which the spectra were obtained by Fourier transform.

Solution spectra were recorded on a Bruker WM-250 spectrometer ($^{31}P\{^1H\}$, $^{195}Pt\{^1H\}$).

[Mesityl(diphenylmethylene)phosphine]bis(triphenylphosphine)platinum(0) (1). Under argon, a solution of mesityl(diphenylmethylene)phosphine (2, 0.593 g, 1.88 mmol) in toluene (4 mL) was added to a suspension of [Pt(PPh$_3$)$_2$C$_2$H$_4$] (1.39 g, 1.86 mmol) in toluene (5 mL). The dark red solution was stirred for 30 min at room temperature. On addition of pentane (100 mL), a red precipitate formed; it was filtered off, washed three times with pentane (10 mL), and dried in vacuo for 30 min; 1 was isolated as red crystals: mp 194–199 °C; 1.66 g, 86%, ^{31}P NMR, see Table I; ^{195}Pt NMR, see Table II; mass spectrum (FD), m/z 1035 (M$^+$·; isotopic pattern expected for 1). Anal. Calcd for C$_{58}$H$_{51}$P$_3$Pt: C, 67.23; H, 4.96; P, 8.97. Found: C, 66.41; H, 5.27; P, 8.41.

Registry No. 1a, 80737-43-5; 1b, 89934-21-4; 3a, 92011-25-1; 3b, 92011-26-2; [Pt(PPh$_3$)$_2$C$_2$H$_4$], 12120-15-9; Pt(PH$_3$)$_2$, 76830-85-8; HP=CH$_2$, 61183-53-7.

Redox Properties of Bis[(η⁵-cyclopentadienyl)dinitrosylchromium] and Related Complexes[1]

Peter Legzdins* and Berend Wassink

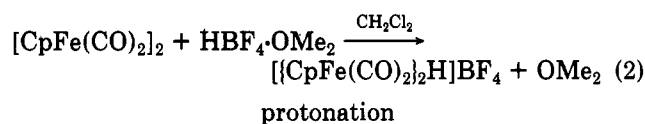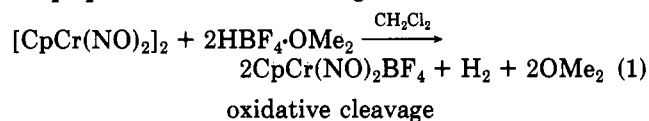*Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Y6*

Cyclic voltammetry studies and bulk electrolyses at controlled potentials establish that [CpCr(NO)$_2$]$_2$ (Cp = η^5-C$_5$H$_5$) undergoes the following principal transformations in CH$_2$Cl$_2$ or CH$_3$CN when electrons are either removed from or added to it. Oxidation of the nitrosyl dimer is an irreversible two-electron process and affords CpCr(NO)$_2^+$ which in CH$_3$CN exists as [CpCr(NO)$_2$(CH$_3$CN)]$^+$. Upon reduction, the cation incorporates one electron and converts to the CpCr(NO)$_2$· radical that then reverts to [CpCr(NO)$_2$]$_2$. Reduction of the nitrosyl dimer is a reversible, one-electron process that results in the formation of the bimetallic radical anion [CpCr(NO)$_2$]$_2^-$·. This redox behavior of [CpCr(NO)$_2$]$_2$ is opposite to that exhibited under similar conditions by its isoelectronic carbonyl analogue, [CpFe(CO)$_2$]$_2$, which retains its bimetallic nature upon oxidation (initially a reversible, one-electron process) and undergoes scission upon reduction (an irreversible, two-electron process). On a preparative scale, these electron-transfer reactions of [CpCr(NO)$_2$]$_2$ are best effected with either HBF$_4$·OMe$_2$ in CH$_2$Cl$_2$ as the oxidant or CpFe(η^6-C$_6$Me$_6$) in Et$_2$O as the reductant. The thermally stable oxidation product CpCr(NO)$_2^+$ is unisolable as such from CH$_2$Cl$_2$ but may be derivatized to CpCr(NO)$_2$Cl in situ. The reduction product, [CpFe(η^6-C$_6$Me$_6$)]$^+$·[{CpCr(NO)$_2$}$_2$]$^-$·, however, is isolable from Et$_2$O, and its spectroscopic properties indicate substantial delocalization of the additional electron density in the radical anion onto the NO ligands. Electrochemical transfer of two electrons to [CpCr(NO)$_2$]$_2$ in CH$_2$Cl$_2$ does not result in the formation of the still unknown [CpCr(NO)$_2$]$^-$ anion but rather affords only low yields of green Cp$_2$Cr$_2$(NO)$_3$(NH$_2$) and orange [CpCr-(NO)(NH$_2$)]$_2$ as the principal nitrosyl-containing products. In contrast to the dinitrosyl dimer, the structurally similar Cp$_2$Cr$_2$(NO)$_3$(NH$_2$) undergoes one-electron reduction more reluctantly and is apparently stabilized against cleavage upon electron removal by virtue of the presence of the better electron-donating μ-NH$_2$ group. Finally, one-electron reduction of CpCr(NO)$_2$Cl effected electrochemically does not produce [CpCr(NO)$_2$]$_2$.

Introduction

During previous investigations[2–6] we have demonstrated that [CpCr(NO)$_2$]$_2$ (Cp = η^5-C$_5$H$_5$) generally exhibits markedly different chemistry than its isoelectronic and isostructural carbonyl analogue, [CpFe(CO)$_2$]$_2$. For instance, treatment of the two dimers with HBF$_4$·OMe$_2$ in CH$_2$Cl$_2$ results in the following conversions:[6]

$$[CpCr(NO)_2]_2 + 2HBF_4·OMe_2 \xrightarrow{CH_2Cl_2} 2CpCr(NO)_2BF_4 + H_2 + 2OMe_2 \quad (1)$$

oxidative cleavage

$$[CpFe(CO)_2]_2 + HBF_4·OMe_2 \xrightarrow{CH_2Cl_2} [\{CpFe(CO)_2\}_2H]BF_4 + OMe_2 \quad (2)$$

protonation

Furthermore, our preliminary electrochemical studies established that under identical experimental conditions the nitrosyl dimer undergoes oxidation at a more positive potential. Consequently, we could conclude that the differing chemical behavior summarized in reactions 1 and 2 is not simply a manifestation of the intrinsically differing tendencies of the two dimers to undergo oxidation but rather probably reflects the relative stabilities of analogous intermediate complexes.[6] We have now completed a more detailed study of the redox properties of [CpCr(NO)$_2$]$_2$ and some related complexes with a view to gaining further insight into the factors responsible for their characteristic chemical behavior and wish to report our observations herein.

Experimental Section

All reactions and subsequent manipulations involving organometallic reagents were performed under anaerobic and an-

(1) Organometallic Nitrosyl Chemistry. 21. For part 20 see: Legzdins, P.; Martin, D. T. *Organometallics* **1983**, *2*, 1785.
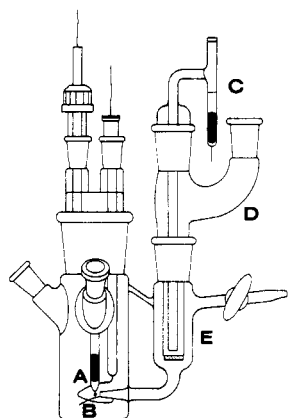
(2) Kolthammer, B. W. S.; Legzdins, P. *J. Chem. Soc., Dalton Trans.* **1978**, 31.

