

# Synthesis, Characterization, and Redox Properties of the 17-Valence-Electron Complexes Cp'Cr(NO)(L)X

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Treatment of CH<sub>2</sub>Cl<sub>2</sub> solutions of [Cp'Cr(NO)I]<sub>2</sub> [Cp' = Cp ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>) or Cp\* ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)] with various P- and N-containing Lewis bases, L, affords good yields of Cp'Cr(NO)(L)I complexes [L = PPh<sub>3</sub>, P(OMe)<sub>3</sub>, P(OPh)<sub>3</sub>, py, or C<sub>5</sub>H<sub>11</sub>N (pip)]. Photolysis of toluene solutions of CpCr(NO)(CO)<sub>2</sub> in the presence of PPh<sub>3</sub> and a source of halogen such as CH<sub>2</sub>Cl<sub>2</sub> results in a 63% isolated yield of CpCr(NO)(PPh<sub>3</sub>)Cl. In donor solvents, S, the ESR-active CpCr(NO)(L)X (X = Cl, I) compounds undergo either L or X substitution to form the 17-valence-electron CpCr(NO)(S)X and [CpCr(NO)(L)(S)]<sup>+</sup> species, respectively. A kinetic analysis of the reaction of CpCr(NO)(THF)I with PPh<sub>3</sub> shows the process to be second-order overall (first-order in each reactant) and associative in nature. The reduction potentials for the various CpCr(NO)(L)X complexes in THF vary from -1.05 to -1.65 V. These reductions are irreversible and are followed by loss of X<sup>-</sup>. Consistently, reduction of CpCr(NO)(PPh<sub>3</sub>)I in THF by Zn in the presence of P(OPh)<sub>3</sub> affords the 18-valence-electron mixed phosphine-phosphite complex, CpCr(NO)(PPh<sub>3</sub>)-[P(OPh)<sub>3</sub>]. The redox chemistry of the CpCr(NO)(L)X complexes is thus unusual in that the odd-electron species are substitutionally less labile than are their 18-electron reduction products.

## Introduction

In recent years, interest in paramagnetic organotransition-metal complexes has increased dramatically.<sup>1-4</sup> By virtue of their odd number of valence electrons, these species possess distinctive electronic properties which can, on occasion, lead to useful reactivity.<sup>5</sup> In general, such complexes are frequently too reactive to be isolated since odd-electron species are usually much more substitutionally labile than are their corresponding diamagnetic analogues.<sup>6</sup> Nevertheless, recent elegant work has shown that some of these radical species can be isolated and do indeed display unique reactivity.<sup>7</sup>

One class of paramagnetic organometallic complexes involves the 17-valence-electron chromium nitrosyl species, Cp'Cr(NO)(L)X [Cp' = Cp ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>), Cp\* ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>); L = Lewis base; X = halide]. Although some members of this class have been known for more than 25 years,<sup>8</sup> the characteristic chemical properties of these compounds have remained largely unexplored. Consequently, we decided to undertake such an investigation, and in this paper we present the characteristic redox and substitution chemistry of these 17-electron halide complexes.

## Experimental Section

General procedures routinely employed in these laboratories have been described previously.<sup>9</sup> Chromatographic separations were effected on alumina I (60-100 mesh, Fisher), and filtrations were performed through Celite 545 diatomaceous earth (Fisher) that had been oven-dried and cooled in vacuo. All reagents were purchased from commercial suppliers or were prepared according to literature methods. Thus, CpCr(NO)(CO)<sub>2</sub>,<sup>10</sup> [CpCr(NO)I]<sub>2</sub>,<sup>11</sup> CpCr(NO)(PPh<sub>3</sub>)I,<sup>11</sup> and CpCr(NO)[P(OPh)<sub>3</sub>]I<sup>11</sup> were prepared by published procedures.

**Solution Molecular-Weight Measurements.** The molecular weight of [CpCr(NO)I]<sub>2</sub> in solution was determined by the Signer method<sup>12</sup> over a period of 30 days using azobenzene as the reference standard. An IR spectrum of the final solution revealed that ca. 10% decomposition of the organometallic complex had occurred, as judged by the intensities of the new IR bands at 1809 and 1711 cm<sup>-1</sup> due to CpCr(NO)<sub>2</sub>I, the decomposition product.

**Electrochemical Measurements.** The detailed methodology employed for cyclic voltammetry (CV) studies in these laboratories has been previously described.<sup>13-15</sup> All potentials experimentally determined are reported versus the aqueous saturated calomel electrode (SCE) and are collected in Table 1. For irreversible features, *E'* is assigned the value of the peak potential, *E*<sub>p,c</sub> or *E*<sub>p,a</sub>, observed under the conditions used in this study. Compensation for *iR* drop was not employed. Ferrocene (Fc) was used as an internal reference during these studies with the redox couple, Fc/Fc<sup>+</sup>, occurring at *E*' = 0.55 V versus SCE in THF and *E*' = 0.34 V versus SCE in MeCN over the range of

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Table 1. Electrochemical Data for CpCr(NO)(L)X Complexes

compd (solvent)	scan rate $\nu$ (V/s)	oxidation potential $E'_{ox}$ vs SCE (V)	reduction potential $E'_{red}$ vs SCE (V)	$E_{pa} - E_{pc}$ for Fc/Fc <sup>+</sup> couple (mV)
CpCr(NO)[P(OMe) <sub>3</sub> ]I (THF)	0.10		-1.05	96
	0.40		-1.09	145
	1.00		-1.14	204
CpCr(NO)(PPh <sub>3</sub> )I (THF)	0.10		-1.14	104
	0.40		-1.18	150
	1.00		-1.22	205
CpCr(NO)(py)I (THF)	0.10		-1.17	94
	0.40		-1.20	135
	1.00		-1.24	183
CpCr(NO)(THF)I (THF)	0.10		-1.27	101
	0.40		-1.34	155
	1.00		-1.40	210
CpCr(NO)(pip)I (THF)	0.10		-1.52	103
	0.40		-1.59	152
	1.00		-1.65	220
Cp*Cr(NO)(py)I (THF)	0.40	0.34	-1.91	16 <sup>a</sup>
CpCr(NO)[P(OMe) <sub>3</sub> ]I (MeCN)	0.40	0.37		
CpCr(NO)(PPh <sub>3</sub> )Cl (MeCN)	0.20	0.78	-1.05	109
CpCr(NO)(PPh <sub>3</sub> )I (MeCN)	0.20	0.34		
CpCr(NO)(PPh <sub>3</sub> )I (MeCN)	0.20	0.84	-1.33	65
Cp*Cr(NO)(PPh <sub>3</sub> )I (MeCN)	0.20	0.54	-1.43	76
Cp*Cr(NO)(PPh <sub>3</sub> )I (MeCN)	0.20	0.55	-1.54	
			-1.75	67

<sup>a</sup> This value is unusually small due to interaction between the substrate and the ferrocene standard.

scan rates used (0.05–1.00 V s<sup>-1</sup>). The ratio of cathodic peak current to anodic peak current,  $i_{pc}/i_{pa}$ , for the oxidation of Fc was unity over all scan rates used. Furthermore, the anodic peak current ( $i_{pa}$ ) increased linearly with  $\nu^{1/2}$ . Diffusion control was tested by observing the behavior of peak currents over at least 1 order of magnitude of scan rate.

