Synthesis and Characterization of 17-Valence-Electron [CpCr(NO)X₂]⁻ Anions: Oxidatively Induced Loss of the Nitrosyl Ligand[1]

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Abstract: Several anionic and paramagnetic [CpCr(NO)X₂]⁻ complexes (X = I [**1**], O₃SCF₃ (OTf) [**2**], Br [**3**], Cl [**4**]) have been prepared as potential precursors to neutral CpCr(NO)X₂ species. Reaction of [CpCr(NO)I]₂ with [NBu₄]I provides [NBu₄][**1**], and halide abstraction from [NBu₄][**1**] with 2 equiv of AgOTf affords [NBu₄][**2**]. The weakly-bound OTf⁻ ligands of [NBu₄][**2**] are readily displaced by Br⁻ to produce [NBu₄][**3**]. The dichloro complexes [NEt₄][**4**] and [PPN][**4**] are obtained by treating [CpCr(NO)Cl]₂ with [NEt₄]Cl and [PPN]Cl, respectively. Use of acetonitrile as reaction solvent allows generation of the requisite [CpCr(NO)Cl]₂ directly from CpCr(NO)(CO)₂ and PCl₅, a marked improvement over previous synthetic routes to this dimer. Similar halogenations of Cp*Cr(NO)-(CO)₂ in NCMe provide access to the previously unknown [Cp*Cr(NO)I]₂ (**5**), and [Cp*Cr(NO)Cl]₂ (**6**), halo-bridged, and dimers. The solid-state molecular structure of [PPN][**4**]·CH₂Cl₂ has been established by single-crystal X-ray crystallography to be a normal three-legged piano stool. The one-electron oxidation of [**4**] has been investigated both chemically (by reaction with [Cp₂Fe]⁺) and electrochemically (by cyclic voltammetry). These studies suggest that upon oxidation a high-spin CpCr(NO)Cl₂ complex is initially formed which then rapidly releases NO. Extended Hückel molecular-orbital calculations have been performed on [**4**], [CpCr(CO)₃]⁻, and [CpCrCl₃]⁻, three CpCr-containing anions with ligands of varying π-bonding capabilities. Correlations between their orbital energies and electron occupancies and a rationale for the lability of the NO ligand in neutral CpCr(NO)Cl₂ are provided.

Introduction

The electronic configurations exhibited by stable organotransition-metal complexes are inexorably linked to the π-bonding capabilities of their ligands. Examination of the development of monocyclopentadienyl chemistry since the first "half-sandwich" compounds were reported in 1954 provides numerous examples of this general principle. The initial, explosive growth of the field can be partly attributed to the predictable adherence of CpM(CO)$_n$X$_m$ (Cp = η^5-C₅H₅; X = halide, hydride, or alkyl)[2] compounds to the eighteen-valence-electron (18e) rule.[3] Indeed, the presence of several π-acidic ligands like CO in the metals' coordination spheres so stabilizes low-valent, inert-gas configurations[4] that one-electron oxidations of these and related complexes generally produce very reactive metalloradical species.[5,6] This strong preference for attaining a diamagnetic electron configuration is markedly *absent* for Cp′ML$_n$X$_m$ compounds (Cp′ = Cp or Cp*(η^5-C₅Me₅), L = phosphine, amine) which contain no π-acidic ligands. Recent studies have demonstrated that stable, paramagnetic (<18e) complexes of this latter type can be synthesized with one, two,

or three unpaired electrons in a variety of relatively high oxidation states.[7−12] Furthermore, attempts to impose an 18e

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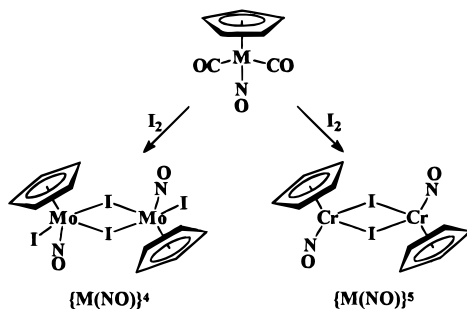(2) Wilkinson, G.; Cotton, F. A. *Prog. Inorg. Chem.* **1959**, *1*, 1.

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Scheme 1

configuration on these carbonyl-free complexes via reduction result in highly reactive, electron-rich species.[13]

Compounds like [CpCr(NO)L_2]^+ that contain only *one* π-acceptor ligand do not fit readily into either of the above categories. For example, [CpCr(NO)(NH_3)_2]^+ is similar to the reactive, substitutionally-labile CpCr(CO)_3 radical species[5a] in that both complexes are paramagnetic, 17e, and contain Cr formally in the +1 oxidation state. However, unlike CpCr-(CO)_3, [CpCr(NO)(NH_3)_2]^+ is kinetically stable and decomposes upon reduction in the absence of trapping ligands. The coordination of additional π-acidic ligands favors the inert-gas configuration, as in the 18e CpCr(NO)(CO)_2, which loses carbonyl ligands when oxidized. In other words, the cationc, 17e, {Cr(NO)}[5] manifold[14] in the [CpCr(NO)L_2]^{+/0} redox couple is stabilized when L is a good σ-donor ligand while the neutral, 18e, {Cr(NO)}[6] configuration is stabilized when L is a π-acceptor ligand.[6]

Comparison of CpCr(NO)-containing complexes with their Mo congeners presents a third possible electronic configuration, namely the {Cr(NO)}[4] manifold. [CpCr(NO)L_2]^+ species and other 17e chromium nitrosyl complexes are accessible via [CpCr(NO)I]_2,[15] the {Cr(NO)}[5] *mono*iodo dimer obtained by the iodine oxidation of CpCr(NO)(CO)_2.[16] As shown in Scheme 1, the reaction of the congeneric CpMo(NO)(CO)_2 with I_2 proceeds differently, affording the {Mo(NO)}[4] *di*iodo dimer, [CpMo(NO)I_2]_2.[17] This and related [CpMo(NO)X_2]_2 dihalo dimers have served as synthetic precursors to a broad spectrum of {Mo(NO)}[4] products,[18,19] most of which have no chromium counterparts. However, the electrochemically reversible reduc-

tion of [CpMo(NO)I_2]_2 to the {Mo(NO)}[5], 17e [CpMo(NO)I_2]^- anion[20] suggests that oxidation of [CpCr(NO)X_2]^- {Cr(NO)}[5] complexes might provide a synthetic route to neutral CpCr-(NO)X_2 {Cr(NO)}[4] products.

In this paper, we detail the synthesis and characterization of [CpCr(NO)X_2]^- compounds (X = I [**1**], O_3SCF_3(OTf) [**2**], Br [**3**], Cl [**4**]). The results of chemical and electrochemical oxidation of [NEt_4][**4**] are consistent with the transient formation of the desired {Cr(NO)}[4] CpCr(NO)Cl_2 followed by rapid loss of NO. Extended-Hückel molecular-orbital calculations have been utilized to rationalize (a) the relative stability of 17e {Cr-(NO)}[5] complexes, (b) the proclivity of [CpCr(NO)Cl_2]^- to lose NO upon oxidation, and (c) the significance of π-donation in stabilizing Cp'Cr(NO)X_2 species.

Results and Discussion

Preparation of [CpCr(NO)X_2]^- Anions. Treatment of known [CpCr(NO)I]_2 with 1 equiv of [NBu_4]I in CH_2Cl_2 effects cleavage of the dimer in a manner similar to that of other Lewis bases,[6,15,21] to generate [NBu_4][**1**] as shown in eq 1.
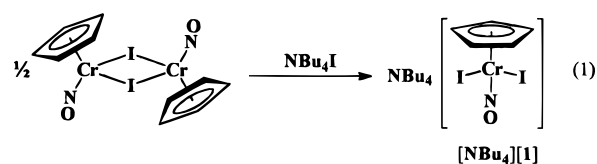
This synthesis and isolation of anion [**1**] suggest that a range of such [CpCr(NO)X_2]^- complexes (X = halide or pseudo-halide) should also be stable species. However, attempts to metathesize the iodide ligands in [**1**] with either Br^- or Cl^- in order to obtain directly the dibromo [**3**] and dichloro [**4**] complexes do not succeed because of scrambling of the halide ligands.[22] Attempts to isolate a single organometallic product from these mixtures have been unsuccessful. However, treatment of [NBu_4][**1**] with 2 equiv of AgOTf in CH_2Cl_2 results in the clean metathesis of the iodide ligands to give [NBu_4][CpCr-(NO)(OTf)_2] ([NBu_4][**2**]) in 85% yield (eq 2).
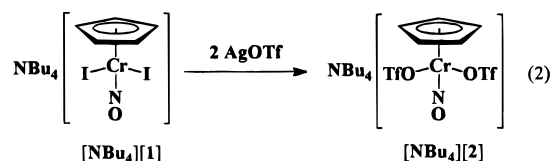
Subsequent metatheses of the triflate ligands in [**2**] for Br^- or Cl^- are more straightforward than the corresponding metatheses of iodide in [**1**], such that reaction of [NBu_4][**2**] with either KBr (eq 3) or KCl results in the clean formation of only [**3**] or [**4**], as judged by both IR and ESR spectroscopies. However, while the dibromo species, [NBu_4][**3**], can be isolated in pure form by recrystallization from CH_2Cl_2/hexanes, the dichloro salt, [NBu_4][**4**], cannot be completely separated from the KOTf byproduct.