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Figure 1. The cyclic voltammetry cell: (A) platinum-bead working electrode with mercury contact; (B) platinum wire spiral auxiliary electrode; (C) saturated calomel electrode; (D) fine-fritted reference electrode holder; (E) reference compartment.

hydrous conditions. General procedures routinely employed in these laboratories have been described previously.[7] The ESR spectrum was recorded at X-band by using the spectrometer and interfaced computer system recently described by Phillips and Herring.[8] The experimental conditions were as follows: microwave frequency, 9.0459 GHz; 50-mG modulation; 5 mW of power; 25.2-G sweep width; 9.5-min scan time, lock-in time constant, 0.125 s; temperature of the sample, 19.10 °C.

Electrochemical Measurements. All operations were effected under an atmosphere of prepurified dinitrogen. CH_2Cl_2 (Fisher spectranalyzed) was not purified further and was simply deaerated prior to use. CH_3CN (Burdick and Jackson, UV grade) was first distilled from CaH_2 and then deaerated with prepurified dinitrogen. Both solvents were stored under N_2 over alumina (Woelm neutral, activity 1) in the dark.[9] The [n-Bu$_4$N]PF$_6$ supporting electrolyte was prepared by metathesis of n-Bu$_4$NI with NH$_4$PF$_6$ in hot acetone[10] and was recrystallized thrice from ethanol. The resulting white crystals were then ground to a fine powder and dried at 50–70 °C in vacuo (5×10^{-3} mm) for 24 h to obtain the desired salt in 86% yield. The solutions employed during cyclic voltammetry studies were typically $(5–7) \times 10^{-4}$ M in the organometallic complex and 0.1 M in [n-Bu$_4$N]PF$_6$.

Electrochemical measurements were accomplished with a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-to-voltage converter and a Model 178 electrometer probe. The probe was mounted external to the potentiostat, the connection being made by a minimum length of a high impedance wire. Cyclic voltammograms were recorded on a Hewlett-Packard Model 7035B X-Y recorder. The same recorder was used in conjunction with an Interstate Electronics Corp. Model F52A function generator to record current–time behavior during bulk electrolysis experiments.

The electrochemical cell employed for cyclic voltammetry was similar in design to that described by van Duyne and Reilley[11] and is shown in Figure 1. A platinum bead sealed in soft borosilicate glass having a similar coefficient of expansion[12] served as the working electrode (designated by A in Figure 1), electrical contact being effected with mercury. The auxiliary electrode (B) consisted of a platinum coil. An aqueous saturated calomel reference electrode (C) was positioned in the side compartment of the cell (E), and its potential was checked periodically against a commercial SCE (Brinkmann Instruments). The reference electrode holder (D) was equipped with a fine porosity frit to minimize the leakage of water. The two compartments of the cell were connected by a Luggin probe, the working electrode being
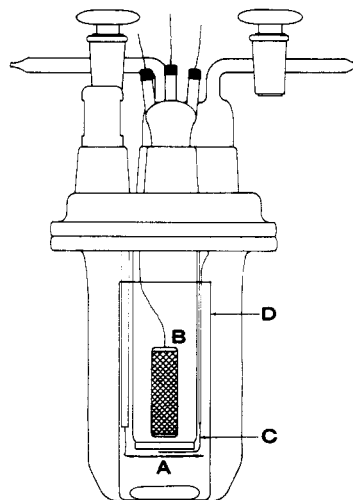
Figure 2. The bulk electrolysis cell: (A) platinum-gauze working electrode; (B) platinum-gauze cylindrical auxiliary electrode; (C) silver-wire quasi-reference electrode; (D) inner glass compartment.

kept at a distance of approximately one diameter of the Pt bead from the tip of the probe (as shown in Figure 1). Before each experiment, the Pt-bead electrode was cleaned by sequential treatment with boiling nitric acid, distilled water, a solution of ferrous ammonium sulfate in 1.0 M H_2SO_4, and distilled water prior to final drying in vacuo.

For bulk electrolysis work, the cell consisted of a 500-mL reaction kettle (Fisher Scientific) and a four-necked lid equipped with ground-glass flanges as depicted in Figure 2. An inner glass compartment (designated by D in Figure 2) that reduced the cell volume to $\sim$150 mL could be introduced if needed. A platinum-gauze sheet and cylinder served as the working (A) and auxiliary (B) electrodes, respectively, and a silver wire situated between them functioned as a quasi-reference electrode (C). The auxiliary and working electrodes were also separated by a glass compartment having a fine-fritted base. The various components such as the auxiliary cell compartment and the different electrodes were held in place by a Teflon plate imbedded in the lid of the cell. Leads from the electrodes were run through a three-necked adapter, each neck being sealed by a 5-mm rubber septum. The other connections shown in Figure 2 permitted the passage of prepurified dinitrogen through the system during an experiment, but the cell was always assembled under N_2 in a Vacuum Atmospheres Corp. Dri-Lab Model HE-43-2 drybox. During operation of the electrolysis cell, the contents of the working compartment were as specified below for each of the processes investigated, and the auxiliary compartment contained only a 0.1 M solution of [n-Bu$_4$N]PF$_6$ in the specified solvent. Prior to each experiment, the working electrode was cleaned in the manner described for the Pt-bead electrode in the preceding paragraph. Except in those cases when products formed were believed to be electroactive or subsequent peaks in the cyclic voltammogram were nearby, bulk electrolyses were usually performed $\sim$200 mV past the peak potential of the appropriate cyclic voltammogram in order to enhance the rate of conversion. Maximum currents attainable were $\sim$150–200 mA.

Oxidation of [CpCr(NO)$_2$]$_2$. The electrolysis cell was charged with [CpCr(NO)$_2$]$_2$[13] (0.20 g, 0.56 mmol), [n-Bu$_4$N]PF$_6$ (8.0 g, 21 mmol), and CH_2Cl_2 (200 mL) at ambient temperature. The stirred solution was electrolyzed at +1.00 V for $\sim$0.5 h whereupon it gradually changed in color from intense red to dark green. Integration of the current vs. time graph showed that a total charge of 89 C (i.e., 0.8 electron/Cr) had been passed. The final green solution was transferred by cannulation to a 300-mL flask, and its volume was reduced to $\sim$20 mL under reduced pressure. An IR spectrum of this solution was devoid of absorptions characteristic of the organometallic reactant but did display two new bands at 1838 (s) and 1731 (s, br) cm^{-1} in the nitrosyl-stretching region. This stirred solution was then treated dropwise with a

