling constants. Such coupling to the ^{95}Mo and ^{97}Mo nuclei is not resolved for either of the molybdenum complexes $[Cp_2Co][CpMo(NO)_2R]$ (R = Me, Et) under similar conditions. Neither is coupling to the ^{183}W nucleus (14.40%; $I = ^1/_2$) resolvable for any of the radical complexes containing tungsten, including $[Cp_2Co][CpW(NO)_2Cl]$ (see Figure 6b).

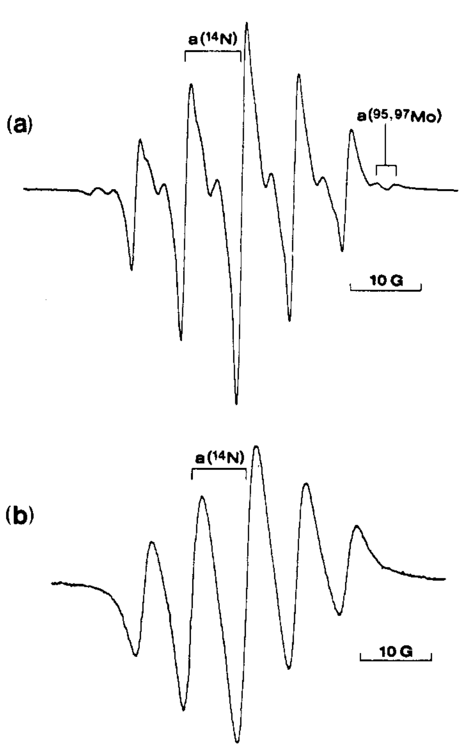

Figure 6. X-band ESR spectra of (a) $[Cp_2Co][CpMo(NO)_2Cl]$ in DMF at ~−25 °C ($a_N \simeq$ 7.4 G; $a_{Mo} \simeq$ 2.5 G) and (b) $[Cp_2Co][CpW(NO)_2Cl]$ in DMF at ~−35 °C ($a_N \simeq$ 7.2 G).

As noted earlier, the $CpM(NO)_2Cl$ (M = Mo or W) compounds cannot be converted to $[CpM(NO)_2]_2$ dimers by treatment with reducing metals such as Na or Zn. This fact is now confirmed to be a manifestation of the intrinsic instability in solutions at room temperature of the initially formed $[CpM(NO)_2Cl]^{\bullet-}$ radical anions which decompose to non-nitrosyl-containing materials under these conditions. It is intriguing also that the isostructural alkyl-containing radical anions are substantially more robust than their chloro analogues. In general, carbonyl-containing alkyls are less stable to heat and air than are their related halides. Some organometallic halo radicals are known (e.g. $Cr(CO)_5I$ and $CpCrCl_2$),[39] but few, if any, are anionic like the $[CpM(NO)_2Cl]^{\bullet-}$ species isolated during this work.

Chemical oxidation of the $[CpMo(NO)_2Cl]^{\bullet-}$ species can be accomplished with $AgBF_4$ in CH_3CN. The neutral $CpMo(NO)_2Cl$ compound is the only isolable nitrosyl complex obtained during this reaction whose occurrence is consistent with the $\{CpMo(NO)_2Cl\}$ structural entity maintaining its integrity upon reduction.

(e) $[CpW(NO)_2L]^{\bullet}$ (L = $P(OMe)_3$, PPh_3). The syntheses of these compounds have been reported by Angelici and co-workers.[8] The precursor cations $[CpW(NO)_2L]PF_6$ [L = PPh_3, $P(OPh)_3$, $P(OMe)_3$] can be reduced by a variety of reductants, i.e.

$$[CpW(NO)_2L]^+ + \text{reducing agent} \rightarrow [CpW(NO)_2L]^{\bullet} \qquad (22)$$

reducing agent = Zn, $N_2H_4 \cdot H_2O$, alkoxides, OH^-

The radical complexes can be isolated in low to moderate yields, depending on the reductant.

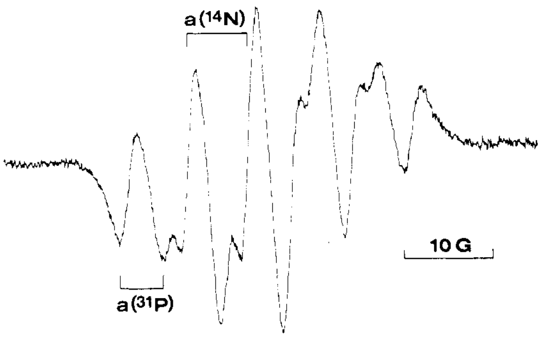

Figure 7. X-band ESR spectrum of $CpW(NO)_2P(OMe)_3$ in CH_3CN at ~-25 °C ($a_N \simeq 6.8$ G; $a_p \simeq 4.5$ G).