**ESR Measurements.** Ambient temperature X-band ESR spectra of ca. 10<sup>-3</sup> M solutions were recorded using a Varian E-3 spectrometer calibrated with a sample of VO(acac)<sub>2</sub> (in THF,  $g = 1.969$ ,  $a_N = 101.7$  G)<sup>16</sup> or were recorded by Dr. F. G. Herring with the Varian spectrometer and interfaced computer system described by Phillips and Herring.<sup>17</sup> Solutions were prepared in an inert atmosphere glovebox and were transferred to capillary tubes which were then sealed with silicone grease. Data obtained in this manner are presented in Table 2.

**Kinetic Studies.** The methodology used in these laboratories for effecting kinetic studies by employing UV-vis measurements has been described in detail previously.<sup>15</sup> Solutions of [CpCr(NO)I]<sub>2</sub> in THF were prepared in an inert atmosphere glovebox, and 3.00-mL aliquots were placed in 1.00-cm UV-vis cells. These cells were placed in a HP-8452A diode array spectrophotometer and were allowed to come to thermal equilibrium before PPh<sub>3</sub> was added. A spectrum was recorded before the addition of phosphine to permit the calculation of the molar absorptivities. Absorption readings were generally recorded for two wavelengths, 460 and 540 nm, but in one case readings were measured at 460 and 520 nm. Measurements were recorded at intervals ranging from 1 to 10 min for periods of 2–24 h, depending on the temperatures used. Shorter reaction times were used for higher temperatures. Beer's law plots for CpCr(NO)(PPh<sub>3</sub>)I and [CpCr(NO)I]<sub>2</sub> in THF at these wavelengths displayed linear behavior over the range of concentrations used. For each set of readings, the simultaneous Beer's law equations were solved for the concentration of each species using absorption data from the two wavelengths measured. The isosbestic point occurred at 500 nm.

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Table 2. ESR Data for CpCr(NO)(L)X Complexes in THF

compd	g value	spectral params
CpCr(NO)(PPh <sub>3</sub> )Cl	1.994	$a_P = 20.4$ G; $a_N = 4.6$ G
CpCr(NO)(PPh <sub>3</sub> )I <sup>a</sup>	2.046	$a_P = 24.5$ G; 75%
CpCr(NO)(PPh <sub>3</sub> )I <sup>b</sup>	2.001	$a_P = 23.7$ G; $a_N = 5.0$ G; 25%
	2.045	$a_P = 24.5$ G; $a_N = 5.0$ G; 80%
	2.001	$a_P = 23.7$ G; $a_N = 5.0$ G; 20%
CpCr(NO)(PPh <sub>3</sub> )I <sup>c</sup>	2.046	$a_P = 24.5$ G; $a_N = 5.0$ G <sup>d</sup>
Cp*Cr(NO)(PPh <sub>3</sub> )I	2.040	$a_P = 27.5$ G; 30%
	2.012	$a_P = 5.0$ G; $a_N = 6.0$ G; 70%
Cp*Cr(NO)(PPh <sub>3</sub> )I <sup>c</sup>	2.039	$a_P = 27.5$ G; $a_N = 5.1$ G <sup>d</sup>
CpCr(NO)[P(OMe) <sub>3</sub> ]I	2.038	$a_P = 31.4$ G
CpCr(NO)[P(OPh) <sub>3</sub> ]I	2.006	$a_P = 24.5$ G
CpCr(NO)(py)I	2.026	$a_{Cr} = 11$ G
Cp*Cr(NO)(py)I	2.004	
Cp*Cr(NO)(py)I <sup>c</sup>	2.004	
CpCr(NO)(pip)I	2.022	$a_{Cr} = 15$ G
CpCr(NO)(THF)I	2.017	$a_N \approx 5$ G; $a_1 \approx 4$ G
		$a_{Cr} = 18$ G

<sup>a</sup> After 5-min reflux. <sup>b</sup> In MeCN. <sup>c</sup> In toluene. <sup>d</sup> Determined from second derivative spectrum.

**Synthesis of CpCr(NO)(L)I [L = P(OMe)<sub>3</sub>, pip, py].** These compounds were prepared by a modification of the procedure described for the synthesis of CpCr(NO)[P(OPh)<sub>3</sub>]I<sup>11</sup> as illustrated below for L = py.

To a stirred, olive green solution ( $\nu_{NO}$  1695, 1673 cm<sup>-1</sup>) of [CpCr(NO)I]<sub>2</sub> (0.27 g, 0.50 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added pyridine (81  $\mu$ L, 1.00 mmol) by syringe. The color changed from dark green to a brighter green over a period of 30 min. The solution was concentrated in vacuo to ca. 10 mL and was then filtered through alumina (1.5  $\times$  3 cm) supported on a medium-porosity frit. The column was washed with CH<sub>2</sub>Cl<sub>2</sub> until the washings were colorless. Hexanes (30 mL) were added to the combined filtrates, and the solution was concentrated under reduced pressure until crystallization had been initiated. The mixture was then cooled to -30 °C overnight to complete crystallization. The solvent was removed by cannulation, and the remaining dark green crystals were washed with pentane (3  $\times$  15 mL). This solid was dried in vacuo to obtain 0.32 g (90% yield) of analytically pure CpCr(NO)(py)I.

Anal. Calcd for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub>CrI: C, 34.02; H, 2.85; N, 7.93. Found: C, 34.15; H, 2.82; N, 7.80. IR (Nujol mull):  $\nu_{NO}$  1651 cm<sup>-1</sup>. FAB mass spectrum:  $m/z$  353 [P<sup>+</sup>].

Data for CpCr(NO)[P(OMe)<sub>3</sub>]I: 0.35 g, 88% yield. Anal. Calcd for C<sub>8</sub>H<sub>14</sub>NO<sub>4</sub>PCrI: C, 24.13; H, 3.54; N, 3.52. Found: C, 24.19; H, 3.54; N, 3.49. IR (Nujol mull):  $\nu_{NO}$  1650 cm<sup>-1</sup>. FAB mass spectrum:  $m/z$  398 [P<sup>+</sup>].