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(14) The Enemark−Feltham notation is a more accurate representation of electronic configuration in metal−nitrosyl complexes than is an assignment of formal oxidation states due to the covalent nature of the M−NO linkage. The {Cr(NO)}[5] configuration can correspond approximately to a d^5, [Cr^I(NO^+)] fragment if the nitrosyl ligand is linear, as it is in the compounds described here. Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

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(18) McCleverty, J. A. *Chem. Soc. Rev.* **1983**, *12*, 331.

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(21) Legzdins, P.; McNeil, W. S.; Shaw, M. J. *Organometallics* **1994**, *13*, 562.

(22) For instance, reaction of either [CpCr(NO)I]_2 or [NBu_4][**1**] with [NEt_4]Cl in CH_2Cl_2 results in a reaction mixture which exhibits an ESR spectrum with three signals, namely one broad singlet attributable to diiodo [**1**], one resolved triplet due to dichloro [**4**], and a third of intermediate *G*-value with an unresolved coupling presumably due to [CpCr(NO)(I)(Cl)]^-.

Synthesis of 17-Valence-Electron [CpCr(NO)X₂]⁻ Anions

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Table 1. Numbering Scheme, Color, Yield and Elemental Analysis Data

			elemental analysis found (calcd)		
complex	compd no.	color (yield, %)	C	H	N
[NBu₄][CpCr(NO)I₂]	[NBu₄][1]	red-brown (90)	39.35 (39.20)	6.47 (6.42)	4.23 (4.35)
[NBu₄][CpCr(NO)(OTf)₂]	[NBu₄][2]	brown (85)	40.30 (40.17)	6.05 (6.01)	4.03 (4.07)
[NBu₄][CpCr(NO)Br₂]	[NBu₄][3]	black (62)	45.91 (45.91)	7.67 (7.52)	5.00 (5.10)
[NEt₄][CpCr(NO)Cl₂]	[NEt₄][4]	black (53)	44.86 (44.84)	7.33 (7.24)	8.04 (8.04)
[PPN][CpCr(NO)Cl₂]^a	[PPN][4]	black (41)	65.57 (65.22)	5.22 (5.23)	3.19 (3.38)
[Cp*Cr(NO)I]₂^b	5	green (62)	35.29 (34.90)	4.38 (4.39)	4.36 (4.07)
[Cp*Cr(NO)Cl]₂	6	green (89)	47.86 (47.53)	6.14 (5.98)	5.49 (5.54)

^{a} Sample for elemental analysis contains one molecule of THF of crystallization per ion pair. ^{b} Reported elemental analysis is the average of three separate runs.

Table 2. Mass Spectral, Infrared, and ESR Data for 17e Species

	FAB-MS (m/z)		IR (cm^{-1})		ESR(CH₂Cl₂)	
complex	(+)	(−)	ν_{NO}(Nujol)	ν_{NO}(CH₂Cl₂)	g-value	coupling (G)
[NBu₄][1]	242 [P⁺]	401 [P⁻]	1637	1644	2.051	
[NBu₄][2]	242 [P⁺]	445 [P⁻]	1697	1690	1.978	$A_N = 5.1; A_{Cr} = 21.3$
[NBu₄][3]	242 [P⁺]	305 307 309 [P⁻]^a	1641		2.011	$A_N = 5.7; A_{Cr} = 18.6$
[NEt₄][4]	130 [P⁺]	217 219 [P⁻]^b	1626	1641	1.986	$A_N = 5.4; A_{Cr} = 20.3$
[PPN][4]	538 [P⁺]	217 219 [P⁻]^b	1622		1.986	$A_N = 5.4; A_{Cr} = 20.4$
5	688 [P⁺]		1647	1650		
6	474 [P⁺−NO]		1648	1645		

^{a} This envelope of peaks is a 1:2:1 isotopic cluster as expected for a mixture of ^{79}Br and ^{81}Br isotopomers, the ^{79}Br/^{81}Br form being most abundant. ^{b} This envelope of peaks is a 3:2 isotopic cluster as expected for a mixture of ^{35}Cl and ^{37}Cl isotopomers, the ^{35}Cl/^{35}Cl form being most abundant.

$$ (3) $$

With this preparative route to [4] thwarted, a route analogous to that shown in eq 1 and utilizing [CpCr(NO)Cl]₂ as the initial reactant appeared to offer an appealing alternative. The problem thus became how best to prepare the requisite bridging-chloro precursor.[23]

Treatment of CpCr(NO)(CO)₂ with Cl₂ in CH₂Cl₂, analogous to the I₂ reaction in Scheme 1, does not afford [CpCr(NO)-Cl]₂.[15] We have now found that effecting the chlorination with PCl₅ as the chlorinating agent and MeCN as the solvent does indeed produce the desired bridging-chloro dimer. Though [CpCr(NO)Cl]₂ isolated from the final reaction mixture as a bright green powder exhibits the expected spectroscopic properties,[24] the IR spectra of these samples also indicate contamination with ~5% of CpCr(NO)₂Cl.[25] The amount of the dinitrosyl contaminant present may be reduced by performing the reaction at lower temperatures, and it can be effectively removed by washing the crude product with Et₂O and recrystallizing the [CpCr(NO)Cl]₂ from toluene at −30 °C. In this connection it should be noted that [CpCr(NO)Cl]₂ is not as thermally robust as its iodo analogue, [CpCr(NO)I]₂.[26]

Finally, reaction of [CpCr(NO)Cl]₂ with [NEt₄]Cl in toluene affords [NEt₄][CpCr(NO)Cl₂] ([NEt₄][4]) in 50−55% yields from CpCr(NO)(CO)₂ (eq 4). For preparative purposes it is more efficient to use crude [CpCr(NO)Cl]₂ and then carry on

(23) [CpCr(NO)Cl]₂ has been obtained in an impure form as the lowest-yield component of four chromium-containing products isolated from the reaction of ClNO with [CpCr(CO)₃]₂ and as a pure solid in low overall yield by treating [CpCr(NO)(OEt)]₂ with HCl gas.[24] However, neither of these reactions represents a viable route for further preparative chemistry.

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directly with chloride addition to prepare [4], since the successful isolation of [4] is not hampered by any contaminating CpCr-(NO)₂Cl which might be present.

$$ (4) $$

Physical and Spectroscopic Properties of CpCr(NO)X₂ Anions. Anions [1] to [4] are monomeric, 17e organometallic species, which as their tetra(alkyl)ammonium salts are essentially insoluble in Et₂O or aliphatic solvents, but are soluble in CH₂-Cl₂ or THF. The yields and analytical data for these complexes are collected in Table 1, and the spectroscopic data are presented in Table 2. The anions are generally more air-sensitive than are their cationic [CpCr(NO)L₂]⁺ counterparts,[6] both as solids and in solutions. The diiodo salt, [NBu₄][1], may be handled in air as a solid for short periods of time, but the bis(triflate), [NBu₄][2], and dibromo, [NBu₄][3], salts both decompose in the atmosphere within minutes to viscous oils. IR spectra of air-exposed solutions show features indicative of the formation of dinitrosyl complexes. As solids, the salts may be stored indefinitely at ambient temperatures under an inert atmosphere without the occurrence of noticeable decomposition.

