

cycle of least squares, anisotropic thermal coefficients were refined for the non-hydrogen atoms and a group isotropic thermal parameter was varied for the hydrogen atoms.] Successful convergence was indicated by the maximum shift/error of 0.076 [0.006 for 2 and 0.001 for 3] in the last cycle. Final refinement parameters are given in Table II. The final difference Fourier map had no significant features. A final analysis of variance between observed and calculated structure factors showed a slight dependence on $\sin \theta$. [For 2 and 3, there were no apparent systematic errors among the final observed and calculated structure factors.]

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Supplementary Material Available: Tables of final atomic coordinates and anisotropic thermal parameters for 1, 2, and 3 and tables of calculated hydrogen atom positions for 1 and 3 (9 pages); listings of final observed and calculated structure factor amplitudes for 1, 2, and 3 (20 pages). Ordering information is given on any current masthead page.

Reduction Behavior of the Complexes $\text{Cp}'\text{M}(\text{NO})\text{X}_2$ ($\text{Cp}' = \text{Cp}$ ($\eta^5\text{-C}_5\text{H}_5$) or Cp^* ($\eta^5\text{-C}_5\text{Me}_5$); $\text{M} = \text{Mo}$ or W ; $\text{X} = \text{Cl}$, Br , or I): Synthesis and Characterization of the $[\text{Cp}'\text{Mo}(\text{NO})\text{X}_2]^-$ Radical Anions^{1,2}

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The reduction behavior of the title series of organometallic complexes has been investigated both by cyclic voltammetry and by chemical means. All the $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2$ complexes in CH_2Cl_2 undergo reversible one-electron reductions, the Cp^* derivatives being more difficult to reduce by ca. 0.2 V. On a preparative scale, these reductions are best effected by utilizing Cp_2Co in THF as the reducing agent. The resulting salts $[\text{Cp}_2\text{Co}]^+[\text{Cp}'\text{Mo}(\text{NO})\text{X}_2]^-$ are isolable in high yields as analytically pure, green to brown solids. The ESR spectra of solutions of these salts reveal that the extra electron density in the $[\text{Cp}'\text{Mo}(\text{NO})\text{X}_2]^-$ anions is not primarily localized in their Mo-NO linkages, as might have been expected. Rather, the ESR signals due to the unpaired electrons on the anions exhibit coupling either only to the molybdenum center ($\text{X} = \text{Cl}$ or I) or to both molybdenum and the halide ($\text{X} = \text{Br}$). The diiodo radical anions are relatively unstable in DMF and convert to $[\text{Cp}'\text{Mo}(\text{NO})\text{I}]_2$ via I^- loss. The congeneric tungsten complexes $\text{Cp}'\text{W}(\text{NO})\text{I}_2$ behave similarly upon the addition of an electron, converting to $[\text{Cp}'\text{W}(\text{NO})\text{I}]_2$ via *EC* mechanisms. On a preparative scale, $[\text{Cp}'\text{W}(\text{NO})\text{I}]_2$ is most cleanly synthesized by reacting equimolar amounts of $\text{Cp}'\text{W}(\text{NO})\text{I}_2$ and $\text{Cp}'\text{W}(\text{NO})(\text{CO})_2$ in refluxing toluene. Finally, ESR spectral evidence for the occurrence of single-electron transfer during the reactions of Grignard reagents RMgX with the $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2$ complexes has been obtained, these observations being of fundamental significance in so far as the successful syntheses of new $\text{Cp}'\text{Mo}(\text{NO})\text{R}_2$ compounds are concerned.

Introduction

Previous work in our laboratories has resulted in the preparation and characterization of several new classes of compounds containing the $\text{CpM}(\text{NO})$ group ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$; $\text{M} = \text{Mo}$ or W). Specifically, alkyl-,³ hydride,⁴ and diene-containing⁵ derivatives have been synthesized by

(1) Organometallic Nitrosyl Chemistry. 40. For part 39 see: Christensen, N. J.; Hunter, A. D.; Legzdins, P. *Organometallics*, in press.

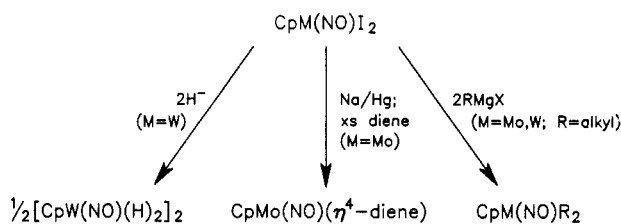
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Scheme I



utilizing the appropriate diiodo precursors, $\text{CpM}(\text{NO})\text{I}_2$,^{6,7} as summarized in Scheme I. From a synthetic point of

(6) The dihalo nitrosyl complexes $\text{Cp}'\text{M}(\text{NO})\text{X}_2$ ($\text{Cp}' = \text{Cp}$ or Cp^* ; $\text{M} = \text{Mo}$ or W ; $\text{X} = \text{Cl}$, Br , or I) possess either monomeric^{6a} or halide-bridged^{7b} dimeric molecular structures in the solid state. On the other hand, the physical and chemical properties of these compounds in solutions are most consistent with their existing as solvated monomers. Consequently, in this paper they are represented exclusively by their monomeric formulae.

view, the most curious aspect of these transformations is that they are highly specific for the product complexes indicated and cannot be readily extended to encompass congeneric derivatives. For instance, the analogous hydride complexes of molybdenum, diene complexes of tungsten, and 16-electron diaryl complexes of both molybdenum and tungsten cannot be prepared in a manner analogous to that depicted above. More perplexing is the fact that the above conversions cannot always be utilized to synthesize the Cp* ($\eta^5\text{-C}_5\text{Me}_5$) analogues of the indicated Cp complexes in an equally facile manner. For example, representative Cp*Mo(NO)R₂ (R = alkyl) compounds can only be obtained in marginally acceptable yields when Cp*Mo(NO)I₂ is employed as the synthetic precursor.⁸

With a view to gaining some insight into why these iodo nitrosyl precursor complexes exhibit such diverse reactivity patterns toward nucleophiles, we undertook an electrochemical investigation of their reduction behavior. [A similar study of organometallic complexes containing the related CpM(NO)₂ groups has enabled us to understand equally perplexing aspects of the chemistry of the dinutrosyl family of compounds.⁹ Eventually, the present study was extended to include an extended series of Cp'M(NO)X₂ complexes (Cp' = Cp or Cp*; M = Mo or W; X = Cl, Br, or I).⁶ In this paper we present the complete results of these electrochemical investigations that have subsequently led to the development of reliable synthetic routes to isolable [Cp'M(NO)X₂]⁻ radical anions and to unequivocal evidence for the occurrence of initial single-electron-transfer (SET) processes during the reactions of the dihalo nitrosyl complexes with representative Grignard reagents.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anhydrous conditions in an atmosphere of prepurified dinitrogen. General procedures routinely employed in these laboratories have been described in detail previously.^{4a} The requisite reagents CpMo(NO)X₂ (X = Cl, Br, or I),¹⁰ [CpMo(NO)I]₂,¹¹ and Cp'W(NO)I₂ (Cp' = Cp¹² or Cp*^{7a}) were prepared by the published procedures. The Cp*Mo(NO)X₂ (X = Cl, Br, or I^{3a}) reactants were prepared by treating Cp*Mo(NO)(CO)₂^{13b} with a stoichiometric amount of elemental X₂ in a manner similar to that employed for the preparation of their perhydro analogues, and their purity was verified by elemental analyses.

IR spectra were recorded on a Nicolet 5DX FT-IR instrument internally calibrated with a He/Ne laser. All ¹H and ¹³C NMR spectra were obtained on a Varian Associates XL-300 or Bruker WP-80 spectrometer, and the chemical shifts of the observed resonances are reported in parts per million downfield from Me₄Si. Low-resolution mass spectra were recorded at 70 eV on an Atlas CH4B or a Kratos MS50 spectrometer using the direct-insertion method.