Data for CpCr(NO)(pip)I: 0.26 g, 74% yield. Anal. Calcd for C<sub>10</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub>CrI: C, 33.44; H, 4.49; N, 7.80. Found: C, 33.23; H, 4.46; N, 7.70. IR (Nujol mull):  $\nu_{NO}$  1651 cm<sup>-1</sup>. FAB mass spectrum:  $m/z$  359 [P<sup>+</sup>].

**Synthesis of CpCr(NO)(PPh<sub>3</sub>)Cl.** A solution of CpCr(NO)(CO)<sub>2</sub> (3.30 g, 16.2 mmol), PPh<sub>3</sub> (3.93 g, 15.0 mmol), and CH<sub>2</sub>Cl<sub>2</sub> (1.00 mL, 15.6 mmol) in toluene (200 mL) was placed in a photoreactor utilizing a medium-pressure mercury lamp (Hanovia L-450W) housed in a water-cooled quartz immersion well. The stirred orange solution was photolyzed for 24 h, during which time it became green and a green precipitate formed. The toluene was removed in vacuo, and the residue was extracted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The green extracts were filtered through Celite supported on a medium-porosity glass frit, and the filtrate was concentrated in vacuo until precipitation had initiated. The mixture was cooled to -30 °C overnight to complete precipitation. The precipitate was collected by filtration and washed with pentane (3  $\times$  20 mL) to obtain 4.80 g (63% yield) of analytically pure CpCr(NO)(PPh<sub>3</sub>)Cl.

Anal. Calcd for C<sub>23</sub>H<sub>20</sub>NOPClCr: C, 62.10; H, 4.54; N, 3.15. Found: C, 62.24; H, 4.54; N, 3.13. IR (Nujol mull):  $\nu_{NO}$  1645 cm<sup>-1</sup>. FAB mass spectrum:  $m/z$  444 [P<sup>+</sup>].

**Synthesis of Cp\*Cr(NO)(PPh<sub>3</sub>)I.** To a stirred orange solution of Cp\*Cr(NO)(CO)<sub>2</sub> (2.10 g, 10.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) was added I<sub>2</sub> (0.97 g, 3.81 mmol). A gas was evolved, the

orange solution became brown, and an IR spectrum of this solution exhibited a new  $\nu_{\text{NO}}$  at 1682  $\text{cm}^{-1}$ , presumably due to  $[\text{Cp}^*\text{Cr}(\text{NO})\text{I}]_2$ . After 10 min,  $\text{PPh}_3$  (2.00 g, 7.63 mmol) was added to the solution which immediately turned green as vigorous effervescence occurred. This solution was stirred for 30 min at room temperature, and then hexanes (60 mL) were added. The reaction mixture was concentrated in vacuo to a volume of ca. 20 mL, and then more hexanes (30 mL) were added. After the mixture had been stirred for an additional 30 min, the precipitate that had formed was collected by filtration. This crude product was recrystallized from  $\text{CH}_2\text{Cl}_2$ /hexanes to obtain 2.77 g (65% yield based on  $\text{I}_2$ ) of  $\text{Cp}^*\text{Cr}(\text{NO})(\text{PPh}_3)\text{I}$  as dark green needles.

Anal. Calcd for  $\text{C}_{28}\text{H}_{30}\text{NOPCrI}$ : C, 55.46; H, 4.99; N, 2.31. Found: C, 55.19; H, 4.97; N, 2.38. IR (Nujol mull):  $\nu_{\text{NO}}$  1632  $\text{cm}^{-1}$ . FAB mass spectrum:  $m/z$  606  $[\text{P}^+]$ .

**Synthesis of  $\text{Cp}^*\text{Cr}(\text{NO})(\text{py})\text{I}$ .** To a stirred orange solution of  $\text{Cp}^*\text{Cr}(\text{NO})(\text{CO})_2$  (1.0 g, 3.7 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added pyridine (0.30 mL, 0.29 g, 3.7 mmol) and  $\text{I}_2$  (0.44 g, 1.7 mmol). The resulting mixture was stirred at reflux for 1 day, whereupon it darkened to green brown and a green precipitate was formed. The reaction mixture was taken to dryness in vacuo. The green residue was first washed with  $\text{Et}_2\text{O}$  ( $5 \times 15$  mL) and then recrystallized in five crops from  $\text{CH}_2\text{Cl}_2$ / $\text{Et}_2\text{O}$  to obtain 0.83 g (57% yield based on  $\text{I}_2$ ) of  $\text{Cp}^*\text{Cr}(\text{NO})(\text{py})\text{I}$  as a dark green solid.

Anal. Calcd for  $\text{C}_{18}\text{H}_{20}\text{N}_2\text{OCrI}$ : C, 42.57, H, 4.76; N, 6.62. Found: C, 42.78; H, 4.89; N, 6.48. IR (Nujol mull):  $\nu_{\text{NO}}$  1624  $\text{cm}^{-1}$ , also 1599 (sh)  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{NO}}$  1642  $\text{cm}^{-1}$ , also 1605 (mw)  $\text{cm}^{-1}$ . FAB mass spectrum:  $m/z$  423  $[\text{P}^+]$ .

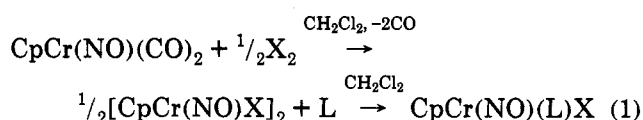
**Reaction of  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  with Zn and  $\text{P}(\text{O}^i\text{Pr})_3$ .** To a stirred suspension of  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  (0.30 g, 0.56 mmol) in THF (15 mL) was added Zn powder (0.20 g, 3.0 mmol) and  $\text{P}(\text{O}^i\text{Pr})_3$  (0.28 mL, 2.0 mmol). The resulting slurry was stirred for 2 days whereupon the color changed from dark green to bright orange. The IR spectrum of this solution displayed a single  $\nu_{\text{NO}}$  band at 1585  $\text{cm}^{-1}$ . The solvent was removed in vacuo, and the residue was extracted with toluene ( $3 \times 5$  mL). The extracts were filtered, and their volume was reduced in vacuo until incipient precipitation. Cooling the resulting mixture to  $-30$   $^\circ\text{C}$  for 2 days afforded 0.15 g (37% yield) of  $\text{CpCr}(\text{NO})(\text{PPh}_3)[\text{P}(\text{O}^i\text{Pr})_3]$  as orange microcrystals.