Each anion exhibits a single strong nitrosyl-stretching absorption in the IR range expected for a linear nitrosyl group. In Nujol-mull spectra, these bands are all between 1626 and 1641 cm^{-1} for the dihalide anions, while the triflate complex, [NBu₄]-[2], exhibits a ν_{NO} at 1697 cm^{-1}. This higher-energy value is a manifestation of the greater electron-withdrawing ability of the triflate ligands. The FAB mass spectra of each of the salts display discrete peaks due to the cation and anion parent ions as well as diagnostic isotope patterns for the dibromo and dichloro anions. As expected for monomeric 17e complexes, each of the anions [1] to [4] exhibits a room-temperature ESR spectrum. The spectrum of the dichloro salt, [NEt₄][4], in CH₂-Cl₂ is typical and is shown in Figure 1. Compounds [2] to [4]

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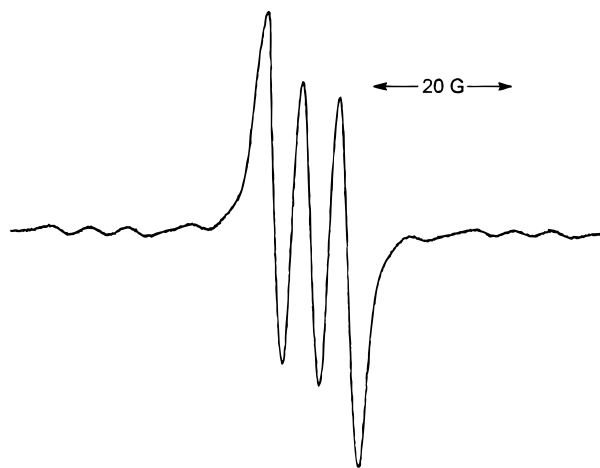
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Figure 1. ESR spectrum of [NBu$_4$][**4**] in CH$_2$Cl$_2$.

display spectra which are qualitatively similar and exhibit coupling to both the nitrosyl nitrogen atom ($I = 1$), which results in a 1:1:1 triplet, and to the 9.55% abundant ^{53}Cr nucleus ($I = {}^3/_2$), which gives rise to satellite signals on either side of the main feature. The coupling constants for these spectra are in the ranges of 5−6 and 18−22 G for the nitrogen and chromium couplings, respectively (Table 2). The ESR spectrum of the diiodo anion is an exception in that it is a broad and featureless singlet. Finally, there is a distinct increase in the *G*-values exhibited by the dihalide anions as the halide ligand is changed from Cl to Br to I, increasing from 1.986 to 2.011 to 2.051. This is exactly the same trend that has been observed for the analogous molybdenum anions, for which the *G*-values increase from 1.982 to 2.010 to 2.060.[20] The trend is also mirrored in complexes of the type CpMoX$_2$(PMe$_3$)$_2$[27] and CpMoX$_2$(dppe)[28] (X = Cl, Br, I), and in the latter cases the diiodo compounds also exhibit much broader ESR signals than do the other species. These effects are likely due to a combination of a varying degree of ligand-atomic-orbital character in the SOMO and an increasing halide-orbital contribution to the moment of the electron spin in going from Cl to Br to I.[27,28]

Solid-State Molecular Structure of [4]. Crystals of [PPN]-[**4**]·CH$_2$Cl$_2$ suitable for X-ray crystallographic analysis were obtained by reacting [CpCr(NO)Cl]$_2$ with [PPN]Cl and subsequent recrystallization of the crude material from CH$_2$Cl$_2$/hexanes. The crystallographic data for [PPN][**4**]·CH$_2$Cl$_2$ are listed in Table 3, and selected bond lengths and bond angles are collected in Table 4. The solid-state molecular structure of the anion in [PPN]CpCr(NO)Cl$_2$]·CH$_2$Cl$_2$ is depicted in Figure 2 with only one of the three possible forms found in the disordered structure being shown. As a result of the disorder and the restraints applied during the solution of the structure (see Experimental Section), the geometry involving the chloride and the nitrosyl ligands is probably less precise than indicated by the standard deviations. Nevertheless, it is clear that [**4**] has a typical three-legged piano-stool structure with intramolecular metrical parameters similar to those exhibited by related CpCr(NO)-containing complexes.[6,29]

Oxidation Chemistry of the Dihalide Anions. We have previously discussed the redox chemistry of {Cr(NO)}^{5} species in our studies of the reduction of neutral CpCr(NO)(L)X[21] and cationic CpCr(NO)L$_2$[6] compounds. While these complexes

(27) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599.

(28) Krueger, S. T.; Owens, B. E.; Poli, R. *Inorg. Chem.* **1990**, *29*, 2001.

(29) (a) Chin, T. T.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1992**, *11*, 913. (b) Greenhough, T. J.; Kolthammer, B. W. S.; Legzdins, P.; Trotter, J. *Acta Crystallogr.* **1980**, *B36*, 795.

Table 3. Crystallographic Data for [PPN][**4**]·CH$_2$Cl$_2$[a,b]

Formula	C$_{42}$H$_{37}$Cl$_4$CrN$_2$P$_2$O
fw	841.52
temp, K	294
color, habit	green, prism
crystal size, mm	0.25 × 0.30 × 0.45
crystal system	triclinic
space group	$P\bar{1}$
a, Å	12.729(2)
b, Å	15.480(2)
c, Å	11.778(2)
α, deg	101.25(1)
β, deg	101.40(1)
γ, deg	111.129(10)
V, Å^3	2029.9(6)
Z	2
ρ_{calc}, g/cm^3	1.377
F(000)	866.00
μ(Mo $K\alpha$), cm^{-1}	6.59
trans. factors (relative)	0.939−1.000
scan type	ω−2θ
scan range, deg in ω	1.05 + 0.35 tan θ
scan rate, deg/min	16.0
data collected	+h,±k,±l
$2\theta_{max}$, deg	55
crystal decay, %	0
total no. of reflcns	9770
no. of unique reflcns	9323
R_{merge}	0.048
no. of reflcns with $I \geq 3\sigma(I)$	2843
R	0.052
R_w	0.044
gof	1.92
max Δ/σ (final cycle)	0.008
residual density, e/Å^3	−0.44 to 0.35 (near Cr)

^{a} Function minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum ||F_o| - |F_c||/\sum |F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and gof = $[\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and gof are based on those reflections with $I \geq 3\sigma(I)$. ^{b} Rigaku AFC6S diffractometer, MO $K\alpha$ radiation ($\lambda = 0.71069$ Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 9 rescans), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count).

Table 4. Selected Metrical Parameters^a for [PPN][**4**]CH$_2$Cl$_2$

atoms	bond length (Å)	atoms	bond angles (deg)
Cr(1)−Cp^b	1.88	Cp−Cr(1)−Cl(1)	120.4
Cr(1)−Cl(1)	2.315(4)	Cp−Cr(1)−Cl(2)	117.7
Cr(1)−Cl(2)	2.314(4)	Cp−Cr(1)−N(1c)	119.8
Cr(1)−N(1c)	1.685(7)	Cr(1)−N(1c)−O(1c)^c	172(4)

^{a} ESD's in parentheses ^{b} Cp refers to the unweighted centroid of the cyclopentadienyl ligand. ^{c} Restrained during refinement.

were not susceptible to electron loss, we now report the 1e oxidation of CpCr(NO)X$_2$ anions.

(a) Cyclic Voltammetry. The cyclic voltammogram of [NBu$_4$][**1**] scanned at 0.4 V/s exhibits an irreversible oxidation feature in THF at $E_{p,a}$ = 0.53 V vs SCE. The dichloro salt, [NEt$_4$][**4**], also displays an irreversible oxidation feature under the same conditions at a similar voltage, $E_{p,a}$ = 0.60 V. If the solvent is changed to CH$_2$Cl$_2$, which allows a wider oxidation window, more features become evident. An oxidative scan of [NEt$_4$][**4**] in CH$_2$Cl$_2$ at 0.1 V/s reveals three irreversible oxidation waves at $E_{p,a}$ = 0.56, 1.15, and 1.74 V. As the scan rate is increased, the first feature remains completely irreversible, and the intensity of this current increases linearly with the square root of the scan rate, as expected. However, at faster scan rates, the current maximum of the second oxidation wave does not increase to the same degree as that of the first feature. This observation indicates that [NEt$_4$][CpCr(NO)Cl$_2$] decomposes
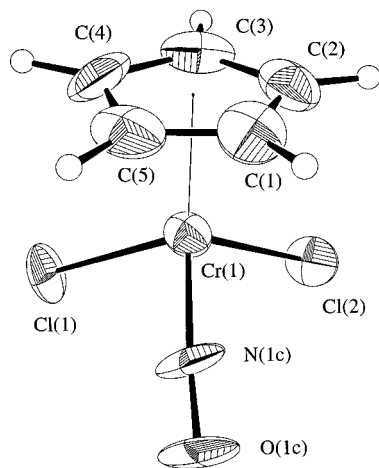
Figure 2. Molecular structure of [**4**] as it occurs in [PPN][**4**]·CH$_2$Cl$_2$; 33% probability thermal ellipsoids shown.

rapidly upon oxidation and that the second oxidation feature is due to a decomposition product of the initially formed CpCr-(NO)Cl$_2$ species, which has only a transient existence.