We now find that cobaltocene can also be used to generate these complexes, i.e.

$$[CpW(NO)_2L]BF_4 + Cp_2Co \xrightarrow{CH_2Cl_2} [CpW(NO)_2L]^{\bullet} + [Cp_2Co]BF_4 \quad (23)$$

$$L = PPh_3, P(OMe)_3$$

The radical complexes can be isolated from the reaction mixtures as purple solids in the manner described in the Experimental Section. These two complexes have been described as being very air- and temperature sensitive.[8] When prepared by using Cp_2Co, however, they are quite thermally stable, decomposing only slightly overnight in CH_2Cl_2 solutions at room temperature. In addition, $[CpW(NO)_2PPh_3]^{\bullet}$ appears to be more air-stable than first reported, exhibiting no obvious decomposition as a solid overnight as evidenced by an IR spectrum (Nujol mull) of a sample of this complex handled in this way. It may be that trace impurities present in the materials obtained via reaction 22 catalyze the decompositions of the $CpW(NO)_2L$ compounds prepared in this manner. It would appear, therefore, that the use of cobaltocene as a reducing agent is somewhat more preferable in these reactions.

The solution IR spectrum of $CpW(NO)_2PPh_3$ (in CH_2Cl_2) prepared by reaction 23 (ν_{NO} = 1598, 1532 cm^{-1}) corresponds fairly well to that reported previously (1595, 1526 cm^{-1}).[8] The difference for the trimethyl phosphite complex is somewhat greater, 1608, 1542 cm^{-1} for the product from reaction 23 and 1605, 1533 cm^{-1} for the species obtained by reaction 22.[8] The trimethyl phosphite complex has also been reported as being too unstable to obtain a solution ESR spectrum.[8] When prepared according to reaction 23, however, $CpW(NO)_2P(OMe)_3$ can be isolated and does exhibit a 10-line ESR spectrum in CH_3CN at ~-25 °C with $a_N \simeq 6.8$ G and $a_P \simeq 4.5$ G (Figure 7), quite similar to that reported for $CpW(NO)_2PPh_3$ in acetone.[8] This is consistent with coupling of the odd electron to two equivalent ^{14}N nuclei (as described above for the other radical anion complexes) and to a ^{31}P nucleus of $P(OMe)_3$.

Oxidation of $CpW(NO)_2P(OMe)_3$ by $AgBF_4$ in CH_2Cl_2 rapidly regenerates $[CpW(NO)_2P(OMe)_3]BF_4$ as indicated by IR monitoring of the reaction's progress. Also, the ^1H NMR spectrum of the isolated green solid in $CDCl_3$ reveals the presence of a coordinated $P(OMe)_3$ ligand [δ 3.88 (d, $^3J_{^{31}P-^1H}$ = 12.0 Hz)].

Overview and Summary

Table III lists the nitrosyl-stretching frequency data of the isolated paramagnetic complexes investigated and the $E_{1/2}$ data of the various precursors in CH_2Cl_2. Plots of $E_{1/2}$ vs ν_{NO} are shown in Figure 8. It seems likely that the oxidation potentials of the $[CpM(NO)_2Y]^{\bullet-}$ (M = Mo, W; Y = Cl, H, Me, Et as appropriate) anions generated during a reduction scan for a given $CpM(NO)_2Y$ compound in CH_2Cl_2 would be the same as those of the $[Cp_2Co][CpM(NO)_2Y]$ isolated compounds or, at least, they would be similar. In other words, $E_{1/2}$ measured for the reduction of $CpM(NO)_2Y$ complex in CH_2Cl_2 should be very similar to $E_{1/2}$ for the oxidation of the radical anion obtained as its $[Cp_2Co]^+$ salt (minor effects due to the cobalticinium counterion notwithstanding). Hence, the correlation observed between $E_{1/2}$ and ν_{NO} in Figure 8 is anticipated to be sound. As would be expected, the lower are the ν_{NO}'s of the isolated complex, the easier it is to oxidize. Such trends are well-known for the oxidation of other nitrosyl complexes. For example, the oxidation potentials of $[Cr(NO)(CNR)_5]PF_6$ (R = alkyl, aryl groups) have been found to be linear with ν_{NO}.[40] Likewise, $E_{1/2}$ (oxidation) and ν_{NO} are linearly related for the complexes $[CpMn(NO)(L)L']^{n+}$ (L, L' = nitrogen- and/or phosphorus-containing two-electron donor ligands and various bidentate sulfur-containing ligands).[41] The reduction potentials of $[(bpy)_2Ru(NO)X]^{n+}$ (X = halides, pseudohalides, and two-electron nitrogen donors) also vary linearly with ν_{NO}.[42] The fact that this dependence of $E_{1/2}$ on ν_{NO} often arises may well reflect the strong π-acidity of NO. Certainly the NO ligands in the new complexes synthesized during this work have a profound influence, markedly stabilizing the reduced species.