Anal. Calcd for  $\text{C}_{41}\text{H}_{38}\text{NO}_4\text{P}_2\text{Cr}$ : C, 68.42; H, 4.90; N, 1.95. Found: C, 68.23; H, 4.95; N, 1.99. IR (Nujol mull):  $\nu_{\text{NO}}$  1585  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (200 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  7.98–6.75 (m, 30H,  $\text{C}_6\text{H}_5$ ), 4.32 (t, 5H,  $^3J_{\text{P-H}} = 3.0$  Hz,  $\text{C}_6\text{H}_5$ ).  $^{31}\text{P}$  NMR (81 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  92.96, 87.43 (2d,  $^2J_{\text{P-P}} = 54.9$  Hz,  $\text{PPh}_3$ ,  $\text{P}(\text{O}^i\text{Pr})_3$ ). FAB mass spectrum:  $m/z$  719  $[\text{P}^+]$ .

The following additional signals attributable to  $\text{CpCr}(\text{NO})[\text{P}(\text{O}^i\text{Pr})_3]_2$  were evident in ca. 3% abundance in the NMR and FAB-MS spectra of  $\text{CpCr}(\text{NO})(\text{PPh}_3)[\text{P}(\text{O}^i\text{Pr})_3]$ .  $^1\text{H}$  NMR (200 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  4.15 (t,  $^3J_{\text{P-H}} = 2.6$  Hz,  $\text{C}_6\text{H}_5$ ).  $^{31}\text{P}$  NMR (81 MHz) ( $\text{C}_6\text{D}_6$ ):  $\delta$  127.99 (s,  $\text{P}(\text{O}^i\text{Pr})_3$ ). FAB mass spectrum:  $m/z$  767  $[\text{P}^+]$ .

## Results and Discussion

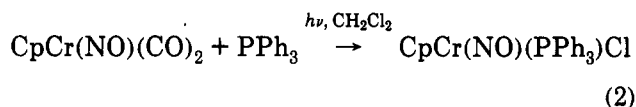
**Syntheses of  $\text{Cp}^*\text{Cr}(\text{NO})(\text{L})\text{X}$  Complexes.** The  $\text{Cp}^*\text{Cr}(\text{NO})(\text{L})\text{X}$  complexes ( $\text{Cp}^* = \text{Cp}$  or  $\text{Cp}^*$ ) can be prepared via the sequential steps shown in eq 1. The iodo complexes are the most convenient members of this class of complexes to synthesize for two reasons. First,  $\text{I}_2$  is



much easier to handle in a quantitative fashion than either  $\text{Cl}_2$  or  $\text{Br}_2$ . Second, the intermediate  $[\text{CpCr}(\text{NO})\text{I}]_2$

compound (eq 1) is more thermally stable in solution and hence does not decompose to the corresponding  $\text{CpCr}(\text{NO})_2\text{X}$  species as readily as do the bromo or chloro dimers.<sup>11</sup> The one-pot approach summarized in eq 1 also provides convenient access to the analogous  $\text{Cp}^*$  compounds such as  $\text{Cp}^*\text{Cr}(\text{NO})(\text{PPh}_3)\text{I}$ . These  $\text{Cp}^*$  complexes have not been previously synthesized since the requisite  $[\text{Cp}^*\text{Cr}(\text{NO})\text{X}]_2$  complexes have not been isolated. Previous attempts to prepare these dimeric compounds resulted in the formation of  $\text{Cp}^*\text{Cr}(\text{NO})_2\text{X}$  complexes.<sup>11</sup> We also find that  $\text{Cp}^*\text{Cr}(\text{NO})_2\text{I}$  begins to form even before all the  $\text{Cp}^*\text{Cr}(\text{CO})_2(\text{NO})$  has been consumed by  $\text{I}_2$  during conversion 1.

This work has also produced another method by which the chloro species can be generated (eq 2). Photolysis of toluene solutions of  $\text{CpCr}(\text{NO})(\text{CO})_2$  in the presence of  $\text{L} = \text{PPh}_3$  and a source of halogen such as  $\text{CH}_2\text{Cl}_2$  results in

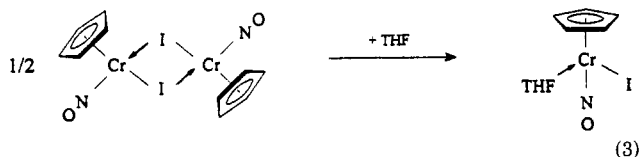


good yields of the desired paramagnetic product,  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{Cl}$ . It has been shown previously<sup>19</sup> that in the absence of  $\text{CH}_2\text{Cl}_2$ , these experimental conditions result in the formation of  $\text{CpCr}(\text{NO})(\text{CO})\text{L}$  and  $\text{CpCr}(\text{NO})\text{L}_2$  complexes.

As solids, the  $\text{CpCr}(\text{NO})(\text{L})\text{X}$  complexes prepared during this work are air-stable. In solutions, they are air-sensitive, and intractable brown solids precipitate from initially green solutions in a matter of hours. The paramagnetic complexes are generally soluble in polar organic solvents, and their solutions exhibit ESR signals at room temperature (Table 2). These signals reveal  $^{53}\text{Cr}$  satellites indicative of coupling of the unpaired electron to the metal center. There is also interaction of the unpaired electron with ligands in the metal's coordination sphere, as evidenced by the observation of coupling to  $^{31}\text{P}$  in phosphorus-containing complexes. The signal due to the chloride complex possesses a sharper line width, and this permits observation of coupling to the nitrosyl nitrogen. The broad line width of the signals due to some iodo complexes obscures such features which are only detectable in the second-derivative spectra (Table 2).

**Solution Studies of  $\text{CpCr}(\text{NO})(\text{L})\text{I}$  Complexes.** By the Gouy method,  $\mu_{\text{eff}}$  for  $[\text{CpCr}(\text{NO})\text{I}]_2$  at 298 K is 0.90  $\mu_{\text{B}}$ , a value consistent with significant electronic interaction between the metal centers.<sup>11</sup> On the other hand, application of Evans' method to an 8% *t*-BuOH in  $\text{CHCl}_3$  solution of the complex affords a value of 1.94  $\mu_{\text{B}}$  for  $\mu_{\text{eff}}$ .<sup>11</sup> Because of this discrepancy between solid-state and solution magnetic measurements, we decided to examine more closely the behavior of  $[\text{CpCr}(\text{NO})\text{I}]_2$  in solution by molecular-weight measurements and by ESR and IR spectroscopy.