(b) Chemical Oxidation of [NEt$_4$][CpCr(NO)Cl$_2$]. The chemical oxidation of [**4**] demonstrates that the initial oxidation product does indeed decompose, and it results in the isolation of two organochromium products. Thus, treatment of [NEt$_4$][CpCr(NO)Cl$_2$] with [Cp$_2$Fe][PF$_6$] results in the formation of a green mixture which contains CpCr(NO)$_2$Cl[25] as the only nitrosyl-containing product (as judged by the solution IR spectrum). Only one-half an equivalent of oxidant is required to consume completely all the starting anion; any excess [Cp$_2$-Fe]$^+$ remains unreacted. Chromatography of the final reaction mixture effects the separation of two organochromium products derived from the decomposition of the initially generated CpCr-(NO)Cl$_2$, namely the dinitrosyl complex CpCr(NO)$_2$Cl and the Cr(III) dimer [CpCrCl(μ-Cl)]$_2$.[30] A balanced equation for this transformation is shown in eq 5.
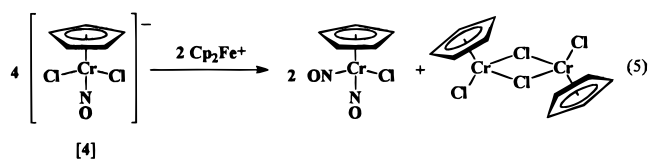
A plausible mechanism that provides a rationale for the formation of the isolated products, for the usual stoichiometry between the reactants, and for the transfer of a nitrosyl ligand is presented in Scheme 2. Removal of an electron from [CpCr(NO)Cl$_2$]$^-$ by [Cp$_2$Fe]$^+$ results in the formation of ferrocene and CpCr(NO)Cl$_2$, a 16e {Cr(NO)}^{4} complex. However, unlike the analogous {Mo(NO)}^{4} compound,[17b] CpCr-(NO)Cl$_2$ is not stable, as indicated by the irreversible electro-chemical oxidation of its 17e anionic precursor. Loss of NO from this complex would yield CpCrCl$_2$, one-half of the Cr(III) dimer isolated from the final reaction mixture. The second product, CpCr(NO)$_2$Cl, could then be formed if the liberated nitric oxide displaces a chloride ligand from unoxidized [NEt$_4$][**4**].[31] Support for the proposed mechanism outlined in

Scheme 2

Scheme 2 comes from the fact that the last step can be effected independently, treatment of [NEt$_4$][**4**] in THF with gaseous NO converting it to CpCr(NO)$_2$Cl.[32]

The loss of nitric oxide from metallonitrosyl complexes is currently a matter of some interest, due to the recently discovered and far-ranging biological effects of NO,[33] including its role as the principal regulator of human blood pressure.[34] Nitroprusside, Na$_2$[Fe(CN)$_5$(NO)], has been used for decades to lower blood pressure during surgery, and is currently the only clinically employed metal−nitrosyl complex.[35] Loss of nitric oxide from this species is triggered by a one-electron reduction process, and is unfortunately accompanied by the release of 2 equiv of toxic cyanide for every molecule of NO, thus requiring concomitant use of a cyanide antidote with the vasodilator.[36] Consequently, design of new metallonitrosyl pharmaceuticals is a subject of some interest, particularly with respect to determination and control of conditions under which nitric oxide is lost from the metal.[37] The development of oxidatively-triggered nitric-oxide-releasing metallonitrosyl compounds could conceivably provide different and complementary pharmaceutical activity to the reductively-triggered nitroprusside ion.

Oxidation of Cp′M(NO)(CO)$_2$ with Halogen Sources. The evident instability of CpCr(NO)Cl$_2$ also helps to account for the metal-dependent difference in products observed when Cp′M(NO)(CO)$_2$ (M = Cr, Mo) complexes possessing {M-(NO)}^{6} configurations are reacted with halogenating agents such as PCl$_5$,[38] Cl$_2$, Br$_2$, or I$_2$ in noncoordinating solvents. For molybdenum, these reactions are remarkably general, and {Mo(NO)}^{4} products of composition [Cp′Mo(NO)X$_2$]$_2$ are isolable in good yields for both Cp[17] and Cp* [39] derivatives. In contrast, no analogous neutral dihalo {Cr(NO)}^{4} complexes are obtained for chromium. Only in the single, specific case

(30) (a) Köhler, F. H.; de Cao, R.; Ackermann, K.; Sedlmair, J. *Z. Naturforsch. B* **1983**, *38*, 1406. (b) Bräunlein, B.; Köhler, F. H.; Strauss, W.; Zeh, H. *Z. Naturforsch. B* **1995**, *50*, 1739.

(31) This mechanism assumes that the NO-transfer mechanism is fast relative to the initial oxidation of [NEt$_4$][**4**]. A perceptive reviewer noted that the oxidation potentials of [NEt$_4$][**4**] and Cp$_2$Fe indicate that the ferrocenium oxidation is endergonic and thus is expected to be slow.

(32) It has been shown previously that [CpCr(NO)Cl]$_2$ also forms CpCr-(NO)$_2$Cl upon reaction with nitric oxide.[24]

(33) (a) Culotta, E.; Koshland, D. E. *Science* **1992**, *258*, 1862. (b) Feldman, P. L.; Griffith, O. W.; Stuer, D. J. *Chem. Eng. News* **1993**, *71*, 26. (c) Nelson, R. J.; Demas, G. E.; Huang, P. L.; Fishman, M. C.; Dawson, V. L.; Dawson, T. M.; Snyder, S. H. *Nature* **1995**, *378*, 383.

(34) Snyder, S. H.; Bredt, D. S. *Sci. Am.* **1992**, *266*, 68.

(35) For other potential medicinal uses for metallonitrosyl complexes currently in development, see: (a) Fricker, S. P. *Platinum Metals Rev.* **1995**, *39*, 150. (b) Schoch, T. K.; Hubbard, J. L.; Zoch, C. R.; Yi, G.-B.; Sørlie, M. *Inorg. Chem.* **1996**, *35*, 4383.

(36) Butler, A. R.; Glidewell, C. *Chem. Soc. Rev.* **1987**, *16*, 361.

(37) Clarke, M. J.; Gaul, J. B. *Struct. Bonding (Berlin)* **1993**, *81*, 148.

(38) For the use of PCl$_5$ as a chlorinating agent in organometallic syntheses, see: (a) Reference 11a. (b) Dryden, N. H.; Legzdins, P.; Batchelor, R. J; Einstein, F. W. B. *Organometallics* **1991**, *10*, 2077. (c) Reference 28.

(39) Gomez-Sal, P.; de Jésus, E.; Michiels, W.; Royo, P.; de Miguel, A. V.; Martinez-Carrera, S. *J. Chem. Soc., Dalton Trans.* **1990**, 2445.

Scheme 3
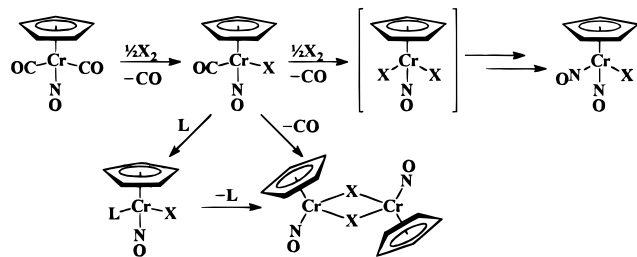
illustrated in Scheme 1 (i.e. Cp′ = Cp; X_2 = I_2) are *any* mononitrosyl chromium products isolable from these reactions. In all other cases, $Cp'Cr(NO)_2X$ products are obtained in <50% yields as the only NO-containing species.[15,21] This lack of a general synthetic route to $[Cp'Cr(NO)X]_2$ compounds from the treatment of $Cp'Cr(NO)(CO)_2$ with X_2 can now be attributed to formation of $Cp'Cr(NO)X_2$ species, as shown in Scheme 3. Once generated, $\{Cr(NO)\}^4$ intermediates like $CpCr(NO)Cl_2$ transfer NO to 17e, $\{Cr(NO)\}^5$ complexes to form the isolated $Cp'Cr(NO)_2X$ products, a reaction sequence analogous to that presented in Scheme 2.