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(9) Ito, N.; Saji, T.; Aoyagui, S. *J. Organomet. Chem.* **1983**, *247*, 301.
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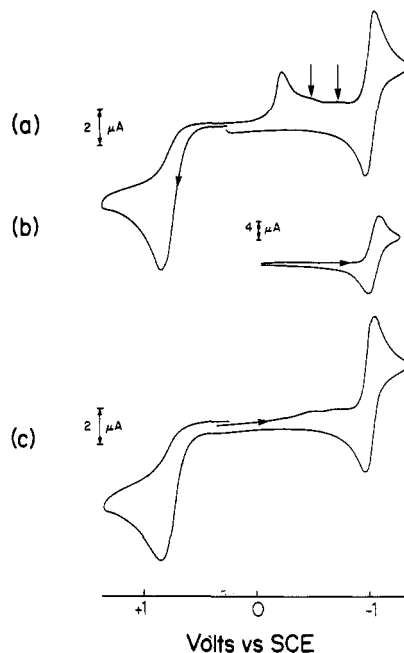(11) Van Duyne, R. P.; Reilley, C. N. *Anal. Chem.* **1972**, *44*, 142.
(12) Other glasses were less satisfactory since the glass–Pt seal rapidly deteriorated. This deterioration was manifested by a drastic increase in the background current which imposed a large slope on the current–voltage trace.

(13) Kolthammer, B. W. S.; Legzdins, P.; Malito, J. T. *Inorg. Synth.* **1979**, *19*, 208.

CH_2Cl_2 solution of $[(Ph_3P)_2N]Cl$ until the latter absorptions were replaced completely by bands at 1816 (s) and 1711 (vs) cm^{-1} in its IR spectrum. The resulting solution was taken to dryness in vacuo, and the remaining residue was extracted with benzene (2 × 25 mL). The combined extracts were concentrated under reduced pressure to ~5 mL and were transferred by syringe to the top of a short (3 × 4 cm) column of Florisil made up in CH_2Cl_2. Elution of the column with CH_2Cl_2 resulted in the development of a single green-brown band that was collected. Removal of solvent from the eluate in vacuo and recrystallization of the residue from CH_2Cl_2–hexanes afforded ~0.1 g of golden $CpCr(NO)_2Cl$ still contaminated with a small amount of $[n-Bu_4N]PF_6$. The organometallic component was readily identifiable by its characteristic spectral properties:[14] IR (CH_2Cl_2) ν_{NO} 1816 (s), 1711 (vs) cm^{-1}; ^{1}H NMR (C_6D_6) δ 4.78 (s); low-resolution mass spectrum (probe temperature 50 °C), m/z 212 (P^+).

Reduction of $[CpCr(NO)_2(CH_3CN)]PF_6$. Addition of $[CpCr(NO)_2(CH_3CN)]PF_6$[15] (0.132 g, 0.364 mmol), $[n-Bu_4N]PF_6$ (6.0 g, 15 mmol), and CH_2Cl_2 (150 mL) to the electrolysis cell produced a green solution. This stirred solution was electrolyzed at −0.40 to −0.47 V for ~1 h until the current had decreased to <1% of its initial value, a total charge of 31 C (i.e., 0.9 electron/Cr) having been passed. The final red solution was cannulated into a 500-mL flask and concentrated in vacuo to ~15 mL. An IR spectrum of this solution exhibited ν_{NO}'s at ~1830 (w), ~1720 (w), and ~1670 (s) cm^{-1}. After removal of the CH_2Cl_2 under reduced pressure, the remaining residue was extracted with benzene (4 × 25 mL), and the combined extracts were reduced in volume to ~10 mL in vacuo. Chromatography of this concentrate on a Florisil column (3 × 10 cm) with benzene as eluant produced a red-brown band that was eluted and collected. Removal of solvent from the eluate under reduced pressure afforded 0.03 g (20% yield based on Cr) of solid $[CpCr(NO)_2]_2$ that was identified by its distinctive spectra:[13,16] IR (CH_2Cl_2) ν_{NO} 1667 (s), 1512 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.17 (s, trans), 4.95 (s, cis); low-resolution mass spectrum (probe temperature 120 °C), m/z 354 (P^+).

Reduction of $[CpCr(NO)_2]_2$. A stirred 0.1 M solution of $[n-Bu_4N]PF_6$ in CH_2Cl_2 (100 mL) also containing $[CpCr(NO)_2]_2$ (0.374 g, 1.06 mmol) was electrolyzed at −1.00 V. The current decayed very slowly as the color of the solution changed from intense red to brown. The electrolysis was stopped after 470 C (i.e., 4.8 electrons/Cr_2) had been passed and the current had dropped to ~2% of its initial value. An IR spectrum of the final solution revealed that the nitrosyl bands characteristic of the organometallic reactant (vide supra) had disappeared completely and had been replaced by a broad, weak absorption at ~1610 cm^{-1}.

In a subsequent experiment, an identical initial mixture was reduced at −1.10 V, but the electrolysis was stopped after 192 C (i.e., 1.9 electrons/Cr_2) had been passed. The resulting brown solution was transferred by cannulation into a 500-mL flask and was taken to dryness in vacuo. The residual solid was extracted with benzene until the extracts were only faintly colored (total volume ~200 mL), and the volume of the extracts was reduced to ~5 mL under reduced pressure. The concentrate was syringed onto a Florisil column (2 × 11 cm) made up in benzene. Elution of the column with benzene first removed a red-brown band that contained 0.013 g (3%) of $[CpCr(NO)_2]_2$ and then a green band that upon collection and solvent removal afforded 0.029 g (8% yield) of $Cp_2Cr_2(NO)_3(NH_2)$, which was identified spectroscopically:[2,17] IR (CH_2Cl_2) ν_{NO} 1642 (s), 1511 (sh), 1503 (m) cm^{-1}; low-resolution mass spectrum (probe temperature 120 °C), m/z 340 (P^+). Further elution of the column with CH_2Cl_2 produced an orange band that was collected and taken to dryness in vacuo to obtain an orange solid (~0.05 g) composed of $[n-Bu_4N]PF_6$ and $[CpCr(NO)(NH_2)]_2$. The latter copompound was also identified spectroscopically:[4] IR (THF) ν_{NO} 1625 (m) cm^{-1}; low-resolution mass spectrum (probe temperature 120 °C), m/z 326 (P^+). Finally, elution of the column with THF resulted in the devel-

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Figure 3. Ambient-temperature cyclic voltammograms of 5 × 10^{-4} M $[CpCr(NO)_2]_2$ in CH_2Cl_2 containing 0.1 M $[n-Bu_4N]PF_6$ measured at a platinum-bead electrode with a scan rate of 110 mV s^{-1}. The individual traces are discussed in the text.

opment of a brown band that was eluted and taken to dryness under reduced pressure to obtain a small amount of a brown solid: IR (THF) ν_{NO} 1656 (s), 1641 (sh) cm^{-1}.