Table III. Nitrosyl-Stretching Frequencies of the Isolated Radical Species and Their Oxidation Potentials

complex^a	ν_{NO}^{b} (cm^{-1})		$E_{1/2}$^{c}
$[CpMo(NO)_2Et]^{\bullet-}$	1527	1458	-0.86
$[CpMo(NO)_2Me]^{\bullet-}$	1526	1443	-0.83
$[CpMo(NO)_2Cl]^{\bullet-}$	1558	1490	-0.59
$[CpW(NO)_2Me]^{\bullet-}$	1511	1427	-0.83
$[CpW(NO)_2H]^{\bullet-}$	1521	1438	-0.79
$[CpW(NO)_2Cl]^{\bullet-}$	1534	1456	-0.62
$[CpW(NO)_2PPh_3]^{\bullet}$	1594	1527	-0.14
$[CpW(NO)_2P(OMe)_3]^{\bullet}$	1593	1533	-0.10

^{a}Anionic complexes as $[Cp_2Co]^+$ salts. ^{b}Nujol mull. ^{c}For the couple $[CpM(NO)_2Y]^{\bullet n-} - e^- \rightleftharpoons [CpM(NO)_2Y]^{(1-n)+}$ (n = 0, 1) in CH_2Cl_2 (V vs SCE).

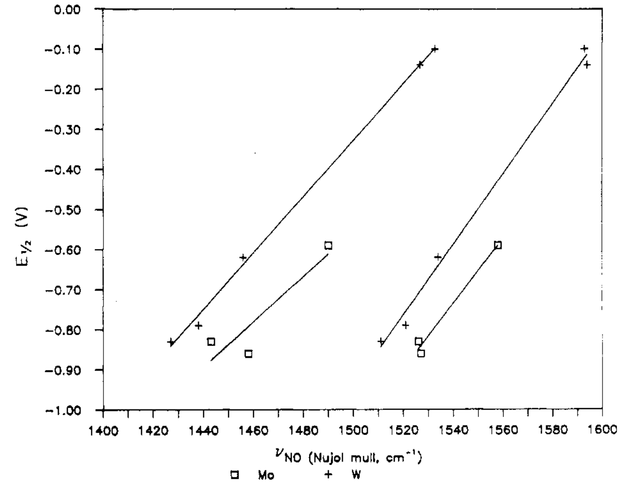

Figure 8. Plots of $E_{1/2}$ for the couple $[CpM(NO)_2Y]^{\bullet n-} - e^- \rightleftharpoons [CpM(NO)_2Y]^{(1-n)+}$ (n = 0, 1) in CH_2Cl_2 vs ν_{NO} (Nujol mull) of $[Cp_2Co][CpM(NO)_2Y]$ and $[CpM(NO)_2Y]^{\bullet}$ complexes (M = Mo, W; Y = Me, Et, H, Cl, PPh_3, $P(OMe)_3$, as appropriate).

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The synthetic strategy employed in preparing the new organometallic nitrosyl radical anions described herein is a simple but effective one. A solvent is chosen in which the reductant and oxidant (i.e. the nitrosyl complex) are both soluble, but the electron-transfer product is not. This facilitates the isolation of the desired ionic compounds as fairly pure solids while avoiding accelerated decomposition rates that they might experience if the products remained in solution. Secondly, the reducing agent becomes a bulky counterion. Other reductants, such as Na or Zn, result in the formation of small counterions that can strongly interact with the nitrosyl ligands[43] and thus destabilize an anionic complex by polarizing the metal–ligand linkage. The syntheses and characterizations of the new radical complexes are of interest in their own right, representing a little explored area of the chemistry of group 6[30] organometallic nitrosyl compounds. The anionic complexes described in this paper join a small family of simple, nitrosyl-containing anions that only in the last five years has begun to grow in number more steadily.[44] Obviously, further work is required to delineate the characteristic chemistry of these anions, particularly their reactivities toward nonoxidizing electrophiles.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and a graduate scholarship to B.W. We are also indebted to Professor F. Geoffrey Herring for his assistance in the acquisition and interpretation of some of the ESR spectra.