Examination of the published IR monitoring of the reaction of $CpCr(NO)(CO)_2$ with I_2 in CH_2Cl_2 reveals how the relative rates of reaction of the various chromium species in solution with iodine favor the clean formation of $[CpCr(NO)I]_2$. The key feature is that only after all the $CpCr(NO)(CO)_2$ is consumed does any excess I_2 present react with the 17e species present to generate absorptions due to $CpCr(NO)_2I$.[15] In other words, I_2 reacts with $CpCr(NO)(CO)_2$ faster than with $CpCr(NO)(CO)I$ or $[CpCr(NO)I]_2$, and so the presence of the dicarbonyl $\{Cr(NO)\}^6$ reactant prevents the formation of $CpCr(NO)I_2$ and the subsequent NO-transfer reactions. Clean generation of other $[Cp'Cr(NO)X]_2$ complexes by the same synthetic methodology is not possible because the relative rates of oxidation encountered with I_2 do not extend to related systems. Thus, when $CpCr(NO)(CO)_2$ is treated with PCl_5, Cl_2, or Br_2 in CH_2Cl_2, or when $Cp^*Cr(NO)(CO)_2$ is reacted with any halogen source, IR bands due to $Cp'Cr(NO)_2X$ species are observed before all of the $\{Cr(NO)\}^6$ dicarbonyl reactant has been consumed.[15,21] In these cases, therefore, X_2 reacts with the various 17e chromium-containing intermediates at rates comparable to its reaction with $Cp'Cr(NO)(CO)_2$, thus hindering isolation of the $\{Cr(NO)\}^5$ bridging-monohalo dimers.

This overoxidation has been avoided by the use of σ-donor ligands (L) to stabilize the 17e, $\{Cr(NO)\}^5$ configuration[6] in order to synthesize complexes having the composition $Cp'Cr(NO)(L)X$ (Scheme 3). Thus, both known 17e $Cp^*Cr(NO)(L)I$ complexes were prepared by adding a trapping ligand (L = PPh_3 or pyridine) immediately after I_2 addition to $Cp^*Cr(NO)(CO)_2$ without attempting to isolate the bridging monoiodide dimer.[21] The σ-donor ligand may also be bound to the chromium center prior to oxidation, as illustrated by the clean conversion of $CpCr(NO)(PR_3)(CO)$ by X_2 to 17e $CpCr(NO)(PR_3)X$.[15] We have now employed a similar synthetic strategy to obtain $[Cp'Cr(NO)X]_2$ dimers by treating $Cp'Cr(NO)(CO)_2$ with PCl_5 or I_2 in a coordinating solvent such as acetonitrile. In MeCN these reactions proceed cleanly for both Cp and Cp* derivatives, with only minimal amounts of $Cp'Cr(NO)_2X$ byproducts being evident by IR spectroscopy. The coordinated MeCN is readily removed in vacuo from the $Cp'Cr(NO)(NCMe)X$ intermediates to obtain the appropriate dimer, including the previously inaccessible $[Cp^*Cr(NO)X]_2$ compounds (**5**,
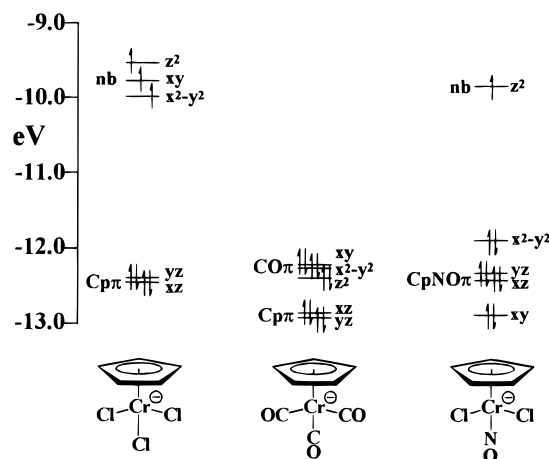
Figure 3. EHMO energy-level diagram for $[CpCrCl_3]^-$, $[CpCr(CO)_3]^-$, and $[CpCr(NO)Cl_2]^-$.

X = I; **6**, X = Cl), as summarized in eq 6 below

$$\text{(6)}$$
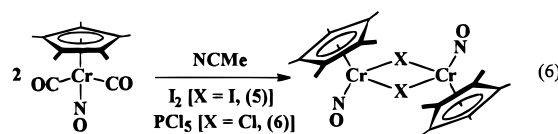
π-Bonding in Cyclopentadienyl Chromium Complexes. The preceding two sections of this report have addressed the oxidation chemistry of $\{Cr(NO)\}^5$ species by invoking that transient $CpCr(NO)X_2$ intermediates are unstable with respect to nitric oxide loss. This instability may appear unusual when contrasted with the substitutionally-inert nature of the $\{Cr(NO)\}^5$ precursors[6,21] and the well-established stability of the analogous $[Cp'Mo(NO)X_2]_n$ complexes.[18,19] To account for this mode of reactivity, we have examined the frontier molecular orbitals of three related $CpCrL_3$ anions, namely $[CpCr(CO)_3]^-$,[40] $[CpCrCl_3]^-$,[41] and $[CpCr(NO)Cl_2]^-$, using extended-Hückel MO calculations.[42,43] These calculations suggest that the $[CpCrL_3]^-$ complexes can be profitably viewed as being pseudo-tetrahedral complexes,[44] with all five of the Cr d-orbitals free to engage in π-bonding (Figure 3).

For $[CpCr(CO)_3]^-$, the alignment of the z-axis along the pseudo-3-fold rotation axis through the Cp centroid allows for

(40) (a) Pasynskii, A. A.; Eremenko, I. L.; Abdullaev, A. S.; Orazsakhatov, B.; Nefedov, S. E.; Stomakhina, E. E.; Ellert, O. G.; Katser, S. B.; Yanovskii, A. I.; Struchkov, Y. T. *Russ. J. Inorg. Chem.* **1990**, *35*, 1285. (b) Rohrmann, J.; Herrmann, W. A.; Herdtweck, E.; Riede, J.; Ziegler, M.; Sergeson, G. *Chem. Ber.* **1986**, *119*, 3544.

(41) (a) Fischer, E. O.; Ulm, K.; Kuzel, P. *Z. Anorg. Allg. Chem.* **1963**, *319*, 253. (b) Reference 30a.

(42) The qualitative, readily-visualized bonding picture achieved through extended-Hückel calculations provides the flexible conceptual framework required for the comparisons we wish to draw, although this is accompanied by an unavoidable loss of quantitative precision. The d-orbital labels are assigned to imply the general shape and relative orientation of the metal-based component of the bonding orbitals, not their exact, quantitative orbital composition. For further discussion of the bonding in Cp′M(NO) complexes (M = Cr or Mo) at a variety of computational levels, see ref 43.

(43) (a) Hoffmann, R. *Science* **1981**, *211*, 995. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592. (c) Reference 14. (d) Herrmann, W. A.; Hubbard, J. L.; Bernal, I.; Korp, J. D.; Haymore, B. L.; Hillhouse, G. L. *Inorg. Chem.* **1984**, *23*, 2978. (e) Legzdins, P.; Rettig, S. J.; Sánchez, L.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1985**, *107*, 1411. (f) Ashby, M. T.; Enemark, J. H. *J. Am. Chem. Soc.* **1986**, *108*, 730. (g) Hunter, A. D.; Legzdins, P.; Einstein, F. W. B.; Willis, A. C.; Bursten, B. E.; Gatter, M. G. *J. Am. Chem. Soc.* **1986**, *108*, 3843. (h) Bursten, B. E.; Cayton, R. H. *Organometallics* **1987**, *6*, 2004. (i) Hubbard, J. L.; McVicar, W. K. *Inorg. Chem.* **1992**, *31*, 910. (j) Reference 6.