Reduction of $CpCr(NO)_2Cl$. A stirred, golden green CH_2Cl_2 solution (100 mL) containing $CpCr(NO)_2Cl$[14] (0.096 g, 0.45 mmol) and $[n-Bu_4N]PF_6$ (4.0 g, 10 mmol) was reduced in the electrolysis cell at −1.00 V until the current had diminished from a peak of 140 mA to 20 mA (6 min). At this point, the current began to increase slightly. Consequently, the potential was reduced to −0.69 V, and electrolysis was continued until the current had decayed to <4 mA. During this time a total charge of 44 C (i.e., 1.0 electron/Cr) had been passed, and the color of the solution had changed to dark brown. The final solution was then cannulated into a 500-mL flask and was concentrated in vacuo to ~15 mL. An IR spectrum of this solution displayed only a single band at ~1640 cm^{-1} attributable to NO stretching. Various attempts to isolate a tractable nitrosyl-containing product from this solution were unsuccessful.

Preparation of $[CpFe(\eta^6-C_6Me_6)][\{CpCr(NO)_2\}_2]$. A stirred, red solution of $[CpCr(NO)_2]_2$ (0.46 g, 1.3 mmol) in Et_2O (250 mL) at room temperature was treated dropwise with a dark green solution of $CpFe(\eta^6-C_6Me_6)$[18] (0.36 g, 1.3 mmol) in the same solvent (50 mL). A gray precipitate formed instantly, and the final mixture was stirred for 15 min to ensure completion of the precipitation. The precipitate was then collected by filtration through a medium-porosity frit, washed with Et_2O (150 mL), and dried in vacuo (5 × 10^{-3} mm) for 30 min at 20 °C to obtain 0.56 g (69% yield) of analytically pure $[CpFe(\eta^6-C_6Me_6)][\{CpCr(NO)_2\}_2]$ as an olive-green, extremely air-sensitive powder: IR (Nujol mull) ν_{NO} 1580 (s), 1331 (s, br) cm^{-1}, also 3177 (w), 3091 (m), 1417 (m), 1392 (sh), 1073 (m), 1011 (m), 796 (s) cm^{-1}.

Anal. Calcd for $C_{27}H_{33}N_4O_4FeCr_2$: C, 50.88; H, 5.22; N, 8.79; O, 10.04. Found: C, 50.76; H, 5.21; N, 8.50; O, 9.95.

Results and Discussion

Cyclic Voltammetry Studies. (a) $[CpCr(NO)_2]_2$. Ambient-temperature cyclic voltammograms (CVs) of $[CpCr(NO)_2]_2$ in CH_2Cl_2 are displayed in Figure 3. From these and the results of bulk electrolyses (vide infra), we infer that the principal transformations undergone by the dimer when electrons are either removed from or added
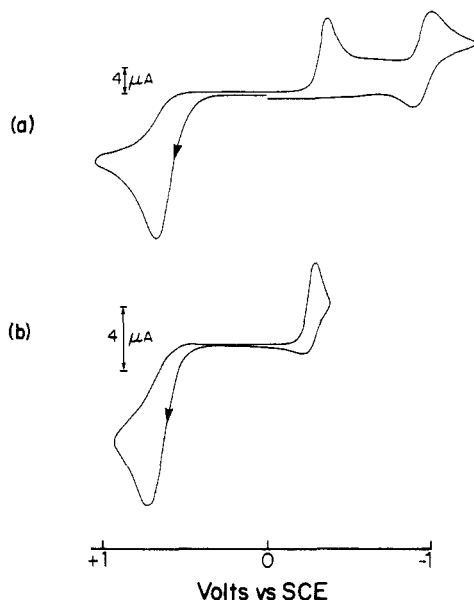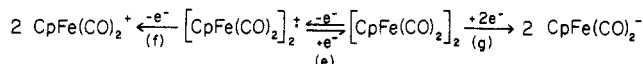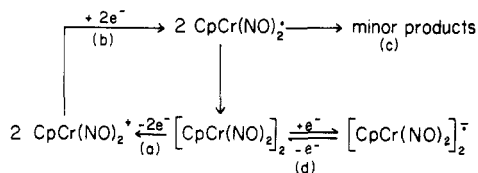
(18) Hamon, J.-R.; Astruc, D.; Michaud, P. *J. Am. Chem. Soc.* **1981**, *103*, 758.

Figure 4. Ambient-temperature cyclic voltammograms of 5 × 10⁻⁴ M [CpCr(NO)₂]₂ in CH₃CN containing 0.1 M [n-Bu₄N]PF₆ measured at a platinum bead electrode with scan rates of (a) 190 mV s⁻¹ and (b) 290 mV s⁻¹, respectively. The individual traces are discussed in the text.

Scheme I

$$2 \text{ CpCr(NO)}_2 \xrightleftharpoons[\text{(a)}]{-2e^-} \left[\text{CpCr(NO)}_2\right]_2 \xrightleftharpoons[-e^-]{+e^-} \left[\text{CpCr(NO)}_2\right]_2^-$$

(with branch: $\xrightarrow[\text{(b)}]{+2e^-} 2 \text{ CpCr(NO)}_2^- \longrightarrow$ minor products (c), and (d))

$$2 \text{ CpFe(CO)}_2^+ \xrightleftharpoons[\text{(f)}]{-e^-} \left[\text{CpFe(CO)}_2\right]_2^+ \xrightleftharpoons[+e^-]{-e^-} \left[\text{CpFe(CO)}_2\right]_2 \xrightarrow[\text{(g)}]{+2e^-} 2 \text{ CpFe(CO)}_2^-$$
(e)

to it are as summarized in the first part of Scheme I. When positive potentials are scanned first (Figure 3a), an irreversible, two-electron oxidation corresponding to step a in Scheme I and having $E_{p,a}$ = +0.85 V vs. SCE at a scan rate of 110 mV s⁻¹ is observed. Reversal of this scan results in the sequential detection of the following features: (1) an irreversible reduction with $E_{p,c}$ = -0.21 V corresponding to step b, (2) two smaller reductions (indicated by arrows in Figure 3a) at $E_{p,c}$ = -0.47 and -0.69 V due to the addition of electrons to the minor products labeled c in Scheme I, and (3) a reversible,[19] one-electron reduction at $E^{o'}$[21] = -1.00 V having ΔE_p = 80 mV and a ratio of peak currents $i_{p,a}/i_{p,c}$[22] = 0.97 that corresponds to step d. Consistent with these assignments is the fact that if a CV is recorded initially between 0 and -1.4 V, only the reversible reduction at -1.00 V is evident (Figure 3b).

(19) The term "reversible" is applied to a particular redox couple in a qualitative sense, and it is based on a comparison of the pertinent CV to that displayed by ferrocene, a compound which is known[20] to undergo a reversible one-electron oxidation. Under the experimental conditions employed throughout this work, this oxidation of Cp₂Fe in CH₂Cl₂ occurs at $E^{o'}$ = +0.47 V and has ΔE_p = 70 mV and $i_{p,c}/i_{p,a}$ = 1.0 at a scan rate of 110 mV s⁻¹.

