Inorg. Chem. **2006**, *45*, 7111–7118

Inorganic Chemistry
Article

# Synthesis of $[(HIPTNCH_2CH_2)_3N]Cr$ Compounds (HIPT = 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$) and an Evaluation of Chromium for the Reduction of Dinitrogen to Ammonia

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Received March 31, 2006

Red-black $[HIPTN_3N]Cr$ (**1**) ($[HIPTN_3N]^{3-} = [(HIPTNCH_2CH_2)_3N]^{3-}$ where HIPT = 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ = HexaIsoPropylTerphenyl) can be prepared from $CrCl_3$, while green-black $[HIPTN_3N]Cr(THF)$ (**2**) can be prepared from $CrCl_3(THF)_3$. Reduction of {**1**|**2**} (which means either **1** or **2**) with potassium graphite in ether at room temperature yields $[HIPTN_3N]CrK$ (**3**) as a yellow-orange powder. There is no evidence that dinitrogen is incorporated into **1**, **2**, or **3**. Compounds that can be prepared readily from {**1**|**2**} include red $[HIPTN_3N]CrCO$ (**4**), blood-red $[HIPTN_3N]CrNO$ (**6**), and purple $[HIPTN_3N]CrCl$ (**7**, upon oxidation of {**1**|**2**} with AgCl). The dichroic (purple/green) Cr(VI) nitride, $[HIPTN_3N]CrN$ (**8**) was prepared from $Bu_4NN_3$ and **7**. X-ray studies have been carried out on **4**, **6**, and **7**, and on two co-crystallized compounds, **7** and $[HIPTN_3N]CrN_3$ (65:35) and $[HIPTN_3N]CrN_3$ and **8** (50:50). Exposure of a degassed solution of {**1**|**2**} to an atmosphere of ammonia does not yield "**Cr**$(NH_3)$" as a stable and well-behaved species analogous to **Mo**$(NH_3)$. An attempt to reduce dinitrogen under conditions described for the catalytic reduction of dinitrogen by $[HIPTN_3N]Mo$ compounds with **8** yielded a substoichiometric amount (0.8 equiv) of ammonia, which suggests that some ammonia is formed from the nitride but none is formed from dinitrogen.

## Introduction

We have been exploring early transition metal complexes that contain a triamidoamine ligand ($[(RNCH_2CH_2)_3N]^{3-}$).[1] Most recently, we have been attracted to Mo complexes that contain the $[(HIPTNCH_2CH_2)_3N]^{3-}$ ligand, where HIPT = 3,5-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$ (HexaIsoPropylTerphenyl; see Figure 1 for a drawing of $[HIPTN_3N]MoN_2$).[2–6] The $[(HIPTNCH_2CH_2)_3N]^{3-}$ ligand was designed to prevent formation of relatively stable and unreactive $\mu$-dinitrogen complexes,[7] maximize steric protection of a monometallic metal coordination site, and provide increased solubility of complexes in nonpolar solvents. Eight of the proposed intermediates in a hypothetical "Chatt-like" reduction of dinitrogen by $[HIPTN_3N]Mo$ complexes (Figure 2) have been prepared and characterized. These include paramagnetic **Mo**$(N_2)$ (**i**, **Mo** = $[HIPTN_3N]Mo$), diamagnetic $[$**Mo**$(N_2)]^-$ (**ii**), diamagnetic **Mo**$-N{=}N-H$ (**iii**), diamagnetic $[$**Mo**$=N-NH_2]BAr'_4$ (**iv**; Ar′ = 3,5-$(CF_3)_2C_6H_3$), diamagnetic **Mo**$\equiv$N (**vii**), diamagnetic $[$**Mo**$=NH]BAr'_4$ (**viii**), paramagnetic $[$**Mo**$(NH_3)]BAr'_4$ (**xii**), and paramagnetic **Mo**$(NH_3)$ (**xiii**). (Kinetic evidence now suggests that the "naked" species, $[HIPTN_3N]Mo$, is *not* an intermediate in the exchange of ammonia for dinitrogen.[8]) With the exception of **vii**, all are extremely sensitive to oxygen. Several of these species were employed successfully to reduce dinitrogen catalytically to ammonia