(44) Bonding in pseudo-tetrahedral complexes has been recently reviewed; see: Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1994**, 1607.
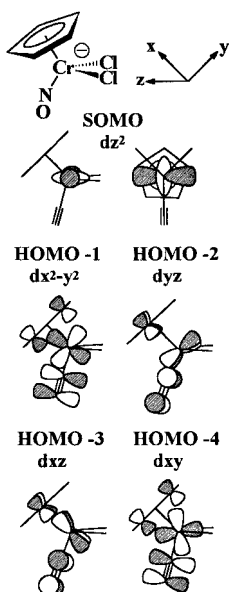
Figure 4. Pictorial representation of the Cp and NO π-bonding interactions with the five Cr 3d orbitals in [CpCr(NO)Cl₂]⁻.

maximum overlap of two orbitals (d_{xz} and d_{yz}) with the two Cp π-symmetry orbitals, while the remaining three orbitals (d_{xy}, $d_{x^2-y^2}$, and d_{z^2}) each form π-bonds with all three carbonyl ligands. All five orbitals are doubly occupied, with the CpCr π-orbitals being slightly lower in energy than the CrCO orbitals. These results agree well with previous molecular-orbital calculations of CpM(CO)₃ compounds.[45] The same orbital orientation holds for the [CpCrCl₃]⁻ complex. The d_{xz} and d_{yz} orbitals are still filled and strongly π-bonding with the Cp ligand, but the d_{xy}, $d_{x^2-y^2}$, and d_{z^2} are now high in energy, singly occupied, and weakly π-antibonding to the filled p-orbitals of the three Cl ligands.

Finally, in the case of [CpCr(NO)Cl₂]⁻, the orbitals mix and reorient in order to maximize Cp and NO π-bonding at the expense of any interaction with the Cl ligands.[46] Four of the five Cr d-orbitals combine with the two Cp and the two NO π-symmetry orbitals to result in four low-energy, filled orbitals, each of which are π-bonding to Cp and NO (Figure 4). The remaining high-energy, singly-occupied d-orbital is nonbonding to the strong π-ligands, although there is some π-antibonding interaction with the weak π-donor Cl ligands.[47]

Comparison of the relative energies, occupancies, and bonding character of the orbitals in Figure 3 suggests an appealing explanation for the ligand control of electronic stability in these cyclopentadienyl chromium complexes. It appears that non-bonding d-orbitals in CpCrL₃ complexes can readily accommodate single, unpaired electrons, thereby resulting in stable paramagnetic species having fewer than 18e. This feature accounts for the stability of 17e [CpCr(NO)L₂]⁺ and

[CpCr(NO)X₂]⁻ complexes, which possess one nonbonding orbital, relative to the 17e CpCr(CO)₃ metalloradical, which has no such orbital.

The remarkable mixing of Cp and NO π-bonding illustrated in Figure 4 is due to the ability of the strong π-acceptor nitrosyl to compete with the π-donor cyclopentadienyl for the available metal π-symmetry orbitals. Similar extensive orbital reorganization resulting from competition between two strong π-donor ligands in four-coordinate compounds has been reported by Schrock and co-workers,[48] who find that "in complexes that contain two different types of 2π, 1σ ligands, the 2π, 1σ ligands are best treated as a unit rather than individually".[49] Research on such compounds has since been largely restricted to high-valent d⁰ and d² complexes of the early transition metals containing strong π-donors such as [η^5-C₅R₅]⁻, [NR]²⁻, and [CR]³⁻ ligands.[44] The EHMO calculations described here suggest that a sufficiently strong π-acceptor ligand may compete significantly with a strong π-donor ligand, leading to M($1\sigma,2\pi$)₂ electronic cores analogous to those found in pseudo-tetrahedral compounds with two π-donor ligands. In other words, our calculations indicate that CpCr(NO) may be considered to be a M($1\sigma,2\pi$)₂ fragment, comparable to Cp′₂Ti,[50] CpV(NR),[51] Cr(NR)₂,[52] and Cp′Cr(CR).[53]

Armed with these perspectives on the bonding in CpCr complexes, we can now more fully appreciate the consequences of performing a one-electron oxidation of [CpCr(NO)Cl₂]⁻. The oxidation presumably effects the removal of the unpaired electron from the high-energy, singly occupied orbital, thereby generating a 16e compound. For the chromium species, this is an irreversible process with removal of the unpaired electron triggering nitrosyl-ligand dissociation. In the case of the congeneric molybdenum compounds, however, this is a reversible process both chemically and electrochemically. To explain this dramatic difference, there must be some electronic property that distinguishes the chromium complex from its molybdenum congener. A strong possibility is that the transient CpCr(NO)-Cl₂ is an open-shell complex, as illustrated in Figure 5.

A recent review of "open-shell organometallics" has high-lighted the importance of release of spin-pairing energy in stabilizing paramagnetic first-row transition-metal complexes as compared to their typically diamagnetic second-row conge-

(45) (a) Lichtenberger, D. L.; Fenske, R. F. *J. Am. Chem. Soc.* **1976**, *98*, 50. (b) Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1977**, *99*, 7546. (c) Hofmann, P.; Schmidt, H. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 837. (d) Reference 5a.

(46) A similar orbital shift in response to ligand asymmetry in CpMLL′X complexes is lucidly described in ref 43b.

(47) Reexamination of the EHMO calculations of [CpCr(NO)(NH₃)₂]⁺ reveals that it possesses an identical "four-below-one" splitting pattern, including two additional Cp and NO π-bonding orbitals lower in energy than the two previously reported.[6] The SOMO is around 0.8 eV lower in energy than the corresponding orbital in [CpCr(NO)Cl₂]⁻. While the difference in charge undoubtedly plays an important role in this variation between the two {Cr(NO)}⁵ complexes, the nature of the ligands (π-donating chloride compared to the purely σ-bonding ammonia) is likely also a contributing factor to this energy difference and the resulting ease of oxidation of the dichloro anion over the bis-ammonia cation.
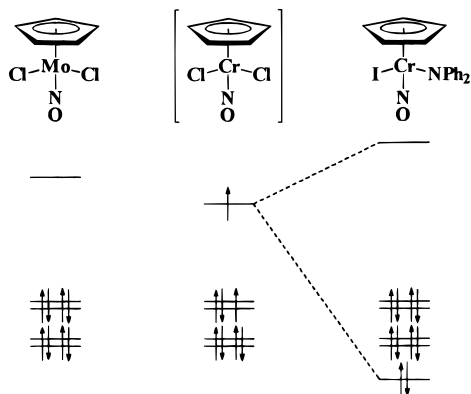
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Figure 5. Qualitative energy-level diagram for closed- and open-shell CpM(NO)X$_2$ complexes.

ners.[54] The reduced orbital size, decreased orbital splitting, and increased pairing energy of the lighter metals all contribute to the formation of high-spin first-row species.[55] Thus, it is probable that whereas CpMo(NO)Cl$_2$ is a low-spin, diamagnetic complex, oxidation of [CpCr(NO)Cl$_2$]$^-$ vacates an orbital of sufficiently low energy that the high-spin configuration becomes accessible to CpCr(NO)Cl$_2$. In a transient open-shell CpCr-(NO)Cl$_2$ complex, the π-bonding orbitals to the nitrosyl are no longer completely filled since one of the electrons in the M−NO π-orbital has been promoted to the orbital above. This change in electron configuration has the effect of weakening the metal−nitrogen bond, thus promoting loss of the nitrosyl ligand. Consequently, invoking the open-shell configuration for the intermediate CpCr(NO)Cl$_2$ complex explains both its instability as compared to its molybdenum congener and its rapid release of nitric oxide as a decomposition path.

If the key difference between stable CpMo(NO)X$_2$ species and unstable CpCr(NO)X$_2$ intermediates is their spin state, perhaps {Cr(NO)}^{4} complexes could be stabilized if the open-shell configuration was rendered inaccessible. One way of doing this is by raising the energy of the empty orbital which is nonbonding to Cp and NO and thereby increasing the energy gap between the LUMO and the four filled π-bonding orbitals of the CpCr(NO) unit. Strong interaction between π-donor X ligands and the π-symmetry LUMO would accomplish just such a distortion of the orbital energies. The importance of π-donation in stabilizing unsaturated complexes has been recently reviewed.[56] Although there is evidence for weak π-donation from the Cl ligands in [CpCr(NO)Cl$_2$]$^-$,[47] this is apparently insufficient to enforce a closed-shell configuration on the transient CpCr(NO)Cl$_2$ species. On the other hand, the stronger π-donation from alkoxide and arylamide ligands appears to be sufficient since Cp*Cr(NO)(O-i-Pr)$_2$[43i] and CpCr(NO)(NPh$_2$)-I[57] have been isolated from halide metathesis reactions of Cp'Cr(NO)$_2$Cl. Both of these {Cr(NO)}^{4} compounds have been characterized by X-ray crystallography,[43i,57] and in both cases alignment of the heteroatom−carbon bond with the Cr−nitrosyl bond in their solid-state molecular structures indicates that the filled heteroatom p-orbital is involved in a π-bonding interaction with the empty metal orbital lying in the plane perpendicular to the Cr−NO axis.[43b,d,i,f] This interaction results in a closed-shell complex, as illustrated pictorially in Figure 5. The importance of this π-donation is especially apparent in the CpCr-(NO)(NPh$_2$)I compound.[57] In the case of the diphenylamide

complex, the π-overlap will be maximized if the Ph−N−Ph plane is parallel to the M−NO vector, and the structure of this compound shows the N−M−N−C(ipso) dihedral angles to be less than 4.9° and 10.1°, actually putting one of the phenyl groups in a sterically unfavorable position with respect to the Cp ring. Consequently, this orientation must be ascribed to an electronic interaction, namely that of the amide group functioning as a π-donor ligand to the metal center.