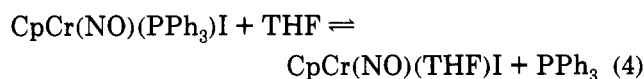
At room temperature,  $[\text{CpCr}(\text{NO})\text{I}]_2$  appears to be dimeric in noncoordinating solvents, but monomeric in donor solvents. For example, in THF the complex exists as monomeric  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$  (eq 3). Thus, the ESR



spectrum of  $[\text{CpCr}(\text{NO})\text{I}]_2$  in  $\text{C}_6\text{H}_6$  and  $\text{CH}_2\text{Cl}_2$  is devoid

of signals, a fact consistent with the view that the compound is dimeric in these solvents and that antiferromagnetic coupling takes place through the iodide bridges. In contrast, the ESR spectrum of [CpCr(NO)I]<sub>2</sub> in THF displays an intense signal which reveals the presence of a single ESR-active radical. This signal displays <sup>53</sup>Cr satellites and reveals hyperfine coupling to other atoms in the metal's coordination sphere (Table 2), all of which are consistent with the formation of the 17-electron, solvo monomer. Consistently, molecular-weight measurements of [CpCr(NO)I]<sub>2</sub> in THF at 19 °C indicate a weight of 340 ± 30, a value close to that expected for monomeric CpCr(NO)(THF)I (346). Further evidence for the monomeric nature of [CpCr(NO)I]<sub>2</sub> in THF comes from IR spectroscopy. The ν<sub>NO</sub> bands of [CpCr(NO)I]<sub>2</sub> in the noncoordinating CH<sub>2</sub>Cl<sub>2</sub> (1695 and 1673 cm<sup>-1</sup>) are very similar to those evident in the solid-state Nujol mull spectrum (i.e. 1682 and 1651 cm<sup>-1</sup>). In contrast, the corresponding spectrum in THF displays a single sharp and symmetric nitrosyl band at 1672 cm<sup>-1</sup>.

The CpCr(NO)(THF)I complex is present to a small, but detectable, extent when some CpCr(NO)(L)I compounds are dissolved in THF. For example, CpCr(NO)(PPh<sub>3</sub>)I in THF undergoes loss of the phosphine ligand to form a small amount of the solvo complex (eq 4), a

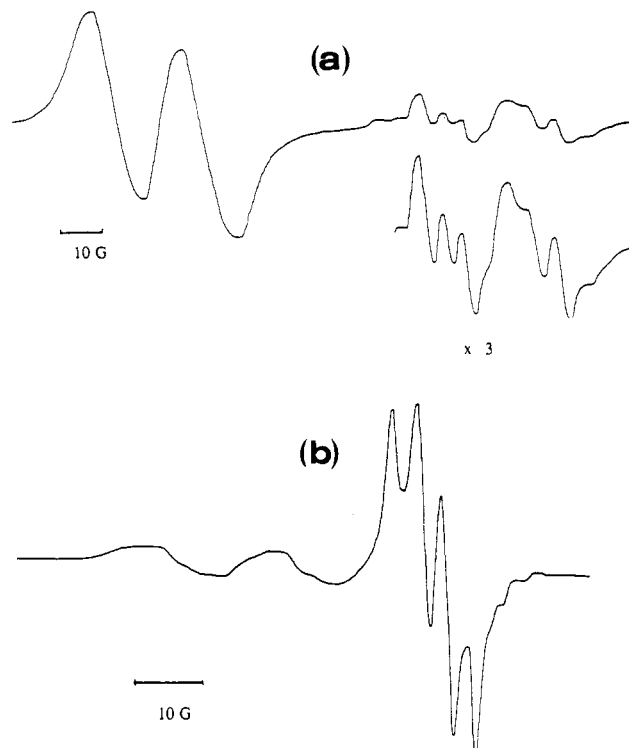


process most conveniently detected by ESR spectroscopy. Thus, the room temperature ESR spectrum of 0.2 M CpCr(NO)(PPh<sub>3</sub>)I in THF displays a small singlet at  $g = 2.017$  which corresponds to the CpCr(NO)(THF)I complex. This feature appears in addition to the doublet characteristic of the phosphine complex (Table 2). The intensity of the former signal indicates that the solvo complex is present in no more than 1% abundance, the equilibrium constant for the ligand metathesis process in eq 4 at room temperature thus being  $K_{\text{eq}} \approx 2 \times 10^{-5}$ . Consistently, ESR monitoring confirms that the same equilibrium is established from CpCr(NO)(THF)I and a slight excess of PPh<sub>3</sub>. As expected, the corresponding spectrum of CpCr(NO)(PPh<sub>3</sub>)I in toluene reveals no signal in addition to that diagnostic of the phosphine complex.

Dissociation of the two-electron donor ligand, L, is not the only reaction that can occur upon dissolution of some CpCr(NO)(L)X complexes. Heating in donor solvents (S) appears to cause partial dissociation of I<sup>-</sup>, a process which results in the formation of ionic species (eq 5). Evidence



for conversion 5 again comes from ESR spectroscopy. For example, the ESR spectrum of a sample of CpCr(NO)(PPh<sub>3</sub>)I which has been briefly refluxed in THF indicates the presence of at least two radicals (Figure 1a). The spectrum displays a doublet and a doublet of 1:1:1 triplets in a 3:1 ratio, the major signal being due to the starting material. The signal due to the minor species obscures the signal due to CpCr(NO)(THF)I (vide supra), but it exhibits  $a_N$ ,  $a_P$ , and  $g$  values which suggest that the identity of the complex responsible for it is [CpCr(NO)(PPh<sub>3</sub>)-



**Figure 1.** (a) ESR spectrum of CpCr(NO)(PPh<sub>3</sub>)I in THF at 298 K after having been heated to reflux for 5 min. (b) ESR spectrum of Cp\*Cr(NO)(PPh<sub>3</sub>)I in THF at 298 K.

(THF)]<sup>+</sup>. Thus, the value of  $a_P$  decreases from 24.5 to 21.0 G, as expected for the formation of a cationic species where the unpaired electron is bound more strongly to the metal center and thus spends less time on the ligands.<sup>20</sup> Furthermore, the values of  $g$  and  $a_N$  are similar to those previously observed for related cations,<sup>21</sup> and treatment of [CpCr(NO)(THF)<sub>2</sub>]<sup>+</sup> 21b in THF with PPh<sub>3</sub> generates a solution which exhibits the same ESR signal as that attributed to [CpCr(NO)(PPh<sub>3</sub>)(THF)]<sup>+</sup>. The fact that this signal is sharper than that of CpCr(NO)(PPh<sub>3</sub>)I also suggests that the iodo ligand is no longer coordinated to the metal, a general feature for these systems.