Electrochemical Measurements. The customary methodology employed during cyclic voltammetry (CV) and bulk electrolysis studies in these laboratories has been outlined in detail elsewhere.¹⁴ The triangular waveform potential required during these studies was obtained with a Wavetek Model 143 function

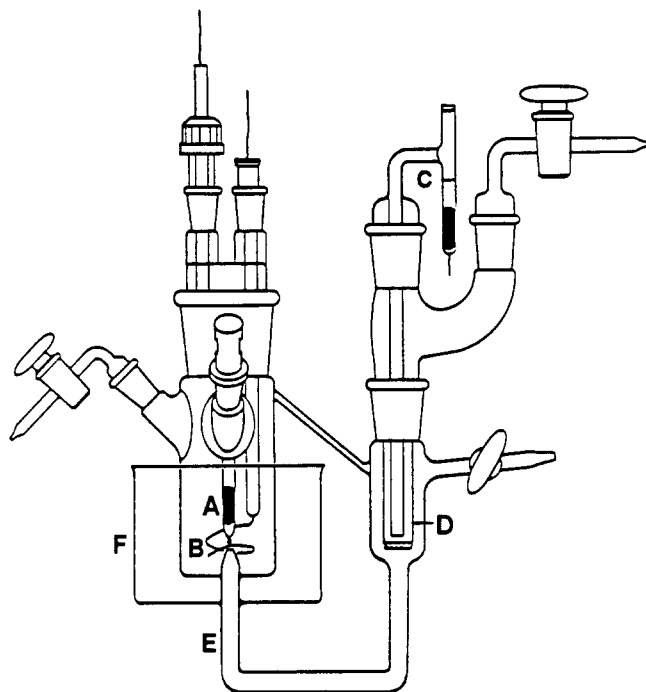


Figure 1. The low-temperature cyclic voltammetry cell: (A) platinum-bead working electrode with mercury contact; (B) platinum wire spiral auxiliary electrode; (C) aqueous saturated calomel reference electrode; (D) fine-fritted reference electrode holder; (E) Luggin probe; (F) glass jacket for coolant.

generator in conjunction with a unity-gain inverter (± 15 V, 50 mA). Cyclic voltammograms were recorded on a Hewlett-Packard Model 7090A X-Y recorder, and a Fisher Model 5000 strip-chart recorder was used for the current-time plots during bulk electrolysis experiments. The electrochemical cell employed for cyclic voltammetry at low temperatures is a modification of a previously described cell¹⁴ and is shown in Figure 1. All potentials are reported versus the aqueous saturated calomel electrode (SCE), and E° values were determined as the average of cathodic and anodic peak potentials, i.e. $[(E_{p,c} + E_{p,a})/2]$. Compensation for iR drop in potential measurements was not employed during this work.

The solutions employed during CV studies were typically $(5\text{--}7) \times 10^{-4}$ M in the organometallic complex and 0.1 M in $[n\text{-Bu}_4\text{N}]\text{PF}_6$, and they were maintained under an atmosphere of N₂. Under the experimental conditions employed throughout this work, the Cp₂Fe/Cp₂Fe⁺ couple in CH₂Cl₂ occurs at $E^{\circ} = +0.46$ V versus SCE, the ratio of the cathodic and anodic peak currents¹⁵ ($i_{p,c}/i_{p,a}$) being 1. In addition, the cathodic peak current ($i_{p,c}$) increases linearly with the square root of scan rate (i.e. $v^{1/2}$),¹⁶ and the separation of the cathodic and anodic peak potentials (ΔE) increases somewhat with increasing scan rate, e.g. from 67 mV at 0.14 V s⁻¹ to 78 mV at 0.28 V s⁻¹. Redox couples that exhibited features similar to that of the reference Cp₂Fe/Cp₂Fe⁺ couple (which is known to be highly reversible¹⁷ at the scan rates employed during this work) were thus considered to be reversible. In general, the reversible processes observed during the CV experiments were first investigated in detail before any irreversible features were studied.

ESR Measurements. Dimethylformamide (DMF) was dried over BaO overnight, filtered through Celite, and then deaerated with N₂ prior to use. Tetrahydrofuran (THF) was distilled from sodium benzophenone and deaerated with N₂. The samples for

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(16) The presence of diffusion control was investigated for all redox processes evident during the cyclic voltammetry experiments by monitoring the behavior of peak currents (i_p) as a function of scan rate (v) over at least 1 order of magnitude in scan rate. All reversible couples observed during this study exhibited a linear variation of i_p with $v^{1/2}$ and not with v .

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Table I. Ambient-Temperature Cyclic Voltammetry Data for the Reduction of Dihalo Nitrosyl Complexes of Molybdenum^a

compound	scan rate ν , V s ⁻¹	E° , ^b V	ΔE , ^c mV	$i_{p,a}/i_{p,c}$ ^d	comments
CpMo(NO)Cl ₂	0.06	-0.10	65	0.85	
	0.13	-0.10	71	0.92	
Cp*Mo(NO)Cl ₂	0.06	-0.35	73	1.00	
	0.25	-0.35	89	1.00	
CpMo(NO)Br ₂	0.09	-0.05	67	0.86	second weak wave at $E_{p,c} = -1.73$ V (0.51 V s ⁻¹)
	0.21	-0.05	89	0.91	
CpMo(NO)Br ₂ ^e	0.14	-0.12	72	0.94	second weak wave at $E_{p,c} = -1.72$ V (0.51 V s ⁻¹)
Cp*Mo(NO)Br ₂	0.06	-0.29	69	0.90	
	0.24	-0.29	80	1.00	
CpMo(NO)I ₂	0.12	-0.04	65	0.93	second weak wave at $E_{p,c} = -1.60$ V (0.44 V s ⁻¹)
	0.24	-0.04	68	0.99	
CpMo(NO)I ₂ ^e	0.24	-0.13	80	0.98	second weak wave at $E_{p,c} = -1.61$ V
CpMo(NO)I ₂ ^f	0.07	-0.21	64	0.90	smaller waves at -1.01 and -1.78 V (0.13 V s ⁻¹)
Cp*Mo(NO)I ₂	0.05	-0.25	57	0.98	second wave at $E_{p,c} = -1.79$ V (0.55 V s ⁻¹)
CpMo(NO)I ₂ (PMePh ₂)	0.12	-0.98	60	0.90	

^a In CH₂Cl₂/0.1 M [*n*-Bu₄N]PF₆ at a platinum-bead electrode unless otherwise noted. Potentials are measured vs SCE. ^b Defined as the average of the cathodic and anodic peak potentials. ^c Defined as the difference between anodic and cathodic peak potentials, i.e. $|E_{p,a} - E_{p,c}|$ in mV. ^d Ratio of anodic peak current to cathodic peak current.¹⁵ ^e In THF. ^f In CH₃CN.

ESR measurements were prepared in a Vacuum Atmospheres Model HE-43 drybox by dissolving a weighed amount of the organometallic complex in enough DMF or THF to make a 5×10^{-5} M solution. A portion of this solution was then transferred by syringe into a sealed melting-point capillary tube to a height of ca. 5 mm. The open end of the capillary tube was then sealed with silicone grease (Dow Corning, high vacuum), and the X-band ESR spectrum of the sample was recorded by using the spectrometer and interfaced computer system described by Phillips and Herring.¹⁸

Reactions of Cp'Mo(NO)X₂ (Cp' = Cp or Cp*; X = Cl, Br, or I) with Cobaltocene. All of these reactions were performed in a similar manner with the procedures varying slightly to obtain the desired product complexes in optimum yields. Representative examples of these procedures are presented below.

Preparation of [Cp₂Co][CpMo(NO)Cl₂]. To a rapidly stirred, green solution of CpMo(NO)Cl₂ (0.22 g, 0.84 mmol) in THF (30 mL) at room temperature was added solid Cp₂Co¹⁹ (0.16 g, 0.83 mmol). A green precipitate formed during 2 min, and the supernatant solution became light brown in color. The precipitate was collected by filtration, washed with THF (2 \times 5 mL), and dried in vacuo (5×10^{-3} mm) at 20 °C for 1 h to obtain 0.31 g (83% yield) of [Cp₂Co][CpMo(NO)Cl₂] as a green, microcrystalline solid.

Anal. Calcd for C₁₅H₁₅ONCl₂MoCo: C, 39.91; H, 3.33; N, 3.10. Found: C, 40.08; H, 3.41; N, 2.91. IR (Nujol mull): ν_{NO} 1552 (s) cm⁻¹; also 3076 (m), 1640 (m), 1527 (sh), 1413 (m), 1063 (w), 1010 (m), 1004 (sh) 864 (m), 805 (m) cm⁻¹.