The existence of these two CpCr(NO)X$_2$ complexes suggests a continuum of three electronic configurations for CpCr(NO) compounds, each selectively stabilized by a particular ligand type: {Cr(NO)}^{6} compounds are stabilized by π-acidic ligands, {Cr(NO)}^{5} configurations are favored for complexes with π-neutral ligands, and {Cr(NO)}^{4} species are stabilized by π-basic ligands. Studies are currently in progress to develop rational synthetic routes to such π-donor stabilized {Cr(NO)}^{4} complexes.

Summary

Despite the chemical and electrochemical reversibility of the [CpMo(NO)X$_2$]$^{0/-}$ redox couple, CpCr(NO)Cl$_2$ is not isolable from the 1e oxidation of [CpCr(NO)Cl$_2$]$^-$. Recovery of CpCr(NO)$_2$Cl and [CpCrCl$_2$]$_2$ from this reaction suggests that the initial oxidation product, CpCr(NO)Cl$_2$, is unstable with respect to NO loss. The difference between stable, diamagnetic {Mo(NO)}^{4} and NO-labile {Cr(NO)}^{4} species may be ascribed to the greater spin-pairing energy of Cr over Mo. If the spin-pairing energy is comparable to the HOMO-LUMO energy gap for CrCr(NO)Cl$_2$, there may be a high-spin configuration available to Cr where it is inaccessible for Mo.[54] The formation of an open-shell, $S = 1$ species relieves spin pairing and regains the single occupancy of the nonbonding orbital by promoting a metal−nitrosyl π-bonding electron, which weakens the Cr−NO bond and enhances NO lability. Furthermore, the stability of both known Cp'Cr(NO)X$_2$ {Cr(NO)}^{4} compounds may now be viewed as depending on π-donation from alkoxide or amide ligands to reinforce the low-spin state.[56]

Recognition of the propensity of high-spin Cp'Cr(NO)X$_2$ species to lose NO has permitted us to rationalize previously inexplicable reaction products and further develop the synthetic chemistry of Cp'Cr(NO)-containing complexes. Performing the halogenation of Cp'Cr(NO)(CO)$_2$ in the coordinating solvent NCMe stabilizes the initial, 17e products, effectively preventing overoxidation and providing a direct route to new [Cp'Cr-(NO)X]$_2$ dimers.[15,21] The solvent dependence of this reaction is of general significance since controlled oxidations of transition-metal carbonyls with halogens constitute an important route to metal−halide complexes, synthetic precursors to a vast number of organotransition-metal compounds.[58]

The apparently anomalous stability of paramagnetic, 17e CpCr(NO)-containing compounds (despite the strong π-acceptor nitrosyl ligand and a lack of an open-shell[54] configuration) can be rationalized through π-bonding considerations. When these compounds are coordinated with π-neutral ancillary ligands, four of the Cr d-orbitals are strongly π-bound to both Cp and NO ligands, consistent with viewing the CpCr(NO) fragment as a M($1\sigma,2\pi$)$_2$ unit.[49] The fifth Cr d-orbital remains higher in energy and essentially nonbonding. EHMO calculations on CpCrL$_3$ anions suggest that such orbitals readily accommodate unpaired electrons, resulting in stable paramagnetic complexes with <18e.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions using an atmosphere of dinitrogen.

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General procedures routinely employed in these laboratories have been described in detail previously.[59] The complexes [CpCr(NO)I]$_2$[15] and CpCr(NO)(CO)$_2$[16] were prepared by published procedures. [Cp$_2$Fe]-[PF$_6$] was prepared by addition of Na[PF$_6$] to an aqueous solution of [Cp$_2$Fe]$_2$[SO$_4$].[60] Cp*Cr(NO)(CO)$_2$[61] was synthesized by treatment of Cp*Cr(CO)$_3$H[62] with Diazald (Aldrich) in THF. All other reagents were used as received from commercial suppliers. Filtrations were performed through Celite (1 × 2 cm) supported on a medium porosity glass frit unless otherwise specified. Ambient-temperature X-band ESR spectra were recorded on an ECS 106 spectrometer with the assistance of Dr. F. G. Herring of this Department and with the microwave frequency being determined with an EIP 625A CW microwave counter. Color, isolated yields, and analytical data for all product complexes are listed in Table 1. Mass, IR, and ESR spectral data are collected in Table 2.

Electrochemical Measurements. General methodology employed during cyclic voltammetry studies in our laboratories has been described previously.[20] The three-electrode cell consisted of either (a) a Pt-bead working electrode (∼1 mm diameter), a coiled Pt-wire auxiliary electrode, and a Ag/AgCl pseudoreference electrode or (b) a Pt-disk working electrode, a Pt-wire auxiliary electrode, and a Ag-wire pseudoreference electrode. Cyclic voltammetry studies employed THF solutions of 1 mM analyte and 0.1 M [*n*-Bu$_4$N][PF$_6$] support electrolyte. The electrochemical cell was assembled and used in a Vacuum Atmospheres model HE-43-2 glovebox. Voltages are reported versus the saturated calomel electrode (SCE) and were measured using an internal ferrocene standard, the highly reversible Cp$_2$Fe/[Cp$_2$Fe]$^+$ couple occurring at $E_{1/2} = +0.55$ V vs SCE in THF under these conditions.

Molecular Orbital Calculations. Extended-Hückel theory calculations were carried out using the commercially available HyperChem for Windows Release 3 and ChemPlus extensions for HyperChem. In all cases, single-point calculations were performed on the structures obtained from single-crystal X-ray crystallographic analyses[40a,41b] using an unweighted Hückel constant of 1.75.

Preparation of [NBu$_4$][CpCr(NO)I$_2$] ([NBu$_4$][1]). [CpCr(NO)I]$_2$ (548 mg, 2.00 mmol) and [NBu$_4$]I (739 mg, 2.00 mmol) were dissolved in CH$_2$Cl$_2$ (30 mL) and stirred for 1 h, and the solvent was then removed in vacuo. The red-brown residue was triturated with Et$_2$O (25 mL), collected on a frit, and further washed with Et$_2$O (2 × 25 mL). The resulting red-brown powder was analytically pure [NBu$_4$][1].

Preparation of [NBu$_4$][CpCr(NO)(OTf)$_2$] ([NBu$_4$][2]). [CpCr-(NO)I]$_2$ (548 mg, 2.00 mmol) and [NBu$_4$]I (739 mg, 2.00 mmol) were dissolved in CH$_2$Cl$_2$ (20 mL) and stirred for 1 h, after which time the solution was cannulated onto AgOTf (1.03 g, 3.99 mmol). A flocculent precipitate formed immediately. The mixture was stirred for 5 min and was then filtered. The brown filtrate was taken to dryness in vacuo, and the residue was triturated with hexanes (2 × 15 mL) to obtain [NBu$_4$][2] as a brown powder.

Preparation of [NBu$_4$][CpCr(NO)Br$_2$] ([NBu$_4$][3]). A mixture of [NBu$_4$][CpCr(NO)(OTf)$_2$] (346 mg, 0.503 mmol) and KBr (120 mg, 1.01 mmol) in CH$_2$Cl$_2$ (15 mL) was stirred for 3 d. The final brown solution was filtered, and the filtrate was taken to dryness in vacuo. The brown residue was recrystallized from CH$_2$Cl$_2$/hexanes to obtain black prisms of [NBu$_4$][3].

Reaction of [NBu$_4$][CpCr(NO)(OTf)$_2$] with KCl. A mixture of [NBu$_4$][CpCr(NO)(OTf)$_2$] (320 mg, 0.465 mmol) and KCl (69 mg, 0.93 mmol) in CH$_2$Cl$_2$ (20 mL) was stirred at ambient temperatures for 1 d, the final green solution was filtered, and the filtrate was taken to dryness in vacuo. The remaining green powder was triturated with hexanes (2 × 15 mL) and recrystallized from CH$_2$Cl$_2$/hexanes to obtain a green crystalline material. This material exhibited spectroscopic properties consistent with its formulation as a salt of [CpCr(NO)Cl$_2$]$^-$, but it could not be obtained analytically pure.