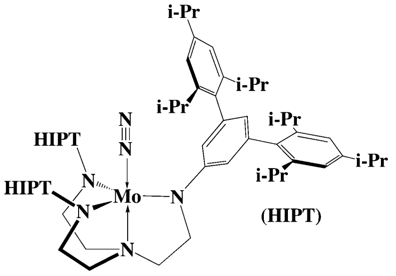

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**Figure 1.** Drawing of $[HIPTN_3N]Mo(N_2)$ = **Mo**$(N_2)$.

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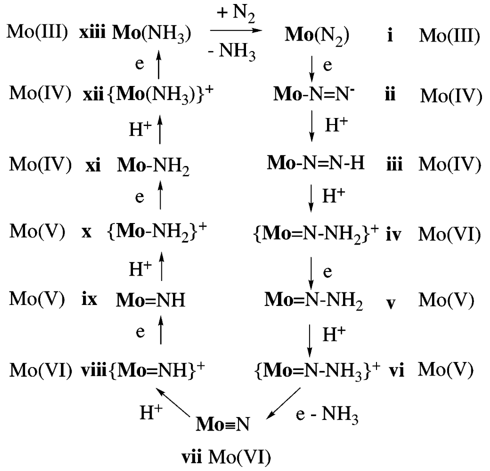

**Figure 2.** Proposed intermediates in the reduction of dinitrogen at a [HIPTN$_3$N]Mo (**Mo**) center through the stepwise addition of protons and electrons.

with protons and electrons,[5] and we have been able to study several important steps in the catalytic cycle.[2]

Many tungsten complexes analogous to the isolated molybdenum catalysts have been prepared and characterized.[9] One important exception is **W**(NH$_3$), the analogue of **Mo**(NH$_3$), which is known to react with dinitrogen to generate ammonia and **Mo**N$_2$. Electrochemical reduction of [**W**(NH$_3$)][BAr′$_4$] in 0.1 M [Bu$_4$N][BAr′$_4$]/PhF at a glassy carbon electrode reveals an irreversible wave at −2.06 V vs FeCp$_2$$^{+/0}$. In contrast, one-electron reduction of [**Mo**(NH$_3$)][BAr′$_4$] is fully reversible both in PhF (0.1M [Bu$_4$N][BAr′$_4$]) at a glassy carbon electrode and THF (0.4 M [Bu$_4$N][PF$_6$]) at a platinum disk and takes place at $E°′$(**Mo**(NH$_3$)$^{+/0}$) = −1.63 V vs FeCp$_2$$^{+/0}$ in PhF (0.1M [Bu$_4$N][BAr′$_4$]). The difference in **M**(NH$_3$)$^{+/0}$ (M = Mo, W) potentials (∼430 mV) suggests that CrCp*$_2$ is much too weak a reducing agent to reduce [**W**(NH$_3$)][BAr′$_4$] to any significant degree. The irreversibility of the [**W**(NH$_3$)][BAr′$_4$] reduction suggests that **W**(NH$_3$) may not be a well-behaved species. In view of these findings, it is perhaps not surprising that no ammonia was formed from dinitrogen in attempted catalytic reductions with **W**(N$_2$).

We became interested in whether [HIPTN$_3$N]Cr complexes can be prepared and whether a compound such as [HIPTN$_3$N]CrN might serve as a catalyst for catalytic reduction of dinitrogen. In this paper, we report the synthesis of a variety of [HIPTN$_3$N]Cr complexes and an exploration of some of their chemistry relevant to the reduction of dinitrogen to ammonia.