Preparations of [Cp₂Co][Cp'Mo(NO)X₂] (Cp' = Cp or Cp*; X = Cl, Br, or I). These complexes were synthesized and isolated in a manner similar to that outlined in the preceding paragraph. On occasion, an equal volume of Et₂O was added to the final reaction mixture to ensure complete precipitation of the desired complex. The product salts obtained in this fashion and their properties are summarized below.

[Cp₂Co][Cp*Mo(NO)Cl₂]: green solid; 80% yield. Anal. Calcd for C₂₀H₂₅ONCl₂MoCo: C, 46.07; H, 4.80; N, 2.69. Found: C, 46.13; H, 4.92; N, 2.67. IR (Nujol mull): ν_{NO} 1523 (s) cm⁻¹; also 3091 (m), 1610 (w), 1415 (m), 1063 (w), 1009 (w), 864 (m), 805 (m) cm⁻¹.

[Cp₂Co][CpMo(NO)Br₂]: green solid; 87% yield. Anal. Calcd for C₁₆H₁₅ONBr₂MoCo: C, 33.33; H, 2.78; N, 2.59. Found: C, 33.44; H, 2.95; N, 2.45. IR (Nujol mull): ν_{NO} 1557 (s) cm⁻¹; also 3090 (m), 1652 (w), 1414 (m), 1063 (w), 1009 (m), 862 (m), 804 (m) cm⁻¹.

[Cp₂Co][Cp*Mo(NO)Br₂]: green solid, 82% yield. Anal. Calcd for C₂₀H₂₅ONBr₂MoCo: C, 39.34; H, 4.10; N, 2.30. Found: C, 39.70; H, 4.09; N, 2.20. IR (Nujol mull): ν_{NO} 1534 (s) cm⁻¹; also 3086 (m), 1638 (w), 1414 (m), 1065 (w), 1009 (m), 864 (m) cm⁻¹.

[Cp₂Co][CpMo(NO)I₂]: brown solid; 84% yield. Anal. Calcd for C₁₅H₁₅ONI₂MoCo: C, 28.39; H, 2.37; N, 2.21. Found: C, 28.30; H, 2.36; N, 2.38. IR (Nujol mull): ν_{NO} 1557 (s) cm⁻¹; also 3065 (w), 1653 (w), 1412 (m), 1059 (m), 1007 (m), 999 (sh), 862 (m), 804 (m) cm⁻¹. Attempts to obtain single crystals of this complex by crystallization from THF/Et₂O at -20 °C only resulted in the formation of black microcrystals of [CpMo(NO)I]₂ which was readily identifiable by its characteristic IR and mass spectra¹¹ and elemental analyses.

[Cp₂Co][Cp*Mo(NO)I₂]: green solid; 70% yield. Anal. Calcd for C₂₀H₂₅ONI₂MoCo: C, 34.09; H, 2.84; N, 1.99. Found: C, 33.76; H, 3.05; N, 1.89. IR (Nujol mull): ν_{NO} 1541 (s) cm⁻¹; also 3083 (w), 1636 (w), 1412 (m), 1113 (w), 1007 (w), 862 (m) cm⁻¹.

Oxidations of [Cp₂Co][Cp'Mo(NO)X₂] (Cp' = Cp or Cp*; X = Cl, Br, or I). As judged by IR spectroscopic monitoring, treatment of all the radical anion complexes with an equimolar amount of [Cp₂Fe]BF₄ in CH₃CN resulted in their clean reconversion to their neutral dihalo precursors.

Attempted Synthesis of [CpFe(η^5 -C₆H₆)] [CpW(NO)-(CH₂SiMe₃)₂]. To a vigorously stirred, violet solution of CpW(NO)(CH₂SiMe₃)₂³ (0.15 g, 0.33 mmol) in Et₂O (20 mL) was added a filtered Et₂O solution (20 mL) of CpFe(η^5 -C₆Me₆)^{20,21} (0.093 g, 0.33 mmol). The reaction mixture became red-brown after 1 min and was stirred for 30 min to ensure complete reaction. Removal of solvent from the final reaction mixture under reduced pressure afforded an intractable red tar.

Preparation of [Cp*W(NO)I₂]. An orange toluene solution (50 mL) of Cp*W(NO)(CO)₂ (1.04 g, 2.57 mmol) was treated with solid Cp*W(NO)I₂ (1.55 g, 2.57 mmol) whereupon it became green in color. The green solution was then refluxed for 2 h during which time its color darkened. The final reaction mixture was allowed to cool to room temperature and was filtered. The filtrate was stored at -20 °C for 3 days to induce the precipitation of a dark green crystalline solid. This solid was collected by filtration, washed with cold toluene (2 \times 5 mL), and dried at 5×10^{-3} mm and 20 °C overnight to obtain 0.89 g (36% yield) of [Cp*W(NO)I]₂ as air-sensitive green crystals.

Anal. Calcd for C₂₀H₃₀O₂N₂I₂W₂: C, 25.21; H, 3.15; N, 2.94. Found: C, 25.29; H, 3.21; N, 2.86. IR (Nujol mull): ν_{NO} 1597 (s) cm⁻¹. ¹H NMR (C₆D₆): δ 1.98 (s). ¹³C{¹H} NMR (C₆D₆): δ 118.68, 114.84, 12.48, 11.57. Low-resolution mass spectrum (probe temperature 120 °C): *m/z* 952 (P⁺).

Results and Discussion

Cyclic Voltammetry Studies of the Molybdenum Complexes. The behavior of all the Cp'Mo(NO)X₂ complexes (Cp' = Cp or Cp*; X = Cl, Br, or I) upon the addition of electrons is quite similar, as evidenced by the

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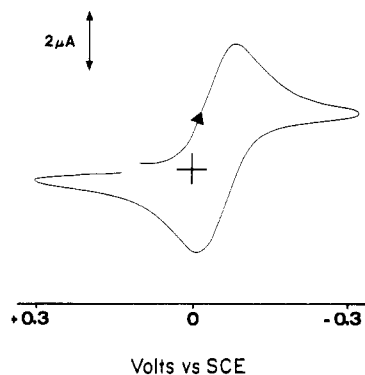


Figure 2. Ambient-temperature cyclic voltammogram of 5×10^{-4} M $\text{CpMo}(\text{NO})\text{I}_2$ in CH_2Cl_2 containing 0.1 M $[\text{n-Bu}_4\text{N}]\text{PF}_6$ measured at a platinum-bead electrode at a scan rate of 0.24 V s^{-1} .

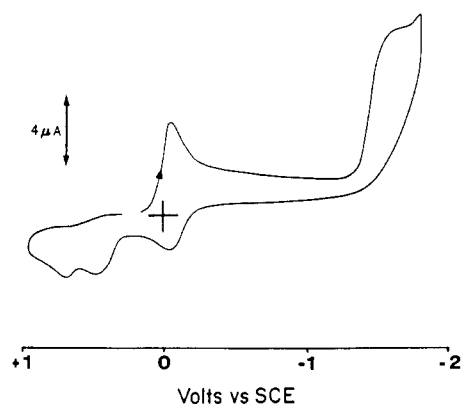
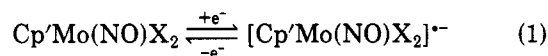


Figure 3. Ambient-temperature cyclic voltammogram of 5×10^{-4} M $\text{CpMo}(\text{NO})\text{I}_2$ in CH_2Cl_2 containing 0.1 M $[\text{n-Bu}_4\text{N}]\text{PF}_6$ measured at a platinum-bead electrode at a scan rate of 0.44 V s^{-1} .

electrochemical data for the reductions of the compounds summarized in Table I.²² All the $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2$ species in CH_2Cl_2 undergo very facile one-electron reductions that can be represented by eq 1. In general, the penta-



methylcyclopentadienyl (Cp^*) derivatives are more difficult to reduce (by ca. 0.2 V) than their perhydro analogues, an observation consistent with the expectation that the former compounds should have the greater electron density at the metal center.²¹ The electrochemical behavior of $\text{CpMo}(\text{NO})\text{I}_2$ is representative of this entire class of complexes, and hence it will now be considered in some detail as an illustrative example.