Stronger donor solvents such as MeCN appear to facilitate loss of the I<sup>-</sup> ligand. Thus, the ESR spectrum of CpCr(NO)(PPh<sub>3</sub>)I in MeCN exhibits two signals (Table 2). Since both of these signals display coupling to <sup>31</sup>P and <sup>14</sup>N, it is likely that the complexes are related by loss of I<sup>-</sup> from the metal's coordination sphere. Unfortunately, attempts to isolate these solvated cationic species by halide abstraction from the parent CpCr(NO)(PPh<sub>3</sub>)I complex with AgPF<sub>6</sub> have been hampered by concomitant decomposition which results in the ultimate formation of the known diamagnetic [CpCr(NO)<sub>2</sub>(PPh<sub>3</sub>)]PF<sub>6</sub>.<sup>22</sup>

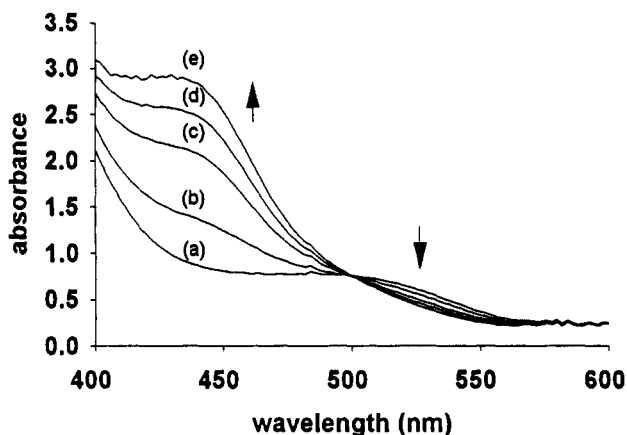
The loss of I<sup>-</sup> is also facilitated by steric crowding at the metal center. Thus, Cp\*Cr(NO)(PPh<sub>3</sub>)I undergoes a more facile loss of the halide ligand than does Cp\*Cr(NO)(py)I and exists in donor solvents primarily as an ionic species. In toluene the Cp\*Cr(NO)(PPh<sub>3</sub>)I complex displays only

(20) Newbound, T. D.; Rheingold, A. L.; Ernst, R. D. *Organometallics* 1992, 11, 1693.

(21) These values agree well with those for the known [CpCr(NO)(MeCN)<sub>2</sub>]BF<sub>4</sub> salt and for other recently observed cations of the type [CpCr(NO)(L)<sub>2</sub>]X. (a) Chin, T. T.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* 1992, 11, 913. (b) The [CpCr(NO)(THF)<sub>2</sub>]<sup>+</sup> cation can be generated in THF solution by treatment of CpCr(NO)(THF)I with silver salts: Legzdins, P.; McNeil, W. S. Manuscript in preparation.

(22) Herring, F. G.; Legzdins, P.; McNeil, W. S.; Shaw, M. J. *J. Am. Chem. Soc.* 1991, 113, 7049.

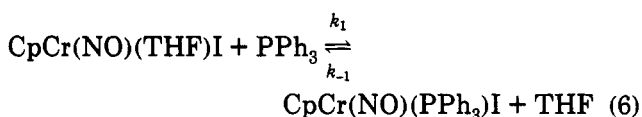
(19) (a) Brunner, H. J. *Organomet. Chem.* 1969, 16, 119. (b) Legzdins, P.; Richter-Addo, G. B. *Metal Nitrosyls*; Oxford University Press: New York, 1992; Chapter 4 (see also references contained therein).



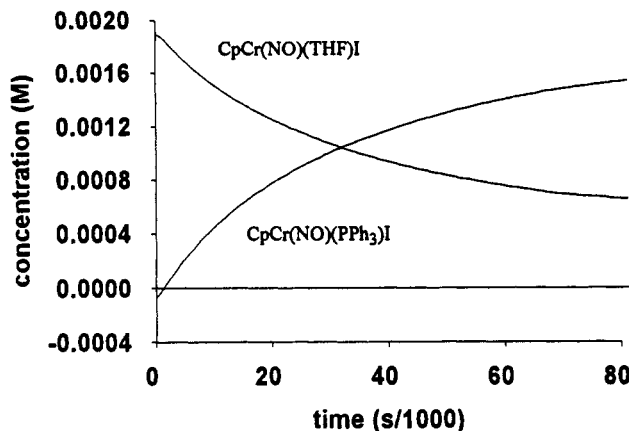
**Figure 2.** Spectral monitoring of the reaction of  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$  with 10 equiv of  $\text{PPh}_3$  at 300 K: (a) 0 min; (b) 20 min; (c) 40 min; (d) 100 min; (e) 180 min.

the expected doublet in its ESR spectrum, but in THF this signal is of relatively low intensity. In the latter solvent, another radical which possesses a lower  $g$  value is the major species, as shown in Figure 1b. This radical displays a sharper signal consisting of an overlapping doublet of triplets due to hyperfine coupling of the signal to  $^{31}\text{P}$  and  $^{14}\text{N}$ . Also, the fact that the value of  $a_{\text{P}}$  decreases from 27.5 to 6.0 G reveals that the unpaired electron is bound more strongly to the metal center, as expected for a cationic radical.<sup>20</sup> Overall, this evidence suggests that in THF solution ( $\nu_{\text{NO}} 1625 \text{ cm}^{-1}$ ) the predominant species is  $[\text{Cp}^*\text{Cr}(\text{NO})(\text{PPh}_3)(\text{THF})]\text{I}$ . In contrast, the ESR spectra of  $\text{Cp}^*\text{Cr}(\text{NO})(\text{py})\text{I}$  in THF and toluene are identical (Table 2), thus confirming that the steric effect of the pyridine ligand is minimal.

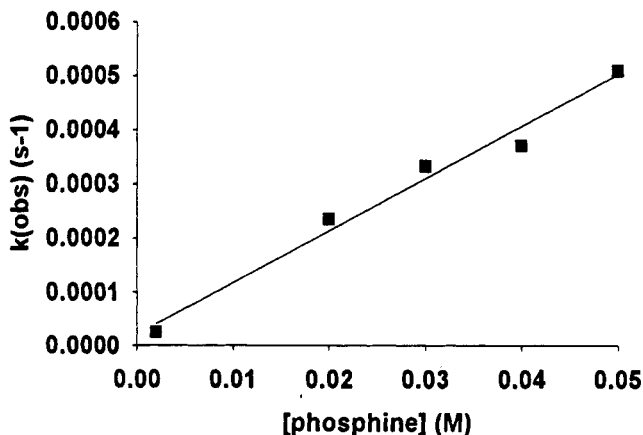
**Kinetic Studies of the Reaction of  $\text{PPh}_3$  with  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$ .** As outlined in the preceding section, the characteristic reactivity of  $\text{CpCr}(\text{NO})(\text{L})\text{X}$  complexes in solution is dominated by ligand-substitution reactions. In order to gain some quantitative information about these processes, we have investigated the reaction of  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$  with  $\text{PPh}_3$  in THF (eq 6) in some detail. This



study has established that the reaction is second-order overall, first-order in each reactant, and is associative in nature.<sup>23</sup> For the purposes of a kinetic study, reaction 6 is best monitored by UV-vis spectroscopy which reveals the presence of an isobestic point at 500 nm (Figure 2). Treatment of a  $2.00 \times 10^{-3} \text{ M}$  THF solution of  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$  with 10 equiv of  $\text{PPh}_3$  at 30 °C results in a color change from orange-brown to green over a period of ca. 2 h (Figure 3). The fact that the reaction is second-order overall is demonstrated by the linearity of a plot of  $[\text{CpCr}(\text{NO})(\text{THF})\text{I}]^{-1}$  vs time for the reaction where both the  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$  and  $\text{PPh}_3$  reagents are initially present in  $2.00 \times 10^{-3} \text{ M}$  concentrations. From the slope of this plot, the rate constant is determined to be  $k_1 = (1.4$