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(22) For details concerning the calculation of the ratio of peak currents see: Roberts, J. L., Jr.; Sawyer, D. T. "Experimental Electrochemistry for Chemists"; Wiley-Interscience: New York, 1974; p 340.
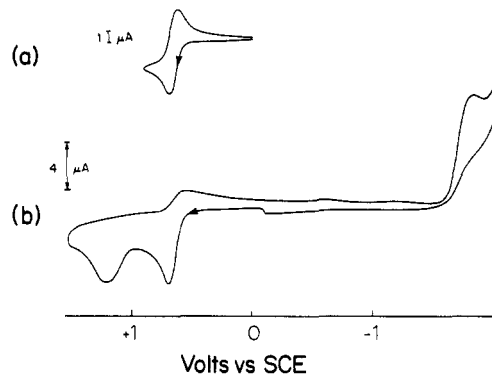

Figure 5. Ambient-temperature cyclic voltammograms of 7 × 10⁻⁴ M [CpFe(CO)₂]₂ in CH₂Cl₂ containing 0.1 M [n-Bu₄N]PF₆ measured at a platinum-bead electrode. Scan rates: (a) 70 mV s⁻¹; (b) 140 mV s⁻¹.

However, after several complete scans of the type shown in Figure 3a, a CV beginning in the reduction region exhibits the peaks at -0.47 and -0.69 V in addition to the dominant feature at -1.00 V (Figure 3c).

Analogous CVs of [CpCr(NO)₂]₂ in CH₃CN are qualitatively similar to those observed in CH₂Cl₂, two representative traces being displayed in Figure 4. The peak potentials shift slightly to more positive values for the oxidation processes and to more negative values for the reduction processes with each successive scan. In CH₃CN, the initial, two-electron irreversible oxidation peak occurs at $E_{p,a}$ = +0.68 V at a scan rate of 190 mV s⁻¹ (Figure 4a), thus indicating that the nitrosyl dimer is more readily oxidized in this solvent. The removal of electrons in this case, i.e., eq 3, is probably facilitated by formation of the

$$[\text{CpCr(NO)}_2]_2 \xrightarrow[\text{CH}_3\text{CN}]{-2e^-} 2[\text{CpCr(NO)}_2(\text{CH}_3\text{CN})]^+ \quad (3)$$
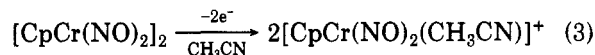
well-known,[15] 18-electron, CH₃CN-containing cation that is more stable than the formally 16-electron [CpCr(NO)₂]⁺ formed by the analogous oxidation in CH₂Cl₂.[23] Consistent with this view is the fact that [CpCr(NO)₂(CH₃CN)]⁺ is somewhat more difficult to reduce in CH₃CN, its reduction being indicated by the CV signal at $E_{p,c}$ = -0.37 V (Figure 4a). Unlike the analogous process in CH₂Cl₂, this reduction is partially chemically reversible, i.e., eq 4. If the CV scan is reversed at -0.50 V (Figure

$$[\text{CpCr(NO)}_2(\text{CH}_3\text{CN})]^+ \xrightleftharpoons[-e^-]{+e^-} [\text{CpCr(NO)}_2(\text{CH}_3\text{CN})]\cdot$$
(4)
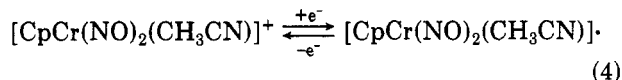
4b), the corresponding anodic peak is detectable at $E_{p,a}$ = -0.30 V. Hence, this redox couple is correctly represented by the parameters $E^{o'}$ = -0.34 V with ΔE_p = 70 mV and $i_{p,a}/i_{p,c}$ = 0.40 at a scan rate of 100 mV s⁻¹. Consistent with the partial chemical reversibility of reaction 4, $i_{p,a}/i_{p,c}$ does increase with increased scan rate. The radical species formed in reaction 4 also appears to be more stable than its analogue formed in CH₂Cl₂, no signals due to to reduction of minor products labeled c in Scheme I being observable in the CVs in Figure 4. This inference is in accord with the recent observation that the congeneric radicals [CpW(NO)₂L]· (L = PPh₃, P(OPh)₃, etc.) are sufficiently thermally stable to be isolable.[24] The chromium-containing radicals evidently undergo dimerization with concomitant expulsion of CH₃CN from each metal's

(23) By analogy to the congeneric CpW(NO)₂BF₄,[1] it is likely that the [CpCr(NO)₂]⁺ cation possesses the PF₆⁻ counterion ligated weakly in a monodentate fashion in these solutions.

(24) Yu, Y. S.; Jacobson, R. A.; Angelici, R. J. *Inorg. Chem.* **1982**, *21*, 3106.

coordination sphere, i.e., eq 5. The final features of the

$$2[CpCr(NO)_2(CH_3CN)] \cdot \rightarrow [CpCr(NO)_2]_2 + 2CH_3CN \quad (5)$$
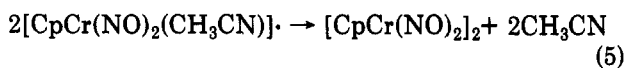
CV shown in Figure 4a thus result from the one-electron reduction of the parent nitrosyl dimer. In CH_3CN, this reduction is less reversible than in CH_2Cl_2 and occurs at $E^{\circ\prime} = -0.95$ V with $\Delta E_p = 120$ mV and $i_{p,a}/i_{p,c} = 0.83$. Consistently, if negative potentials are scanned first, the CV of $[CpCr(NO)_2]_2$ in CH_3CN exhibits only the signals due to this redox couple (step d of Scheme I).

The electron-transfer processes engaged in by [CpCr-$(NO)_2]_2$ contrast with those in which its isoelectronic carbonyl analogue, $[CpFe(CO)_2]_2$, is a participant. The latter transformations are summarized for comparison in the second part of Scheme I, and their occurrence can be inferred from the CVs presented in Figure 5. Thus, a CV of the carbonyl dimer in CH_2Cl_2[25] between 0 and +0.91 V (Figure 5a) shows only a reversible, one-electron oxidation at $E^{\circ\prime} = +0.67$ V having $\Delta E_p = 70$ mV and $i_{p,c}/i_{p,a} = 0.93$. This corresponds to step e of Scheme I. If, however, the oxidation scan is extended to +1.6 V (Figure 5b), a second oxidation corresponding to step f occurs irreversibly at $E_{p,a} = +1.21$ V[27] and the initial signal at $E^{\circ\prime} = +0.67$ V becomes less reversible. Successive oxidation scans result in broadening of the observed signals probably because of contamination of the electrode surface by decomposition products.[30] At negative potentials, the carbonyl dimer in CH_2Cl_2 displays only an irreversible two-electron reduction with $E_{p,c} = -1.84$ V that corresponds ultimately[31] to the formation of $[CpFe(CO)_2]^-$ (i.e., step g), a feature that has been previously observed by other investigators. Each successive scan of the complete CV of $[CpFe(CO)_2]_2$ in CH_2Cl_2 results in the irreversible oxidation potential becoming more positive and the reduction potential becoming more negative.