A cyclic voltammogram of $\text{CpMo}(\text{NO})\text{I}_2$ in CH_2Cl_2 is displayed in Figure 2. Under the experimental conditions employed throughout this study, this compound exhibits a reversible one-electron reduction at $E^{\text{D}^\circ} = -0.04 \text{ V}$ vs SCE. At a scan rate (v) of 0.12 V s^{-1} , the separation in peak potentials (ΔE) is 65 mV, and the anodic to cathodic peak current ratio ($i_{\text{p,a}}/i_{\text{p,c}}$)¹⁵ is 0.93. The $i_{\text{p,a}}/i_{\text{p,c}}$ value increases with an increase in scan rate from 0.93 at 0.12 V s^{-1} to 0.99 at 0.24 V s^{-1} . Furthermore, $i_{\text{p,c}}$ varies linearly with $v^{1/2}$ over the scan-rate range employed, and the peak potentials separate somewhat with increasing scan rate, being 65 mV at 0.12 V s^{-1} and 68 mV at 0.24 V s^{-1} . Bulk electrolysis of a THF solution of $\text{CpMo}(\text{NO})\text{I}_2$ consumes 1 F/mol of the monomeric complex. All of these facts are consistent

(22) All the $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2$ complexes undergo irreversible oxidations which were not investigated further at the present time. Only the oxidations of $[\text{CpMo}(\text{NO})\text{I}_2]$ were examined as part of the current study.

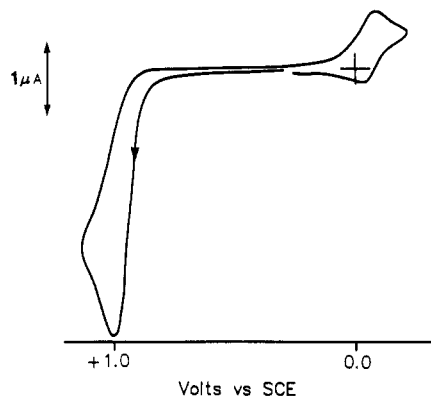
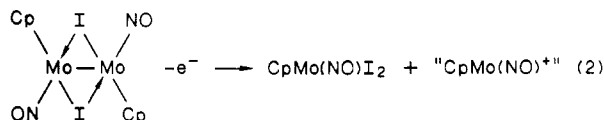


Figure 4. Ambient-temperature cyclic voltammogram of 5×10^{-4} M $[\text{CpMo}(\text{NO})\text{I}_2]$ in CH_2Cl_2 containing 0.1 M $[\text{n-Bu}_4\text{N}]\text{PF}_6$ measured at a platinum-bead electrode at a scan rate of 0.14 V s^{-1} .

with the stoichiometry of the reduction of the 16-electron $\text{CpMo}(\text{NO})\text{I}_2$ species being as indicated in eq 1 when $\text{Cp}' = \text{Cp}$ and $\text{X} = \text{I}$. As shown in Figure 3, if the scan is extended to the solvent limit (ca. -2 V), a second reduction wave is evident at $E_{\text{p,c}} = -1.60 \text{ V}$ (0.44 V s^{-1}) which gives rise to corresponding anodic peaks (at $+0.46$ and $+0.69 \text{ V}$) reflecting the release of I^- into the solution.²³ This second reduction wave is attributed to $[\text{CpMo}(\text{NO})\text{I}_2]^-$ which arises from the decomposition of the initially formed $[\text{CpMo}(\text{NO})\text{I}_2]^-$ radical anion.²⁴ This assignment is confirmed by the fact that a cyclic voltammogram of authentic $[\text{CpMo}(\text{NO})\text{I}_2]$ (recorded under the same experimental conditions) exhibits a single irreversible reduction peak at -1.60 V .

Interestingly, oxidation of $[\text{CpMo}(\text{NO})\text{I}_2]$ results in heterolytic cleavage of the $\text{Mo}(\mu\text{-I})_2\text{Mo}$ unit to regenerate $\text{CpMo}(\text{NO})\text{I}_2$ as summarized in eq 2, the cyclic voltam-



gram indicating this particular chemical transformation being displayed in Figure 4. Thus, when the anodic scan is reversed after the oxidation peak at $+1.05 \text{ V}$, a reversible redox couple is observable at -0.04 V which reflects the formation of $\text{CpMo}(\text{NO})\text{I}_2$ (vide supra). The formally 13-electron $\text{CpMo}(\text{NO})^+$ byproduct of reaction 2 probably decomposes in the absence of any appropriate trapping ligands. The lower $i_{\text{p,a}}/i_{\text{p,c}}$ ratios of the redox couples exhibited by the other $\text{Cp}'\text{Mo}(\text{NO})\text{X}_2$ complexes upon reduction at low scan rates and the observation (at least for some of these complexes, Table I) of second reduction waves at more negative potentials are features consistent with the initially formed $[\text{Cp}'\text{Mo}(\text{NO})\text{X}_2]^-$ radical anions undergoing similar slow decompositions to their respective $[\text{Cp}'\text{Mo}(\text{NO})\text{X}]_2$ monohalo dimers.²⁵

Preparation of the $[\text{Cp}'\text{Mo}(\text{NO})\text{X}_2]^-$ Radical Anion Complexes. The reductions of the nitrosyl complexes summarized in eq 1 are best effected on a preparative scale by utilizing cobaltocene, a moderately potent, one-electron

(23) These anodic peaks are enhanced by the addition of $[\text{n-Bu}_4\text{N}]\text{I}$ and are thus assigned to the oxidation of I^- and I_3^- ; see: Samuel, E.; Guery, D.; Vedel, J. *J. Organomet. Chem.* 1984, 263, C43.

(24) It is unlikely that this peak is due to further reduction of the radical anion to the corresponding dianion since the current value is so low. Nevertheless, it should be noted that it has been reported that $[\text{Cp}_2\text{ZrI}_2]^-$ is indeed reducible to its dianion; see: El Murr, N.; Chaloyard, A.; Tirouflet, J. *J. Chem. Soc., Chem. Commun.* 1980, 446.

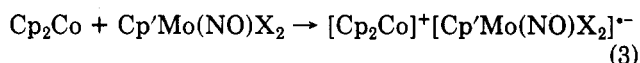
(25) Other examples of such halide loss are known; see: Connelly, N. G.; Geiger, W. E. *Adv. Organomet. Chem.* 1984, 23, 1.

Table II. Comparison of the Nitrosyl-Stretching Frequencies of the New 17-Electron Radical Anion Complexes with Their Neutral Precursors^a

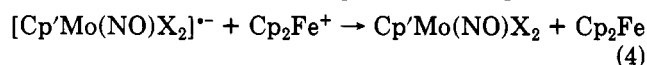
complex	$\nu_{\text{NO}}, \text{cm}^{-1}$					
	X = Cl		X = Br		X = I	
	Cp' = Cp	Cp' = Cp*	Cp' = Cp	Cp' = Cp*	Cp' = Cp	Cp' = Cp*
Cp'Mo(NO)X ₂	1665	1647	1670 ^b	1649	1670 ^b	1663
[Cp'Mo(NO)X ₂] ^{-c}	1552	1523	1557	1534	1557	1541

^a As Nujol mulls unless indicated otherwise. ^b As KBr pellets. ^c As cobalticinium salts.

reductant.^{26,27} When solid Cp₂Co is added to THF solutions of the Cp'Mo(NO)X₂ compounds, reaction 3 occurs,



the 17-electron [Cp'Mo(NO)X₂]⁻ radical anions precipitating as their cobalticinium salts. Isolable by filtration, these radical anion salts are obtainable in high yields as analytically pure, green to brown solids that are very soluble in DMF, slightly soluble in THF, and insoluble in Et₂O. These salts are air- and moisture-sensitive, especially in solutions. As solids, the chloro and bromo derivatives are thermally stable at -10 °C under N₂ for at least 3 weeks, but the congeneric iodo complexes decompose in less than 2 days even at -20 °C. Not surprisingly, treatment of the various [Cp'Mo(NO)X₂]⁻ complexes in CH₃CN with oxidants such as [Cp₂Fe]BF₄²⁸ cleanly regenerates the neutral dihalo precursor complexes, i.e.