Registry No. $CpMo(NO)_2Me$, 57034-48-7; $CpMo(NO)_2Cl$, 12305-00-9; $CpW(NO)_2Me$, 57034-45-4; $CpW(NO)_2BF_4$, 87189-85-3; $CpW(NO)_2Cl$, 53419-14-0; $[Cp_2Co][CpW(NO)_2Me]$, 111469-36-4; Cp_2Co, 1277-43-6; $[Cp_2Co][CpMo(NO)_2Me]$, 111469-38-6; $CpCr(NO)_2Me$, 53522-59-1; $CpFe(\eta^6\text{-}C_6Me_6)$, 70414-92-5; $CpW(NO)_2H$, 69532-01-0; $[Cp_2Co][CpW(NO)_2H]$, 111469-40-0; $[Cp_2Co][CpW(NO)_2D]$, 111469-42-2; $CpW(NO)_2D$, 69532-02-1; $[Cp_2Co][CpW(NO)_2Cl]$, 111469-44-4; $[Cp_2Co][CpMo(NO)_2Cl]$, 111469-46-6; $CpW(NO)_2P(OMe)_3$, 82044-74-4; $P(OMe)_3$, 121-45-9; $[CpW(NO)_2P(OMe)_3]BF_4$, 111469-47-7; $CpW(NO)_2PPh_3$, 82044-73-3; $[CpW(NO)_2PPh_3$, 87189-86-4; $[Cp_2Co]BF_4$, 52314-53-1; Cp_2Fe, 102-54-5; $[CpCr(NO)_2(CH_3CN)]PF_6$, 74924-59-7; $CpCr(NO)_2Cl$, 12071-51-1; $[CpMo(NO)_2PPh_3]BF_4$, 111469-48-8; $CpMo(NO)_2Et$, 57034-47-6; $CpW(NO)_2Et$, 87189-91-1; $[Cp_2Co][CpMo(NO)_2Et]$, 111409-66-6; $[Cp_2Fe]BF_4$, 1282-37-7.

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Reaction of Organoboranes with Olefinic α,β-Unsaturated Nitro Compounds

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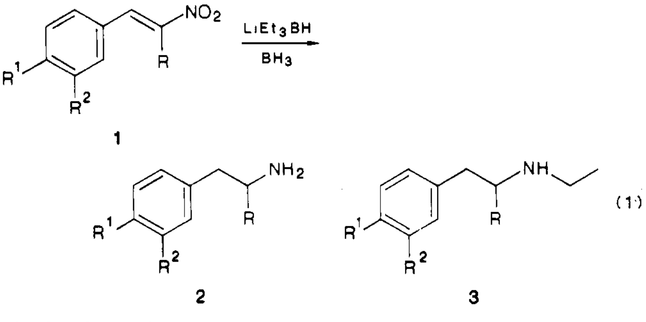
The reaction of lithium triethylborohydride with nitroalkenes in the presence of borane results in the unexpected formation of *N*-ethylamine derivatives. Evidence supports a reaction sequence involving the 1,2-addition of triethylborane to a nitroso intermediate.

Introduction

α,β-Unsaturated nitroalkenes have proven to be versatile synthetic intermediates.[1] They react with a variety of reducing agents to yield nitroalkanes,[2] amines,[3] oximes,[4] ketones,[5] and hydroxylamines.[6] In the course of recent investigations involving the reaction of borohydrides with conjugated nitroalkenes, we noted the consistent formation of *N*-ethylamines as byproducts in reactions utilizing lithium triethylborohydride (eq 1). Interestingly, N-alkylated products were not produced when other alkylborohydrides were used.



Earlier studies had established that borohydride-catalyzed, borane reductions of conjugated nitroalkenes proceed via *aci*-nitro derivatives which are then further reduced to hydroxylamines and, finally, amines.[7] Alternatively the *aci*-nitro intermediates may be hydrolyzed to carbonyl compounds. The observation that N-ethylation products are formed leads to the conclusion that a Grignard-like addition reaction between an alkylborane and a nitroso intermediate can also occur.[8]

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[8] The formation of *N*- hydroxyldialkylamines via a Grignard-like reaction between a trialkylborane and nitrosoalkane has never been reported. Yashida and his co-workers observed the formation of trace quantities dicyclohexylamine when they reacted nitrosyl chloride with tricyclohexylborane, a product which, logically, could be derived from the corresponding *N*-hydroxyldicyclohexylamine. See: Yoshida, Z.; Ogushi, T.; Manabe, O.; Hiyama, H. *Tetrahedron Lett.* **1965**, 753. Okushi, T.; Manabe, O.; Hiyama, H.; Yoshida, Z. *Kogyo Kagaku Zasshi* **1965**, *68*, 1685.

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