**Figure 3.** Plots of concentration vs time for the reaction between  $2.00 \times 10^{-3} \text{ M}$   $\text{CpCr}(\text{NO})(\text{THF})\text{I}$  and  $2.00 \times 10^{-3} \text{ M}$   $\text{PPh}_3$  at 303 K.



**Figure 4.** Plot of  $k_{\text{obs}}$  vs  $[\text{PPh}_3]$  for the reaction of  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$  with  $\text{PPh}_3$ .

$\pm 0.1) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ . This rate constant is several orders of magnitude less than the  $(9.09 \pm 0.81) \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  recently found for the related reaction of  $\text{CpCr}(\text{CO})_3$  with  $\text{PPh}_3$ ,<sup>24</sup> thus indicating that the nitrosyl system is much less substitutionally labile than the sterically similar carbonyl system.

Obviously, the above treatment is valid only if the reaction is first-order in both  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$  and  $\text{PPh}_3$ . To establish conclusively the order of reaction with respect to  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$ , the method of initial reaction rates was used.<sup>25</sup> The slope of the plot of  $\ln(\nu)$  vs  $\ln(C_0)$  for this reaction is  $1.11 \pm 0.05$ , thereby establishing that the reaction is indeed first-order in  $\text{CpCr}(\text{NO})(\text{THF})\text{I}$ . The value of  $\ln[k_{\text{obs}}]$ , obtained from the intercept of this plot, yields  $k_{\text{obs}} = (3.5 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$  and  $k_1 = (1.7 \pm 0.3) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ . This value of  $k_1$  is consistent with that obtained above.

A plot of the initial concentration of  $\text{PPh}_3$  vs  $k_{\text{obs}}$  for several different concentrations of  $\text{PPh}_3$  proves to be linear with a  $y$ -intercept close to zero, as shown in Figure 4. The linearity of this graph establishes that the reaction is first-order in phosphine, and its slope of  $(9.6 \pm 0.7) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$  provides yet another measure of  $k_1$  which is again consistent with the other treatments of the data.

To evaluate the activation parameters  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  for conversion 6, the reaction between  $2.00 \times 10^{-3} \text{ M}$   $\text{CpCr}$

(23) This treatment ignores the effect of the back-reaction. However, since the equilibrium constant for the dissociation reaction is about  $2 \times 10^{-5}$ , the back reaction has a rate constant of  $k_{-1} = 3 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$ . The back-reaction is thus relatively unimportant, given the fact that initial rates of reaction are used in the determination of the parameters of the forward reaction.

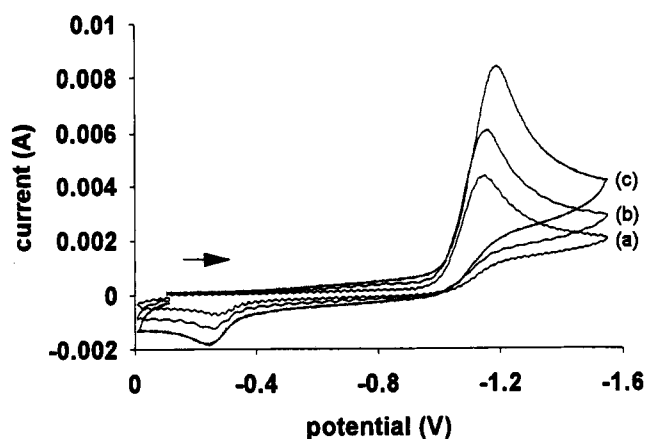
(24) Watkins, W. C.; Hensel, K.; Fortier, S.; Macartney, D. H.; Baird, M. C.; McLain, S. J. *Organometallics* 1992, 11, 2418.

(25) Laidler, K. J. *Chemical Kinetics*, 3rd ed.; Harper and Row: New York, 1987; Chapter 1.

(NO)(THF)I and  $2.00 \times 10^{-2}$  M  $\text{PPh}_3$  was studied in the temperature range from 15 to 55 °C in 5-deg intervals. This study produced values of  $\Delta H^\ddagger = 62 \pm 10$  kJ/mol and  $\Delta S^\ddagger = -79 \pm 10$  J/(mol K), as determined from the appropriate Eyring plot of  $\ln(k/T)$  vs  $1/T$ . The relatively low value for  $\Delta H^\ddagger$  and the negative value of  $\Delta S^\ddagger$  clearly establish that this reaction is associative in nature. This result is consistent with what is currently known about the mechanisms of ligand-exchange reactions for other 17-electron compounds.<sup>2,26,27</sup> It is also instructive to compare these values to the activation parameters which have been determined recently for the related reaction of  $\text{CpCr}(\text{CO})_3$  with  $\text{PPh}_3$ .<sup>24</sup> In the carbonyl case,  $\Delta H^\ddagger = 30 \pm 10$  kJ mol<sup>-1</sup> and  $\Delta S^\ddagger = -170 \pm 32$  J mol<sup>-1</sup> K<sup>-1</sup>. Evidently, more significant bond cleavage occurs in the attainment of the transition state by the nitrosyl complex, as indicated by its higher  $\Delta H^\ddagger$  value. In contrast, its  $\Delta S^\ddagger$  is less negative than that for the carbonyl reaction, thus indicating that less ordering has to occur for the nitrosyl system to reach its transition state. Possible explanations of these thermodynamic data are that the substitution of the nitrosyl complex is aided by some degree of Cp ring slippage or NO ligand bending in the transition state. It may also be noted that by the principle of microscopic reversibility the ligand dissociation which occurs when  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  is dissolved in THF (eq 4, the reverse of eq 6) must also occur associatively.

**Redox Properties of CpCr(NO)(L)X Compounds.** The reduction potentials for the various  $\text{CpCr}(\text{NO})(\text{L})\text{X}$  complexes in THF vary from -1.05 to -1.65 V (Table I). No oxidation features are detectable within the solvent limits. The shifts in reduction potentials are consistent with the donor properties of the ligands, L, with more potent bases giving rise to complexes having more negative reduction potentials. This trend is as expected since an increase in the amount of electron density on the metal center should render the complex more difficult to reduce.