The nitrosyl-stretching frequencies exhibited by the various [Cp'Mo(NO)X₂]⁻ radical anions are listed in Table II where they are compared with the analogous IR data of their neutral precursors. As expected, a decrease in ν_{NO} of ca. 120 cm⁻¹ occurs in going from the neutral to the corresponding anionic species, a manifestation of the increased back-bonding to the nitrosyl ligands extant in the latter complexes.²⁹ Nevertheless, the ν_{NO} values exhibited by the anions are still consistent with their nitrosyl ligands being linear and terminal. Indeed, the nitrosyl-stretching frequencies of the anionic, 17-electron [Cp'Mo(NO)X₂]⁻ complexes are in the same range as those of the neutral, 18-electron CpMo(NO)L₂ compounds (L = phosphine or phosphite).³¹ For instance, [Cp₂Co][CpM(NO)I₂] displays a ν_{NO} of 1570 cm⁻¹ in THF, a value quite comparable to the 1568 cm⁻¹ exhibited by CpMo(NO)(Ph₂PCH₂CH₂PPh₂) in the same solvent.³¹ Consequently, it appears that the increased back-donation of electron density to the nitrosyl ligands in the [Cp'Mo(NO)X₂]⁻ complexes is not sufficiently great to cause these ligands to adopt a bent coordination geometry. Consistently, Fenske-Hall molecular orbital calculations suggest that the lowest unoccupied molecular orbital (LUMO) of the related 16-electron model

(26) Morris, M. D.; Kok, G. L. In *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1979; Vol. 13, Chapter 1.

(27) Under the experimental conditions employed throughout this study, the Cp₂Co/Cp₂Co⁺ couple in CH₂Cl₂ occurs at -0.82 V vs SCE. This E⁰ value is sufficiently negative of the first reduction features exhibited by the dihalo nitrosyl complexes (Table I) and yet sufficiently positive of the second reduction features to make cobaltocene the ideal reducing agent for effecting the desired single-electron transfer on a preparative scale.

(28) The Cp₂Fe⁺ cation is a well-known one-electron oxidant in organometallic chemistry; see: Schumann, H. *J. Organomet. Chem.* **1986**, *304*, 341.

(29) For comparison, a decrease in ν_{NO} of 180–200 cm⁻¹ occurs upon reduction of the dinitrosyl complexes CpM(NO)₂X (M = Mo or W) to their corresponding 19-electron monoanions.³⁰

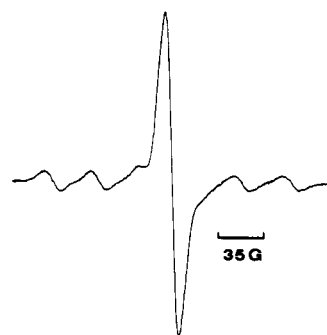
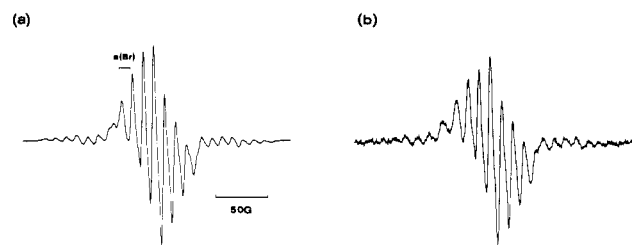
(30) Legzdins, P.; Wassink, B. *Organometallics* **1988**, *7*, 482.

(31) Hunter, A. D.; Legzdins, P. *Organometallics* **1986**, *5*, 1001.

Table III. Electron Spin Resonance Data for the [Cp'Mo(NO)X₂]⁻ Radical Anion Complexes^{a,b}

complex	g value	temp, °C
[CpMo(NO)Cl ₂] ⁻	1.9819	14.5
[Cp*Mo(NO)Cl ₂] ⁻	1.9840	22.6
[CpMo(NO)Br ₂] ⁻	2.0103	22.7
[Cp*Mo(NO)Br ₂] ⁻	2.0092	22.8
[CpMo(NO)I ₂] ^{-c}	2.0596	18.5
[Cp*Mo(NO)I ₂] ^{-c}	2.0582	19.9

^a As cobalticinium salts. ^b As DMF solutions unless indicated otherwise. ^c As THF solutions.

**Figure 5.** X-Band ESR spectrum of [Cp₂Co][CpMo(NO)Cl₂] in DMF at 14.5 °C.**Figure 6.** (a) X-Band ESR spectrum of [Cp₂Co][Cp*Mo(NO)Br₂] in DMF at 22.8 °C. (b) X-Band ESR spectrum of an equimolar mixture of Me₃SiCH₂MgCl and Cp*Mo(NO)Br₂ in DMF at 20 °C (g = 2.0106).

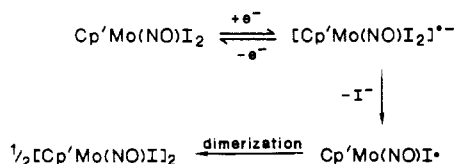
compound CpMo(NO)Me₂ is localized on the metal center and contains no NO 2π character.³ Therefore, reduction of the dimethyl complex to its 17-electron [CpMo(NO)Me₂]⁻ radical anion is also not expected to alter the mode of coordination of the nitrosyl ligand in the process. In contrast, the added electron density in [CpMo(NO)(CO)₂]⁻ (obtained by electroreduction of its 18-electron precursor) is largely localized in its Mo–NO group, a feature that is believed to result in bending of the Mo–NO linkage.³² That the extra electron density in the [CpMo(NO)X₂]⁻ anions is not primarily localized in their Mo–NO linkages is also indicated by their ESR spectra.

The ESR data for all six radical anion complexes synthesized during this study are collected in Table III. The observed change in the g value reflects increasing spin-orbit coupling for the halogens which suggests in turn that

(32) Geiger, W. E.; Rieger, P. H.; Tulyathan, B.; Rausch, M. D. *J. Am. Chem. Soc.* **1984**, *106*, 7000.

the overall electron distribution is quite similar in all the molecules. The ESR spectra for the dichloro and diiodo species are similar, each consisting of a single, strong central resonance flanked by molybdenum satellite signals. The spectrum of $[\text{Cp}_2\text{Co}][\text{CpMo}(\text{NO})\text{Cl}_2]$ is shown in Figure 5 as a representative example of these spectra. The central resonance in this spectrum ($g = 1.9819$) clearly displays five broad satellite signals due to ^{95}Mo and ^{97}Mo hyperfine coupling ($I = 5/2$, natural abundance 15.9% and 9.6%, respectively).³³ No ^{14}N or ^1H hyperfine coupling is evident in this spectrum or any of the other spectra, the first observation indicating the minimal delocalization of the extra electron density onto the nitrosyl ligands of the radical anions. The coupling to molybdenum is approximately 35 G indicating that roughly 3% of the extra electron density is localized in s-type orbitals on the metal center. In contrast to the ESR spectra displayed by the dichloro and diiodo anions, those of the dibromo analogues do exhibit halide hyperfine interactions. For example, the ESR spectrum of $[\text{Cp}_2\text{Co}][\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2]$ in DMF (shown in Figure 6a) consists of a 7-line central pattern (1:2:3:4:3:2:1) reflecting coupling of the unpaired electron to two Br nuclei ($I = 3/2$; ^{79}Br , 50.54% natural abundance; ^{81}Br , 49.46% natural abundance; $a_{\text{Br}} = 10.4$ G).³⁴ Nevertheless, the observed coupling to Br only corresponds to approximately 0.1% of the unpaired electron density being localized in s-type orbitals on the halide ligand. The fact that the ESR spectra of all the radical anions exhibit such small isotropic coupling thus suggests that the odd electron is primarily localized in a π -type orbital, the small couplings being due to spin polarization of s-type orbitals. However, confirmation of this view must await a detailed molecular orbital analysis of these species. The spectrum of the perhydrocyclopentadienyl analogue $[\text{Cp}_2\text{Co}][\text{CpMo}(\text{NO})\text{Br}_2]$ also exhibits a splitting pattern quite similar to that shown in Figure 6a. Like their dichloro analogues, these dibromo radical anions persist in DMF solutions for at least 3 h at ambient temperatures.

In contrast, the diiodo species are relatively unstable in DMF. For instance, the ESR spectrum of $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2]^-$ as its cobalticinium salt in DMF initially displays a strong central resonance ($g = 2.0142$) and molybdenum satellite signals identical with those shown in Figure 5. Within an hour, the central signal is gradually replaced by a new, broad signal ($g = 2.064$) attributable to the neutral $\text{Cp}^*\text{Mo}(\text{NO})\text{I}^{\bullet}$ radical that results from the loss of I^- from the $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2]^-$ radical anion.³⁵ In other words, these observations are in accord with the cyclic voltammetry results (vide supra) and indicate the occurrence of the following sequence of reactions upon reduction of the $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$ complexes.