Improved Preparation of [CpCr(NO)Cl]$_2$. Orange CpCr(NO)-(CO)$_2$ (812 mg, 4.00 mmol) was dissolved in MeCN (∼15 mL), and the solution was cooled to −30 °C. PCl$_5$ (407 mg, 1.95 mmol) was added, and the stirred mixture was allowed to warm slowly to room temperature. The warming was accompanied by a color change to deep green and the evolution of gas. The solvent was removed from the final mixture in vacuo, and the green residue was washed with pentane (2 × 15 mL). The crude green powder thus isolated (674 mg) exhibited spectroscopic properties characteristic of [CpCr(NO)Cl]$_2$, but its IR spectrum indicated the presence of a small amount of CpCr(NO)$_2$Cl[25] in the sample. The green powder was washed with Et$_2$O (3 × 10 mL) and then recrystallized from toluene to obtain green microcrystals of analytically pure [CpCr(NO)Cl]$_2$.

Preparation of [NEt$_4$][CpCr(NO)Cl$_2$] ([NEt$_4$][4]). [CpCr(NO)-Cl]$_2$ was prepared as described above from 4.00 mmol of CpCr(NO)-(CO)$_2$. The resulting green powder and [NEt$_4$]Cl (650 mg, 3.92 mmol) were suspended in toluene and stirred for 3 h, whereupon a color change from green to brown occurred. The solvent was removed from the final mixture in vacuo, the remaining solid was extracted into CH$_2$Cl$_2$/hexanes (20 mL, 4:1 ratio), and the mixture was filtered. Cooling of the filtrate to −30 °C resulted in the deposition of [NEt$_4$][4] as narrow black blocks.

Preparation of [PPN][CpCr(NO)Cl$_2$] ([PPN][4]). [PPN]Cl (205 mg, 0.357 mmol) was added to recrystallized [CpCr(NO)Cl]$_2$ in toluene (∼5 mL), and the mixture was stirred at ambient temperature. After 1 h, the solvent was removed in vacuo, the residue was extracted with CH$_2$Cl$_2$, the extracts were filtered through Celite, and a small amount of hexanes was added. Cooling the solution to −30 °C resulted in the crystallization of [PPN][4]·CH$_2$Cl$_2$ as black blocks (112 mg, 41% yield) suitable for X-ray crystallographic analysis.

Reaction of the Dichloro Salt, [Et$_4$N][4], with [Cp$_2$Fe][PF$_6$]. THF (∼10 mL) was vacuum transferred onto [Et$_4$N][4] (347 mg, 1.03 mmol) and [Cp$_2$Fe][PF$_6$] (170 mg, 0.514 mmol), and the resulting solution was stirred at room temperature for 1 h. The solvent was removed in vacuo, the residue was extracted into CH$_2$Cl$_2$ (2 × 15 mL), the combined extracts were filtered through Florisil (1 × 2 cm), and the Florisil plug was washed with an additional amount (45 mL) of CH$_2$-Cl$_2$. Solvent was removed from the combined filtrates in vacuo, and the remaining residue was extracted with Et$_2$O (2 × 15 mL). The insoluble green powder left behind was recrystallized from CH$_2$Cl$_2$/hexanes to obtain [CpCrCl$_2$]$_2$ (25 mg, 13% yield based on [4]).[30] The Et$_2$O extracts were combined and taken to dryness, and the resulting yellow powder was dissolved in Et$_2$O (15 mL). The Et$_2$O solution was transferred to the top of a column of Florisil (2 × 8 cm) made up in hexanes. Elution of the column with Et$_2$O led to the development and collection of two bands, the first orange-yellow in color and the second yellow-gold. The first eluate was stripped of solvent to obtain bright orange Cp$_2$Fe (35 mg, 37% yield). The second was taken to dryness in vacuo to obtain CpCr(NO)$_2$Cl (52 mg, 50% yield based on NO).[25]

Reaction of the Dichloro Salt, [NEt$_4$][4], with NO. [NEt$_4$][4] (174 mg, 0.500 mmol) was suspended in THF (15 mL), and nitric oxide was bubbled slowly through the mixture for a total of 30 min. The dark brown-gold solution was taken to dryness under reduced pressure, the residue was extracted with CH$_2$Cl$_2$ (2 × 20 mL), and the extracts were filtered through neutral alumina I (2 × 3 cm). Solvent was removed from the filtrate in vacuo to obtain (43 mg, 40% yield) CpCr-(NO)$_2$Cl.[25]

Preparation of [Cp*Cr(NO)I]$_2$ (5). MeCN (∼30 mL) was vacuum transferred onto Cp*Cr(NO)(CO)$_2$ (123 mg, 0.450 mmol), and the orange chromium complex dissolved as the solution was warmed in an ice bath. Iodine (0.056 g, 0.441 mmol) was added, and the solution was stirred for 6 h while being slowly warmed to ambient temperature, after which time only peaks attributable to Cp*Cr(NO)(CO)$_2$ remained in the solution's IR spectrum. The solution was heated with a 55 °C water bath for ∼35 min, and the solution was then taken to dryness in vacuo. The remaining green residue was dissolved in THF (15 mL) and taken to dryness four times, and then triturated with Et$_2$O (30 mL, also removed in vacuo) four times. The residue was washed extensively with hexanes and then extracted into toluene, filtered through Celite, and recrystallized at −30 °C from toluene:hexanes.

Preparation of [Cp*Cr(NO)Cl]$_2$ (6). MeCN (∼20 mL) was

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vacuum transferred onto Cp*Cr(NO)(CO)$_2$ (1.48 g, 5.41 mmol) and the orange solution was warmed to -30 °C. PCl$_5$ (0.550 g, 2.64 mmol) was added, and the reaction mixture was stirred at -30 °C for $\sim$20 min and then allowed to warm slowly to room temperature. After 90 min, Et$_2$O (10 mL) was added to the green solution, and the solution was filtered. The plug of Celite was washed with Et$_2$O (3 $\times$ 5 mL), and the combined filtrates were taken to dryness in vacuo. The remaining residue was triturated with Et$_2$O (10 mL) and washed extensively with pentane (7 $\times$ 5 mL). Remaining solvent was removed under static vacuum to obtain crude [Cp*Cr(NO)Cl]$_2$ as a green powder (1.22 g). Analytically pure samples of the complex were obtained as dark green microcrystals by recrystallizing the powder overnight at -30 °C from a $\sim$2:1 toluene:hexanes solvent mixture.

X-ray Structure Determination of [PPN][CpCr(NO)(Cl)$_2$]·CH$_2$-Cl$_2$ ([PPN][4]·CH$_2$Cl$_2$). Crystallographic data appear in Table 3. The final unit-cell parameters were obtained by least-squares analysis on the setting angles for 25 reflections with $2\theta = 18.0-25.9°$. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, showed only minor random fluctuations. The data were processed[63] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans).

The structure was solved by the Patterson method. The structure analysis was initiated in the centrosymmetric space group $P\bar{1}$, this choice being confirmed by subsequent calculations. The NO and Cl ligands are disordered, all three sites being occupied by both types of ligand. Geometric restraints were employed for the three partial nitrosyl ligands. As a result of the disorder and the restraints, the geometry involving the chloride and nitrosyl ligands is probably less precise than indicated by the standard deviations. All non-hydrogen atoms except the low-occupancy nitrosyl N and O atoms were refined anisotropically. The hydrogen atoms were fixed in calculated positions with C$-$H = 0.98 Å and $B_H = 1.2$ $B_{bonded\ atom}$. No secondary extinction correction was necessary. Neutral atom scattering factors and anomalous dispersion corrections were taken from the *International Tables for X-Ray Crystallography.*[64]

Selected bond lengths and bond angles appear in Table 4. Tables of final atomic coordinates and equivalent isotropic thermal parameters, anisotropic thermal parameters, complete tables of bond lengths and angles, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information.

Supporting Information Available: Tables of fractional coordinates and displacement parameters, intramolecular distances and angles, supplementary crystallographic data for the structure determination, hydrogen atom coordinates, anisotropic thermal parameters, torsion angles, nonbonded contacts out to 3.80 Å, and least-squares planes for [PPN][4]·CH$_2$Cl$_2$ (27 pages). See any current masthead page for ordering and Internet access instructions.

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