The fundamental difference between the two dimeric complexes considered in Scheme I is thus their behavior upon electron addition. The iron carbonyl dimer undergoes scission with a net two-electron reduction, i.e., eq 6, whereas the chromium nitrosyl dimer retains its bi-

$$[CpFe(CO)_2]_2 \xrightarrow{+2e^-} 2[CpFe(CO)_2]^- \quad (6)$$
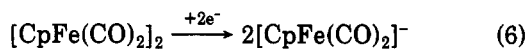
metallic nature upon one-electron reduction, i.e., eq 7. A

$$[CpCr(NO)_2]_2 \xrightarrow{+e^-} [CpCr(NO)_2]_2^- \cdot \quad (7)$$

possible explanation of these observations is that the greater π acidity of the NO ligands results in a greater delocalization of the extra electron density in [CpCr-$(NO)_2]_2^-\cdot$ and, consequently, a diminished tendency for the bimetallic anion to undergo cleavage. In a complementary fashion, the occurrence of reactions 6 and 7 may be viewed as reflecting the inherently differing natures of the lowest unoccupied molecular orbitals of the two dimers, that for

$[CpCr(NO)_2]_2$ evidently being a relatively low-energy nonbonding or bonding orbital. Obviously, the confirmation of this latter inference must await a detailed theoretical analysis. Nevertheless, the experimental results presented here clearly indicate why previous attempts[2] to synthesize the still unknown $[CpCr(NO)_2]^-$ anion by reduction of the parent dimer were unsuccessful.

(b) $CpCr(NO)_2BF_4$. Treatment of a 4×10^{-4} M solution of $[CpCr(NO)_2]_2$ in CH_2Cl_2 with 2 equiv of $HBF_4 \cdot OMe_2$ results in the generation of a 8×10^{-4} M solution of $CpCr(NO)_2BF_4$ according to eq 1. A CV of this solution recorded at a scan rate of 150 mV s^{-1} displays the familiar signals due to an irreversible reduction at $E_{p,c} = -0.24$ V, two less intense reductions at -0.45 and -0.71 V, and finally a reduction at $E^{\circ\prime} = -0.99$ V that exhibits some degree of reversibility. These features correspond reasonably well to the CV presented in Figure 3a at negative potentials and confirm the sequential reduction processes that originate at $[CpCr(NO)_2]^+$ as outlined in Scheme I.[23]

(c) $[CpCr(NO)_2(CH_3CN)]PF_6$. As expected on the basis of the preceding results, CH_3CN solutions of this isolable complex[15] exhibit CVs in the reduction region essentially identical with those presented in Figure 4. When CH_2Cl_2 is employed as the solvent, the first reduction of the complex occurs irreversibly at $E_{p,c} = -0.27$ V at a scan rate of 100 mV s^{-1}. The resulting [CpCr-$(NO)_2(CH_3CN)] \cdot$ radical is apparently not as stable in CH_2Cl_2 as it is in CH_3CN, since a small reduction peak is also detectable at $E_{p,c} = -0.71$ V that may again be attributed to the transfer of electrons to minor products derived from this radical (vide supra). Nevertheless, the presence in the CV of the strong and ubiquitous signals due to the reversible reduction of $[CpCr(NO)_2]_2$ again confirm the occurrence of the transformations summarized in the first part of Scheme I.

(d) $CpCr(NO)_2Cl$. The redox properties of this compound are of interest in comparison to those displayed by the complexes formally containing the $[CpCr(NO)_2]^+$ cation. The CV of $CpCr(NO)_2Cl$ in CH_2Cl_2 is devoid of any features corresponding to oxidation of the compound out to the solvent limit (+1.7 V). When negative potentials are scanned, the only observable feature is an irreversible reduction of the compound at $E_{p,c} = -0.68$ V and a scan rate of 70 mV s^{-1}. Hence, $CpCr(NO)_2Cl$ is somewhat more difficult to reduce than $[CpCr(NO)_2]^+$ in CH_2Cl_2, and no electrochemically detectable amounts of $[CpCr(NO)_2]_2$ or its precursors are produced in the process.

(e) $Cp_2Cr_2(NO)_3(NH_2)$. The molecular structure of this bimetallic nitrosyl complex in the solid state resembles that of $[CpCr(NO)_2]_2$, a bridging NO ligand in the latter simply having been replaced by a bridging NH_2 group.[32] Its reduction behavior in solution is also qualitatively similar. If a CV of the amido complex in CH_2Cl_2 is recorded initially between 0 and -1.6 V at a scan rate of 100 mV s^{-1}, only a quasi-reversible, one-electron reduction at $E^{\circ\prime} = -1.27$ V having $\Delta E_p = 110$ mV and $i_{p,a}/i_{p,c} = 0.94$ is evident. [The $E_{p,c}$ value (-1.33 V at 100 mV s^{-1}) shifts to more negative potentials as the scan rate is increased.] The effects of the μ-NH_2 ligand, a non-π-acid, are thus to make the amido complex relatively more difficult to reduce and the process shown in eq 8 less reversible. In contrast to

$$Cp_2Cr_2(NO)_3(NH_2) \underset{-e^-}{\overset{+e^-}{\rightleftharpoons}} [Cp_2Cr_2(NO)_3(NH_2)]^- \cdot \quad (8)$$
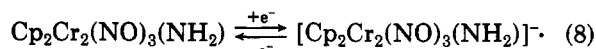
$[CpCr(NO)_2]_2$ (Figure 3), however, the bimetallic amido complex undergoes two successive, quasi-reversible one-

(25) The electrochemical oxidation of $[CpFe(CO)_2]_2$ in a variety of solvents has been investigated previously.[26]

(26) Ferguson, J. A.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 1025.

(27) In our hands, controlled potential electrolysis of $[CpFe(CO)_2]_2$ in CH_2Cl_2 at +0.80 V in the presence of [n-Bu₄N]PF₆ yields CpFe(CO)₂PF₆ ($\nu_{CO} = 2076$ (s) and 2030 (s) cm^{-1})[28] that can be derivatized with [(Ph₃P)₂N]Cl to obtain the well-known CpFe(CO)₂Cl.[29]

(28) Mattson, B. M.; Graham, W. A. G. *Inorg. Chem.* **1981**, *20*, 3186.

(29) Piper, T. S.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1956**, *3*, 104.

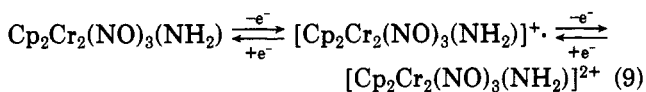(30) Sharp, P. R.; Bard, A. J. *Inorg. Chem.* **1983**, *22*, 2689.

(31) (a) Dessy, R. E.; Weissman, P. M.; Pohl, R. L. *J. Am. Chem. Soc.* **1966**, *88*, 5117. (b) Miholová, D.; Vlček, A. A. *Inorg. Chim. Acta* **1980**, *41*, 119. (c) Davies, S. G.; Simpson, S. J.; Parker, V. D. *J. Chem. Soc., Chem. Commun.* **1984**, 352.

(32) Chan, L. Y. Y.; Einstein, F. W. B. *Acta Crystallogr., Sect. B* **1970**, *B26*, 1899.