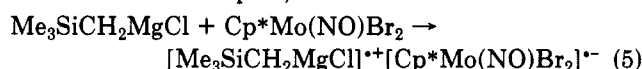
(33) The individual contributions of the ^{95}Mo and ^{97}Mo isotopes to this spectrum are unresolved, a not unusual feature; see: (a) Atherton, N. M.; Denti, G.; Ghedini, M.; Oliva, C. *J. Magn. Reson.* 1981, 43, 167. (b) Hanson, G. R.; Wilson, G. L.; Bailey, T. D.; Pilbrow, J. R.; Wedd, A. G. *J. Am. Chem. Soc.* 1987, 109, 2609.

(34) The magnitude of the hyperfine coupling in this complex is similar to that reported for the $[\text{Cp}_2\text{MoBr}_2]^+$ cation for which $a_{\text{Br}} = 15.8$ G; Cooper, R. L.; Green, M. L. H. *J. Chem. Soc. A* 1967, 1155.

(35) A similar inference has been drawn concerning the electrogeneration of the neutral $\text{HB}(\text{Me}_2\text{pz})\text{Mo}(\text{NO})\text{I}^{\bullet}$ radical ($\text{Me}_2\text{pz} = 3,5$ -dimethylpyrazolyl): Briggs, T. N.; Jones, C. J.; McCleverty, J. A.; Neaves, B. D.; El Murr, N.; Colquhoun, H. M. *J. Chem. Soc., Dalton Trans.* 1985, 1249.

Consistent with this inference is the fact that attempts to grow single crystals of $[\text{Cp}_2\text{Co}][\text{CpMo}(\text{NO})\text{I}_2]$ only result in the formation of $[\text{CpMo}(\text{NO})\text{I}]_2$ as the only nitrosyl-containing species. It is probable, therefore, that the analogous dichloro and dibromo radical anions eventually undergo similar conversions to their monohalo dimers, albeit at much slower rates than those observed for the diiodo species.³⁶

Evidence for the Occurrence of Single-Electron Transfer (SET) during the Reactions of Grignard Reagents with the $\text{Cp}^*\text{Mo}(\text{NO})\text{X}_2$ Complexes: Implications for the Improved Syntheses of the Corresponding $\text{Cp}^*\text{Mo}(\text{NO})\text{R}_2$ Compounds. An equimolar mixture of $\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2$ and $\text{Me}_3\text{SiCH}_2\text{MgCl}$ in DMF exhibits an ESR spectrum (shown in Figure 6b) that is qualitatively similar to that displayed by $[\text{Cp}_2\text{Co}][\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2]$ (Figure 6a). This observation provides direct evidence for the occurrence of (at least some)³⁷ single-electron transfer (SET) from the Grignard reagent to the dibromo complex,⁴⁰ i.e.



Reaction 5 is presumably facilitated by the relatively low potential required to effect the reduction of $\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2$ (Table I). The formation of the $[\text{Cp}^*\text{Mo}(\text{NO})\text{Br}_2]^{-\bullet}$ radical anion in this manner is of fundamental significance since very little mechanistic information concerning the reactions of Grignard reagents with organometallic halides is presently available.⁴¹ Furthermore, the occurrence of reaction 5 thus suggests that dihalo radical anions are the initial intermediates during the metathesis reactions between RMgCl and $\text{Cp}^*\text{Mo}(\text{NO})\text{X}_2$ to produce $\text{Cp}^*\text{Mo}(\text{NO})\text{R}_2$. For these conversions to proceed to completion, the intermediate radical anions must have a sufficiently long lifetime for the requisite R for X exchange to occur. Otherwise, the radical anions will simply decompose to other products (e.g. $[\text{Cp}^*\text{Mo}(\text{NO})\text{X}]_2$ etc.), and the desired organometallic product complexes will not be obtained. The relative stability of the $[\text{Cp}^*\text{Mo}(\text{NO})\text{X}_2]^{-\bullet}$ anions both in solutions (as ascertained by their ESR spectra) and in the solid state (as ascertained by their IR spectra) is $\text{X} = \text{Cl} > \text{Br} \gg \text{I}$. Consequently, this line of reasoning would suggest that the *dichloro* precursors should be used in order to effect the cleanest syntheses of the various $\text{Cp}^*\text{Mo}(\text{NO})\text{R}_2$ complexes. Gratifyingly, the

(36) In this connection, it is tempting to speculate that the very weak bands at ca. 1620 cm^{-1} evident in the Nujol mull IR spectra of the $[\text{Cp}_2\text{Co}][\text{Cp}^*\text{Mo}(\text{NO})\text{X}_2]$ complexes may well be due to the nitrosyl ligand of $\text{Cp}^*\text{Mo}(\text{NO})\text{X}^{\bullet}$, thereby reflecting partial decomposition of the radical anion in the solid state.

(37) Integration of the ESR signal to ascertain the concentration of the radical anion has not been performed. In related organic systems, such integrations (concentrations) have been found to be dependent on the nature of the organic group attached to magnesium³⁸ and even the purity of the elemental magnesium used to prepare the Grignard reagent.³⁹

(38) Ashby, E. C.; Goel, A. B. *J. Am. Chem. Soc.* 1981, 103, 4983.

(39) Ashby, E. C.; Wiesemann, T. L. *J. Am. Chem. Soc.* 1978, 100, 189.

(40) It is entirely possible that the $[\text{Me}_3\text{SiCH}_2\text{MgCl}]^{+\bullet}$ radical cation depicted in eq 6 is stabilized by some means such as solvation or aggregation: Maruyama, K.; Katagiri, T. *J. Am. Chem. Soc.* 1986, 108, 6263.

(41) RMgX species are known to function as SET agents to various organic compounds⁴² and to organic ligands attached to transition metals.⁴³

(42) Leading references dealing with this topic include: (a) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; Chapter 17. (b) Jones, P. R. *Adv. Organomet. Chem.* 1977, 15, 274. (c) Ashby, E. C.; Bowers, J.; Depriest, R. *Tetrahedron Lett.* 1980, 21, 3541. (d) Ashby, E. C. *Pure Appl. Chem.* 1980, 52, 545. (e) Reference 38.

(43) (a) Top, S.; Jaouen, G. *J. Organomet. Chem.* 1987, 336, 143. (b) Astruc, D. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Ed.; Wiley-Interscience: Chichester, 1987; Vol. 4, p 630.

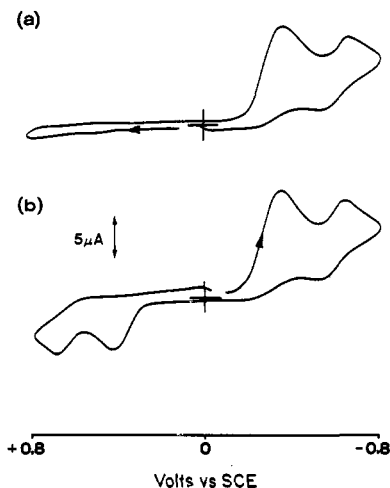
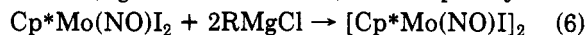


Figure 7. Ambient-temperature cyclic voltammograms of 5×10^{-4} M CpW(NO)I₂ in CH₂Cl₂ containing 0.1 M [n-Bu₄N]PF₆ measured at a platinum-bead electrode at a scan rate of 0.32 V s⁻¹: (a) scanning positive potentials first; (b) scanning negative potentials first.

results of preliminary preparative experiments in our laboratories (e.g. reactions 6 and 7) are completely in ac-



cord with this expectation, thereby providing new synthetic routes to previously inaccessible compounds (e.g. R = Ph^{7b} or CH₂SiMe₃⁸). In summary, it thus appears that sufficiently stable radical anion intermediates resulting from initial SET are a prerequisite for successfully effecting halide-for-organic group metathesis in these nitrosyl systems. In this connection, it should be noted that we have not as yet been successful in our attempts to effect monoalkylation of the dihalo precursors by employing RMgX or RLi reagents.⁴⁴ However, such monoalkylation of the cyclopentadienyl dibromo precursor has recently been achieved by employing the less nucleophilic Me₃Al as a gentler alkylating agent; [CpMo(NO)(Br)Me]₂ is the organometallic product obtained in good yield.⁴⁵

Cyclic Voltammetry Studies of the Tungsten Complexes. (A) Cp'W(NO)I₂ Compounds. Unlike the congeneric molybdenum species which exhibit similar reduction behavior in CH₂Cl₂ regardless of the nature of the cyclopentadienyl ligand, the Cp'W(NO)I₂ complexes display somewhat different electrochemical behavior when Cp' = Cp than when Cp' = Cp*. The cyclic voltammograms of CpW(NO)I₂ in CH₂Cl₂ are displayed in Figure 7 as a representative example. The experimental traces indicate that the complex undergoes an irreversible reduction at $E_{p,c} = -0.35$ V and a somewhat reversible reduction at $E_{o'} = -0.64$ V ($\Delta E = 88$ mV). The first reduction remains irreversible even at scan rates up to 15 V s⁻¹. The observed anodic peaks at positive potentials (Figure 7b) again reflect the release of I⁻ into the solution (vide supra), and these peaks due to the I⁻/I₃⁻ system are also evident if only the first reduction wave is passed in the scan shown in Figure 7b.