The redox properties of  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  are typical of this class of complexes. A  $7.5 \times 10^{-5}$  M solution of  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  in THF displays an irreversible reduction feature in its cyclic voltammogram at ca. -1.2 V vs SCE. As expected for irreversible reduction features, the value of  $E'$  depends on the scan rate, as illustrated in Figure 5. The compound displays no oxidation features in its cyclic voltammograms, except for features at potentials both more positive and more negative than 0 V vs SCE which appear only after the reduction feature has been scanned. The feature at ca. -0.25 V (Figure 5) is attributed to oxidation of an organometallic reduction product whose exact nature remains to be ascertained. However, since no feature attributable to the initially formed  $[\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}]^-$  anion is evident, the lifetime of this anion must be much less than the time required (ca. 0.5 s) to scan from the switching potential to the potential where such an oxidation may be reasonably expected (ca. -1.1 V). Thus, the rate of decomposition of  $[\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}]^-$  is orders of magnitude faster than the rate of the simple ligand substitution reaction (6). In

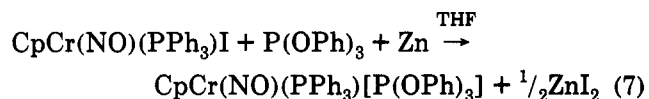


**Figure 5.** Cyclic voltammograms of  $7.5 \times 10^{-5}$  M  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  in THF at scan rates of (a) 0.10 V/s, (b) 0.40 V/s, and (c) 1.00 V/s.

other words, the 17-electron  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  is less substitutionally labile than is its 18-electron congeneric anion.

The new features that appear above 0 V in the cyclic voltammograms after the reduction feature has been scanned are anodic peaks at ca. +0.30 and +0.55 V which are due to liberated  $\text{I}^-$ .<sup>14</sup> This conclusion may be confirmed by adding NaI to the electrochemical cell, an operation which causes the observed oxidation features to increase in intensity. It should be emphasized that the evidence for  $\text{I}^-$  is present in the cyclic voltammograms only after initial reduction of the  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  complex has occurred. This observation confirms that the complex must initially retain the  $\text{I}^-$  ligand in the metal's coordination sphere under the conditions used for the electrochemical measurements. However, as discussed above, the  $\text{I}^-$  ligand can dissociate from the metal center under some conditions and form ionic species in solution. Not surprisingly, therefore, there are complications in the electrochemical investigations of the  $\text{CpCr}(\text{NO})(\text{L})\text{X}$  compounds upon changing the solvent from THF to MeCN. The fact that these complexes become partially ionized in MeCN and form a number of species in solution explains both the differences in the reduction potentials from those found in THF and the concomitant observation of oxidation features (Table I).

The results of chemical reduction of the  $\text{CpCr}(\text{NO})(\text{L})\text{X}$  complexes are consistent with the electrochemical studies. For instance, reaction of  $\text{CpCr}(\text{NO})(\text{PPh}_3)\text{I}$  with  $\text{P}(\text{O}Ph)_3$  and Zn dust in THF generates the 18-valence-electron mixed phosphine-phosphite complex,  $\text{CpCr}(\text{NO})(\text{PPh}_3)[\text{P}(\text{O}Ph)_3]$  (eq 7). Conversion 7 is consistent with



previous studies in which solutions containing  $[\text{CpCr}(\text{NO})\text{I}]_2$  and excess ligand, L, were reduced with Na/Hg to obtain the corresponding  $\text{CpCr}(\text{NO})(\text{L})_2$  complexes.<sup>18</sup> Essentially, both reactions can be viewed as proceeding via initial reduction which causes halide loss, followed by trapping of the coordinatively unsaturated " $\text{CpCr}(\text{NO})(\text{L})$ " fragments with another equivalent of ligand.

## Summary

In contrast to most 17-electron compounds which are mild oxidants,<sup>28a</sup> the  $\text{CpCr}(\text{NO})(\text{L})\text{X}$  complexes are rel-

(26) Trogler, W. C. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Chapter 9.

(27) (a) Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Elsevier: New York, 1990; Chapter 3 and references contained therein. (b) Shen, J. K.; Freeman, J. W.; Hallinan, N. C.; Rheingold, A. L.; Arif, A. M.; Ernst, R. D.; Basolo, F. *Organometallics* 1992, 11, 3215.

atively difficult to reduce. In addition, the redox chemistry of the  $\text{CpCr}(\text{NO})(\text{L})\text{X}$  complexes is unusual in that it is the odd-electron species which are substitutionally less labile. Usually, 17-electron compounds are more substitutionally labile than the corresponding 18-electron species obtained by their reduction.<sup>26</sup> However, in the chromium systems the situation is reversed as electron transfer induces lability, leading to loss of  $\text{I}^-$  and the formation of neutral Cr-containing materials. To the best of our knowledge, there is only one other system, namely  $\text{CpMoI}_2(\text{PMe}_3)_2$ , which exhibits this kind of greater lability after electron transfer to or from paramagnetic species.<sup>28</sup>

The 17-valence-electron  $\text{CpCr}(\text{NO})(\text{L})\text{X}$  species also possess unusual chemical properties. In moderate donor solvents they are in equilibrium with solvated species via a ligand-dissociation process. In strong donor solvents, on the other hand, they lose  $\text{I}^-$  and form ionic species. By conventional criteria,<sup>6,29</sup> they are not substitutionally

labile, although like other 17-electron species their ligand metatheses reactions appear to occur associatively via second-order reactions. They are not easily oxidized, but upon reduction to compounds containing an even number of electrons, their lability increases and they undergo halide substitution to form diamagnetic  $\text{CpCr}(\text{NO})(\text{L})_2$ -type species. Their relative ease of reduction shows a strong dependence on the identity of the two-electron donor ligand, L, bound to the metal center, the more electron-rich complexes being harder to reduce.

**Acknowledgment.** We are grateful to the Natural Sciences and Engineering Research Council of Canada for support of this work in the form of grants to P.L. and a postgraduate scholarship to W.S.M. We also thank Professor F. G. Herring of this Department for assistance with some of the ESR measurements.

OM930569R

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(28) (a) Abugideiri, F.; Kelland, M. A.; Poli, R.; Rheingold, A. L. *Organometallics* **1992**, *11*, 1311. (b) Abugideiri, F.; Kelland, M. A.; Poli, R. *Organometallics* **1992**, *11*, 1303. (c) Poli, R.; Owens, B. E.; Linck, R. G. *J. Am. Chem. Soc.* **1992**, *114*, 1302.

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(29) Taube, H. *Chem. Rev.* **1952**, *50*, 69.