Volts vs SCE
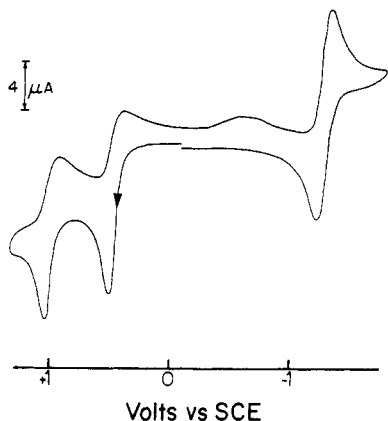
Figure 6. Ambient-temperature cyclic voltammogram of 5×10^{-4} M $Cp_2Cr_2(NO)_3(NH_2)$ in CH_2Cl_2 containing 0.1 M [n-Bu$_4$N]PF$_6$ measured at a platinum-bead electrode with a scan rate of 100 mV s^{-1}.

electron oxidations in CH_2Cl_2 when positive potentials are scanned first (Figure 6). The probable transformations involved, i.e., eq 9, occur at $E^{\circ\prime} = +0.45$ V with $\Delta E_p = 120$

$$Cp_2Cr_2(NO)_3(NH_2) \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Cp_2Cr_2(NO)_3(NH_2)]^+ \cdot \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}}$$
$$[Cp_2Cr_2(NO)_3(NH_2)]^{2+} \quad (9)$$

mV and $E^{\circ\prime} = +0.98$ V with $\Delta E_p = 140$ mV at a scan rate of 180 mV s^{-1}, respectively. The first oxidation occurs more readily than for $[CpCr(NO)_2]_2$ and is again a manifestation of the relatively better electron-donating properties of the NH$_2$ group. Indeed, the presence of the bridging amido ligand apparently stabilizes $Cp_2Cr_2(NO)_3(NH_2)$ considerably against undergoing scission upon electron removal. Reversal of the CV scan after the oxidative processes also reveals the presence of a small and broad set of reduction peaks in the region between -0.39 and -0.57 V (Figure 6) that are probably associated with small amounts of byproducts derived from the oxidized complexes in reactions 9. If the CV scan is reversed before the second oxidation occurs, a similarly shaped envelope of reduction peaks is observable in this region.

Bulk Electrolyses. The interpretations of the CVs discussed in the preceding paragraphs are substantiated by the following independent experiments, complete details of which are presented in the Experimental Section.

(A) Controlled potential electrolysis of an intensely red solution of $[CpCr(NO)_2]_2$ in CH_2Cl_2 (with [n-Bu$_4$N]PF$_6$ as support electrolyte) at +1.00 V results in the removal of 0.8 electron/chromium atom and the nearly quantitative formation of green $CpCr(NO)_2PF_6$[15] [IR (CH_2Cl_2) ν_{NO} 1838 (s), 1731 (s, br) cm^{-1}]. The oxidation process is substantially slower than that for ferrocene under analogous experimental conditions. The unisolable organometallic product can be converted in situ to tractable $CpCr(NO)_2Cl$ by metathesis with [(Ph$_3$P)$_2$N]Cl.

(B) Bulk reduction of green $[CpCr(NO)_2(CH_3CN)]PF_6$ in CH_2Cl_2 at -0.45 V is quite slow and consumes 0.9 electron/chromium atom. IR monitoring of the progress of the conversion verifies that the principal nitrosyl-containing product formed is $[CpCr(NO)_2]_2$ that is isolable by chromatography on Florisil. The IR spectrum of the final electrolyzed solution also displays two weak nitrosyl absorptions at ~1830 and ~1720 cm^{-1} reminiscent of those exhibited by the dinitrosyl complexes, $CpCr(NO)_2X$ where X = a halide or a pseudohalide.[33] While we have not as

yet succeeded in isolating and characterizing this minor product, it is likely that transfer of electrons to this complex produces the small reduction peak at $E_{p,c} = -0.71$ V in the CV of $[CpCr(NO)_2(CH_3CN)]PF_6$ in CH_2Cl_2 (vide supra).

(C) Exhaustive reduction of $[CpCr(NO)_2]_2$ in CH_2Cl_2 at -1.00 V requires the transfer of 4.8 electrons/dimer in order to consume the reactant completely. Evidently the initially formed bimetallic radical anion decomposes to other electroactive species. If the controlled potential electrolysis is effected at -1.10 V and is stopped after 1.9 electrons/dimer have been transferred, the final solution still contains a small amount of $[CpCr(NO)_2]_2$. The nitrosyl-containing products formed in low yields are the bridging amido compounds green $Cp_2Cr_2(NO)_3(NH_2)$ and orange $[CpCr(NO)(NH_2)]_2$ and a brown complex as yet unidentified, all of which are separable by column chromatography on Florisil. A similar distribution of products is known to result when the neutral dinitrosyl dimer is treated with reducing agents such as Na/Hg or Na[H$_2$-Al(OCH$_2$CH$_2$OCH$_3$)$_2$].[4] These dimeric solid products probably result from further reactions of $[CpCr(NO)_2]_2^-$. However, the dominant mode of reactivity when electrons are added to the bimetallic radical anion or its derivatives is the formation of non-nitrosyl products. The $[CpCr(NO)_2]^-$ anion is not formed even transiently in spectroscopically detectable amounts.

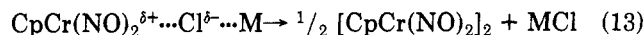(D) Complete electrochemical reduction of $CpCr(NO)_2Cl$ in CH_2Cl_2 results in the transfer of 1.0 electron/chromium atom and in the formation of a brown product complex [IR (CH_2Cl_2) ν_{NO} ~1640 (br) cm^{-1}] whose identity remains to be ascertained. The fact that no $[CpCr(NO)_2]_2$ is formed as a product indicates that during its chemical synthesis, i.e., eq 10, where reducing agent = Zn/Hg in THF[34] or

$$CpCr(NO)_2Cl \xrightarrow[\text{agent}]{\text{reducing}} [CpCr(NO)_2]_2 \quad (10)$$
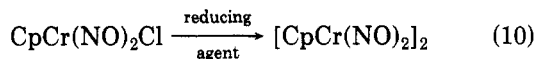
Na/Hg in benzene,[13] the initial step does not involve the simple electron transfer shown in eq 11. Consequently,

$$CpCr(NO)_2Cl + e^- \rightarrow [CpCr(NO)_2Cl]^- \cdot \quad (11)$$
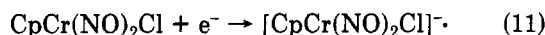
transformation 10 probably proceeds via the sequential reactions 12 and 13, where M = Na or $^1/_2$ Zn. The hete-

$$CpCr(NO)_2Cl + M \rightarrow CpCr(NO)_2^{\delta+}\cdots Cl^{\delta-}\cdots M \quad (12)$$

$$CpCr(NO)_2^{\delta+}\cdots Cl^{\delta-}\cdots M \rightarrow {}^1/_2 [CpCr(NO)_2]_2 + MCl \quad (13)$$

rolytic cleavage of the polar Cr–Cl linkage[35] involved in the first step would be facilitated by the electropositive reductant and/or a polar solvent, and the electron transfer involved in the second step would proceed via $CpCr(NO)_2 \cdot$ radical as shown in Scheme I.