Cyclic voltammograms of the permethylcyclopentadienyl analogue Cp*W(NO)I₂ in CH₂Cl₂ are shown in Figure 8 for comparison. In this case, the first reduction of the complex now occurs at $E_{o'} = -0.52$ V and is largely re-

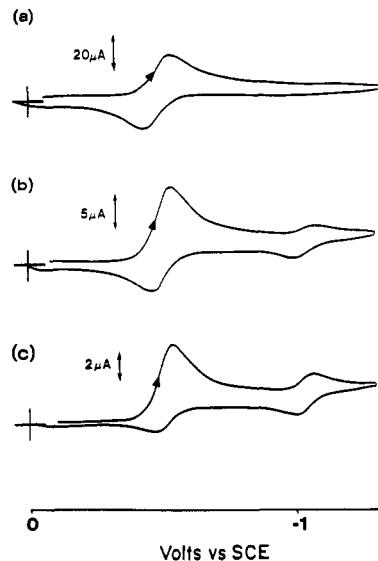


Figure 8. Ambient-temperature cyclic voltammograms of 5×10^{-4} M Cp*W(NO)I₂ in CH₂Cl₂ containing 0.1 M [n-Bu₄N]PF₆ measured at a platinum-bead electrode at the different scan rates (a) 2.64 V s⁻¹, (b) 0.53 V s⁻¹, and (c) 0.13 V s⁻¹.

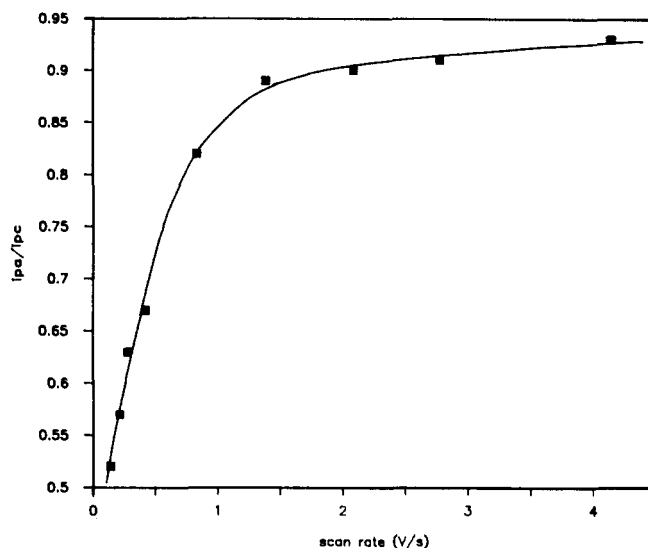


Figure 9. Plot of $i_{p,a}/i_{p,c}$ vs scan rate for the first reversible redox couple of Cp*W(NO)I₂ in CH₂Cl₂.

versible. The magnitude of the return anodic current for this couple is also greater at higher scan rates, as $i_{p,a}/i_{p,c}$ approaches unity. Furthermore, the intensity of the wave for the second redox couple at $E_{o'} = -1.06$ V is more enhanced at lower scan rates (Figure 8c) and is further enhanced by the addition of an authentic sample⁴⁶ of [Cp*W(NO)I]₂ to the cyclic voltammetry cell. Clearly, [Cp*W(NO)I]₂ is being generated (probably by the rapid dimerization of the 15-electron Cp*W(NO)I[•] radicals) as a result of the electrochemical reduction of Cp*W(NO)I₂. In this sense, this behavior of both Cp'W(NO)I₂ compounds parallels that exhibited by the analogous molybdenum complexes considered earlier; the one difference is that in the tungsten cases the [Cp'W(NO)I]₂ dimers so formed are then reversibly reduced, presumably to the corresponding bimetallic radical anions, i.e. [Cp'W(NO)-I]₂^{•-}.

(44) In this connection, it may be noted that *p*-tolyllithium is reported to react with the related HB(Me₂ppz)₃Mo(NO)I₂ to form a product complex formulated as HB(Me₂ppz)₃Mo(NO)I₂Li(OEt₂).³⁵

(45) Alegre, B.; de Jesús, E.; de Miguel, A. V.; Royo, P.; Lanfredi, A. M. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* 1988, 819.

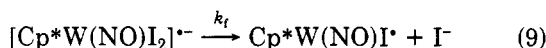
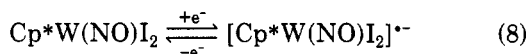
(46) As described in the Experimental Section of this paper, [Cp*W(NO)I]₂ may be synthesized independently by reacting equimolar quantities of Cp*W(NO)(CO)₂ and Cp*W(NO)I₂ in refluxing toluene. A similar method has been used previously to prepare [CpMo(NO)I]₂,¹¹ but the tungsten derivatives have remained unreported until now.

Table IV. Cyclic Voltammetry Data for the Electroreduction of Cp*W(NO)I₂ in CH₂Cl₂ at a Variety of Scan Rates at 19 °C

scan rate ν , V s ⁻¹	$E^{\circ'}$, V	current $i_{p,c}$, μ A	ΔE , mV	$i_{p,a}/i_{p,c}^a$	k_f^b , s ⁻¹
0.14	-0.52	5.52	58	0.52	0.94
0.21	-0.52	6.57	59	0.57	1.13
0.28	-0.52	7.58	64	0.63	1.16
0.42	-0.52	9.42	66	0.67	1.46
0.83	-0.52	12.8	68	0.82	1.25
1.38	-0.52	16.7	78	0.89	1.32

^a Ratio of anodic peak current to cathodic peak current.¹⁵ ^b Rate constant for the irreversible chemical reaction (C₁) following the reversible electron transfer (E_r); estimated from $i_{p,a}/i_{p,c}$ by using the method of Nicholson and Shain,^{47c} assuming a simple first-order reaction.

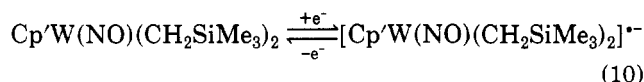
In the specific case of the pentamethylcyclopentadienyl-containing system, the overall process to generate [Cp*W(NO)I₂] via Cp*W(NO)I[•] may be viewed as a reversible electron transfer (E_r , eq 8) followed by an irreversible chemical reaction (C₁, eq 9).⁴⁷ The $i_{p,a}/i_{p,c}$



dependence on the scan rate for the E_r step (eq 8) is shown in Figure 9, and the observed trend of higher $i_{p,a}/i_{p,c}$ values (increased chemical reversibility) at greater scan rates is consistent with the occurrence of an E_r C₁ mechanism.⁴⁷ The variation of $i_{p,a}/i_{p,c}$ for the electroreduction as a function of the scan rate may then be used to estimate the rate constant (k_f in s⁻¹) for the coupled chemical reaction by employing the method of Nicholson and Shain.^{47c} If this is done, the results collected in Table IV are obtained. The calculated average value for k_f of 1.21 s⁻¹ at 19 °C is of the same order of magnitude as that reported previously for some ferrocenyl-containing complexes that display similar electrode processes.⁴⁸

As might have been expected, the stability of the electrogenerated [Cp*W(NO)I₂]^{-•} radical anion is greatest at lower temperatures, a fact clearly illustrated by the bar graphs presented in Figure 10.⁴⁹ For instance, the redox couple for the first reduction in THF at $E^{\circ'} = -0.49$ V (at a scan rate of 0.07 V s⁻¹) exhibits an $i_{p,a}/i_{p,c}$ value of 0.74 at -30 °C, whereas at 0 °C this ratio is only 0.46. These observations suggest that the [Cp*W(NO)I₂]^{-•} radical anion may well be chemically accessible at these lower temperatures.

(B) The Dialkyl Complexes Cp'W(NO)(CH₂SiMe₃)₂. Cyclic voltammetry of the title compounds reveals that they are both reduced reversibly, i.e.



When Cp' = Cp, the reversible redox couple occurs in CH₂Cl₂ at $E^{\circ'} = -1.51$ V ($\nu = 0.15$ V s⁻¹, $\Delta E = 90$ mV, $i_{p,a}/i_{p,c} = 0.97$), and for Cp' = Cp*, it occurs at $E^{\circ'} = -1.64$ V ($\nu = 0.19$ V s⁻¹, $i_{p,a}/i_{p,c} = 0.90$). The cathodic shift in the $E^{\circ'}$ value as Cp is replaced by Cp* again reflects the

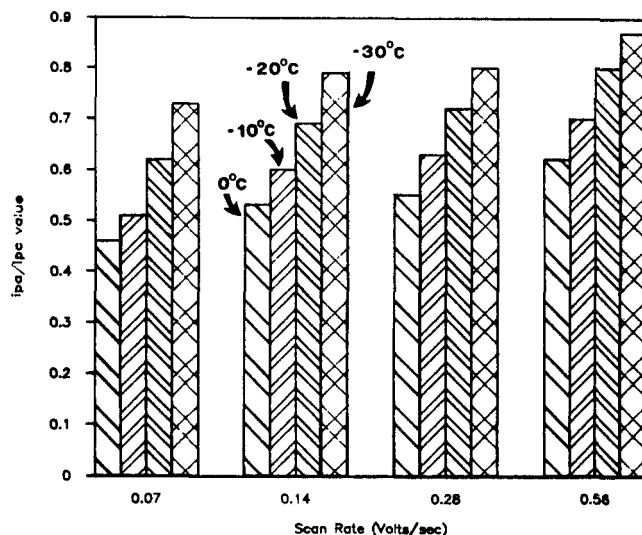


Figure 10. Temperature dependence of $i_{p,a}/i_{p,c}$ values as a function of scan rate for the first reversible redox couple of Cp*W(NO)I₂ in THF.

increased electron density at the metal center due to the greater electron-donating ability of the pentamethylcyclopentadienyl ligand. These dialkyl complexes are significantly more difficult to reduce than their dihalo precursors, a manifestation, no doubt, of the fact that alkyl ligands are better electron donors than are halide ligands.⁵⁰ Regrettably, our attempts to effect reductions 10 on a preparative scale and to isolate the [Cp'W(NO)-(CH₂SiMe₃)₂]^{-•} radical anions have so far been unsuccessful.^{51,52} No reaction occurs between Cp₂Co and CpW(NO)(CH₂SiMe₃)₂ in Et₂O at room temperature during 3 h, the cobaltocene ($E^{\circ'} = -0.82$ V, vide supra) apparently not being a sufficiently potent reagent to effect the reduction of the dialkyl complex ($E^{\circ'} = -1.61$ V). When CpW(NO)(CH₂SiMe₃)₂ in Et₂O is treated with the more potent reductant CpFe(η^6 -C₆Me₆) ($E_{1/2} = -1.78$ V),²⁰ only an intractable tar results.

Epilogue

In addition to establishing the fundamental reduction properties of the Cp'M(NO)X₂ complexes and related species, this work has also demonstrated that [Cp'M(NO)X₂]^{-•} radical anions are probable intermediates during the reactions of the dihalo nitrosyl complexes with nucleophiles. This, in turn, has led to predictions concerning the synthetic methodology to be employed for the successful preparation of new Cp'M(NO)-containing derivatives. While initial experiments designed to test the validity of these predictions have proven to be successful, it is clear that more work will have to be done to establish properly just when these predictions may be reliably applied.

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Registry No. CpMo(NO)Cl₂, 120311-08-2; Cp*Mo(NO)Cl₂, 120311-09-3; CpMo(NO)Br₂, 120311-10-6; Cp*Mo(NO)Br₂, 120311-11-7; CpMo(NO)I₂, 61495-99-6; Cp*Mo(NO)I₂, 115364-37-9; CpMo(NO)I₂(PMePh₂), 100898-79-1; [CpMo(NO)Cl₂]⁺, 120311-12-8; [Cp*Mo(NO)Cl₂]⁺, 120311-20-8; [CpMo(NO)Br₂]⁺,

120311-13-9; [Cp*Mo(NO)Br₂]⁺, 120311-14-0; [CpMo(NO)I₂]⁺, 120311-15-1; [Cp*Mo(NO)I₂]⁺, 120311-16-2; [Cp₂Co][Cp*Mo(NO)Br₂], 120311-17-3; Me₃SiCH₂MgCl, 13170-43-9; CpW(NO)I₂, 120311-18-4; Cp*W(NO)I, 115364-39-1; [Cp₂Co][CpMo(NO)Cl₂], 120311-19-5; [Cp₂Co][Cp*Mo(NO)Cl₂], 120311-21-9; [Cp₂Co][CpMo(NO)Br₂], 120311-22-0; [Cp₂Co][CpMo(NO)I₂], 120311-23-1; [Cp₂Co][Cp*Mo(NO)I₂], 120311-24-2; [CpFe(η⁶-C₆H₆)] [CpW(NO)(CH₂SiMe₃)₂], 120311-26-4.

Electrochemical Study of Iron(0)-Carbene Complexes: Electrochemical Dimerization of the Carbene Ligand and Synthesis of Tetrathiafulvalene Derivatives

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The electrochemical properties of (carbene)iron(0) complexes Fe:(CSC(CO₂Me)=C(CO₂Me)S)(CO)₂(L)₂ (**2**; L = PMe₃, **a**; L = PMe₂Ph, **b**; L = PMePh₂, **c**; L = PPh₃, **d**; L = PPh₃ and CO, **e**) are reported. Cyclic voltammetry shows that they undergo a one-electron oxidation between -0.1 and -0.3 V vs SCE and that the stability of 2⁺ is markedly affected by the nature of both solvents and ligands. Controlled potential electrolysis of **2d** in acetonitrile affords TTF derivative **3** arising from the dimerization of the carbene ligand, and coulometric measurements reveals that the dimerization is electrocatalyzed (TN ≥ 100). The formation of TTF derivative **3** from **2d** can be initiated either by electrochemical oxidation or by chemical oxidation with AgCF₃SO₃, I₂, or [Fe(C₅H₅)₂]PF₆. The stoichiometric chemical oxidation of **2b** with Ag⁺ or Fe(C₅H₅)₂⁺ salts leads to a mixture of two cationic diamagnetic isomers corresponding to (2b)₂²⁺ derivatives. A mechanism of the electrocatalyzed dimerization of carbene ligand is proposed and is shown to involve one-electron oxidation, dimerization of the resulting cation, and ligand elimination.

Introduction

Metal-carbene complexes are useful reagents for the selective formation of carbon-carbon bonds and the synthesis of organic compounds.² Dimerization of carbene ligands, with carbon-carbon double bond formation, is of special interest for the direct access to functional olefins displaying specific properties. Especially, the dimerization of the 1,3-dithiol-2-ylidene ligand of complexes of type I, easily produced by the cycloaddition of alkynes to Fe(η²-CS₂) complexes,³ shows potential for the one-step synthesis of tetrathiafulvalene derivatives II which behave as one-electron donating compounds for the formation of charge-transfer complexes.⁴ The dimerization of carbene ligands into olefins has already been achieved by the thermolysis of Fischer-type metal-carbene complexes.^{5,6} As for carbene-olefin coupling reactions⁷ or metal-carbene-initiated alkyne polymerization,^{8,9} the initial step of

Chart I



the carbene ligand dimerization process involves the generation of a vacant site, by thermal or photochemical dissociation of a metal-ligand bond.^{10,11} In addition, it has been established that the thermal dimerization does not proceed with the release of the uncoordinated carbene species but via a bimetallic intermediate¹⁰ (Chart I).

We have already shown that tetrathiafulvalene derivatives II could be produced directly from (1,3-dithiol-2-ylidene)iron complexes (I) by either thermolysis or even addition of iodine.¹¹ The latter observation led us to investigate the role of oxidation on the dimerization of the carbene ligand, and we report herein the electrochemical study of iron-carbene complexes of type I that gives evidence for the electron-transfer catalysis and the controlled influence of ancillary PR₃ ligands in carbene ligand dimerization.

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