At the outset of this work it was our hope that, having acquired information about the redox properties of $[CpCr(NO)_2]_2$ from the cyclic voltammetry studies, it would be possible to effect specific oxidations and reductions on a preparative scale by employing appropriate bulk electrolytic methods. However, the realization of this expectation has been thwarted by two factors, namely, (1) the difficulty of separating the desired organometallic products, particularly ionic species, from the excess of the (n-Bu$_4$N)PF$_6$ support electrolyte always present and (2) the inherent difficulties associated with carrying out electrolyses of long duration in CH_2Cl_2.[36] [For example,

(33) Hames, B. W.; Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1978**, *17*, 3644, and references contained therein.

(34) Hoyano, J. K.; Legzdins, P.; Malito, J. T. *J. Chem. Soc., Dalton Trans.* **1975**, 1022.

(35) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr., Sect. B* **1980**, *B36*, 795.
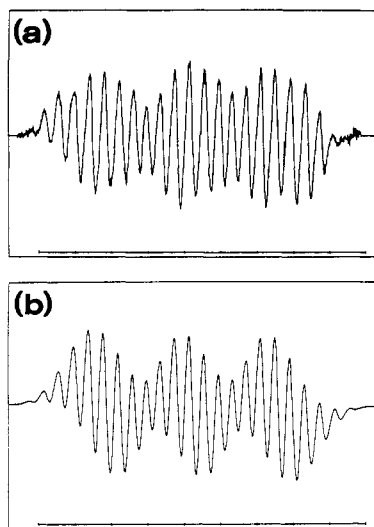
Figure 7. X-Band ESR spectrum of [CpFe(η⁶-C₆Me₆)][{CpCr-(NO)₂}₂] in DMF. (a) experimentally observed; g value = 1.997540. (b) Simulated employing the following spin Hamiltonian parameters: a_{N_1} = 5.89 G, a_{N_2} = 0.89 G, a_H = 1.05 G, p–p line width = 0.56.

during bulk reductions in our system (Figure 2), the oxidation product formed in the auxiliary compartment is a gas (probably resulting from the oxidation of PF_6^-) whose evolution enhances the vaporization of CH_2Cl_2 and consequently diminishes the auxiliary cell volume.] As a result, we have had to resort to chemical means to effect the redox conversions of [CpCr(NO)₂]₂ on a synthetically useful scale.

Preparative Work. As we have recently reported,[6] the two-electron oxidation of [CpCr(NO)₂]₂ to CpCr(NO)₂⁺ in CH_2Cl_2 may be conveniently carried out on a preparative scale by employing 2 equiv of a protonic acid as the oxidant (e.g., eq 1). The unsolvated product cation is quite thermally stable but is unisolable as such.[6] Nevertheless, it may be used in situ as a synthetic precursor to a wide variety of organometallic dinitrosylchromium complexes. Unlike its tungsten congener,[1] CpCr(NO)₂⁺ cannot be generated conveniently in CH_2Cl_2 by treatment of CpCr-(NO)₂Cl with an equimolar amount of a halide abstractor such as Ag^+.[37]

The one-electron reduction of the neutral nitrosyl dimer is best effected synthetically in Et_2O with CpFe(η⁶-C₆Me₆), a homogeneous and potent one-electron reductant,[18] i.e., eq 14. Under these conditions, the desired bimetallic

$$[CpCr(NO)_2]_2 + CpFe(\eta^6\text{-}C_6Me_6) \xrightarrow{Et_2O}$$

$$[CpFe(\eta^6\text{-}C_6Me_6)]^+[\{CpCr(NO)_2\}_2]^- \quad (14)$$
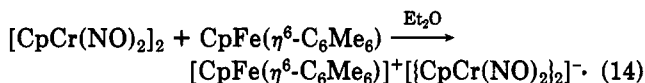
radical anion precipitates as its [CpFe(η⁶-C₆Me₆)]⁺ salt and is thus precluded from being reduced further (vide supra). The product salt from reaction 14, isolable in 69% yield, is a paramagnetic, olive green solid that is air-sensitive both in solution and in the solid state. It dissolves readily in polar organic solvents having good solvating abilities[38] to form intense brown solutions. Its Nujol mull IR spectrum

displays two strong nitrosyl absorptions at 1580 and 1331 cm^{-1} attributable to terminal and bridging NO groups, respectively. These absorptions occur ~90 and ~175 cm^{-1}, respectively, lower in energy than those exhibited by [CpCr(NO)₂]₂ [IR (Nujol mull) ν_{NO} 1669 (s, br), 1505 (s) cm^{-1}] and indicate substantial delocalization of the extra electron density in the radical anion onto the NO ligands, particularly the bridging nitrosyl groups. Consistent with this interpretation is the fact that the ESR spectrum of the salt in DMF (Figure 7a) indicates strong coupling of the electron to one nitrogen atom (a_{N_1} = 5.89 G) and weaker couplings to a second nitrogen atom (a_{N_2} = 0.89 G) and ten equivalent cyclopentadienyl protons (a_H = 1.05 G) (Figure 7b). This spectrum also indicates that in DMF the bimetallic radical anion does not possess a centrosymmetric molecular structure analogous to that found for the parent nitrosyl dimer in the solid state.[39] Consequently, no inference concerning the atomic orbitals that contribute to the lowest unoccupied molecular orbital of [CpCr(NO)₂]₂ may readily be drawn. We are presently endeavoring to grow single crystals of [CpFe(η⁶-C₆Me₆)][{CpCr(NO)₂}₂] suitable for X-ray work as well as investigating its reactivity in solution.

Epilogue

In addition to establishing the fundamental redox properties of [CpCr(NO)₂]₂ and related complexes, this work has shown that because of the electronic perturbations that occur when M–CO linkages are replaced by formally isoelectronic M′–NO bonds,[40] the redox behavior of organometallic nitrosyl complexes cannot necessarily be inferred from that exhibited by their isoelectronic and isostructural carbonyl analogues. Furthermore, these studes have verified that the formal 16-electron cation CpCr(NO)₂⁺ is more readily accessible than its 18-electron anionic analogue, [CpCr(NO)₂]⁻, which remains unknown. This experimental observation is in accord with recent theoretical predictions[41] and demonstrates once again that the presence of nitrosyl ligands can impart distinctive chemical characteristics to a complex.[1]

(36) Iversen, P.; Lund, H. In "Organic Electrochemistry"; Baizer, M. M., Ed.; Marcel Dekker: New York, 1973; Chapter 4.

(37) Hartmann, G.; Fröböse, R.; Mews, R.; Sheldrick, D. M. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 1234.

(38) Drago, R. S. *Pure Appl. Chem.* **1980**, *52*, 2261.

(39) Calderón, J. L.; Fontana, S.; Frauendorfer, E.; Day, V. W. *J. Organomet. Chem.* **1974**, *64*, C10.

(40) (a) Morris-Sherwood, B. J.; Kolthammer, B. W. S.; Hall, M. B. *Inorg. Chem.* **1981**, *20*, 2771. (b) Hubbard, J. L. Ph.D. Dissertation, The University of Arizona, 1982.

(41) Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1984**, *106*, 2554.