## Results

**Syntheses of [HIPTN$_3$N]Cr Complexes.** Suitable starting materials for chromium chemistry are CrCl$_3$ and CrCl$_3$(THF)$_3$. [HIPTN$_3$N]Cr (**1**; $\mu_{eff}$ = 3.03 $\mu_B$, Evans method) can be prepared from CrCl$_3$ and [HIPTN$_3$N]Cr(THF) (**2**; $\mu_{eff}$ = 2.46 $\mu_B$) can be prepared from CrCl$_3$(THF)$_3$, although no crystals of either **1** or **2** suitable for X-ray studies have been obtained. Both are extraordinarily soluble in organic solvents and are difficult to crystallize. [HIPTN$_3$N]Cr is analogous to [*t*-BuMe$_2$SiN$_3$N]Cr[10] and [Me$_3$SiN$_3$N]Cr.[11] (Comments concerning measurements of $\mu_{eff}$ can be found later.)

Green-black **2** is prepared as shown in eq 1, a method that is analogous to the synthesis of [HIPTN$_3$N]MoCl from MoCl$_4$(THF)$_2$.[3] The nature of the adduct that is formed upon

$$CrCl_3(THF)_3/THF \xrightarrow[2.\ 3(TMS)_2NLi]{1.\ H_3[HIPTN_3N]} \underset{\text{green-black}}{[HIPTN_3N]Cr(THF)\ (\mathbf{2})} \tag{1}$$

stirring H$_3$[HIPTN$_3$N] with CrCl$_3$(THF)$_3$ in THF for 1 h is not known. The synthesis of red-black **1** consists of generating Li$_3$[HIPTN$_3$N] in situ from H$_3$[HIPTN$_3$N] and 3 equiv of LiN(TMS)$_2$ in ether, adding CrCl$_3$, and stirring the heterogeneous mixture for 2 days. Compound **1** is converted into **2** upon addition of THF to a solution of **1**, while application of heat and/or vacuum to solid **2** yields **1**. Interconversion of **2** and **1** in this manner appears to be entirely reversible. The two compounds also appear to react entirely analogously as described below. It should be noted that **1** and **2** show no absorption that can be ascribed to an N$_2$ stretch in IR spectra in heptane (Figure 3). The absorptions shown are ascribed to ligand modes that are comparable to those seen in the **Mo** and **W** systems.

Reduction of {**1**|**2**} (which means either **1** or **2**) with potassium graphite in ether at room-temperature yields **Cr**K (**3**; $\mu_{eff}$ = 3.77 and 3.71 $\mu_B$) as a yellow-orange powder. (See Scheme 1 for the reactions of **1** or **2**.) The solution IR spectrum of **Cr**K in heptane is identical to the IR spectra for **1** and **2** shown in Figure 3, i.e., there is no evidence that dinitrogen is incorporated before or after reduction of Cr(III) to yield "{[HIPTN$_3$N]Cr(N$_2$)}K," which would be an analogue of various derivatives of {[HIPTN$_3$N]Mo(N$_2$)}$^-$.[3] The IR spectra of {[HIPTN$_3$N]Mo(N$_2$)}$^-$ derivatives have an absorption for $\nu_{NN}$ in the region 1680−1830 cm$^{-1}$, depending upon the nature of the metal cation and its degree of solvation.[4] **Cr**K is believed to be the potassium salt of the Cr(II) anion with no substituent in the apical pocket except the potassium ion, which is likely to be supported through interaction with one or more aryl rings, as found in a variety of anions that contain arylated amido ligands in the literature.[9,12−15a] Another possibility is a structure related to that found in [Me$_3$SiN$_3$N]CrK(THF)$_2$, where the alkali metal is bound to two of the amido nitrogens and two molecules of THF.[15b] X-ray-quality single crystals of **Cr**K have not yet been obtained. In an attempt to obtain a more crystalline species, 18-crown-6 was added to an ethereal solution of **Cr**K to yield "**Cr**K(18-crown-6)". This species

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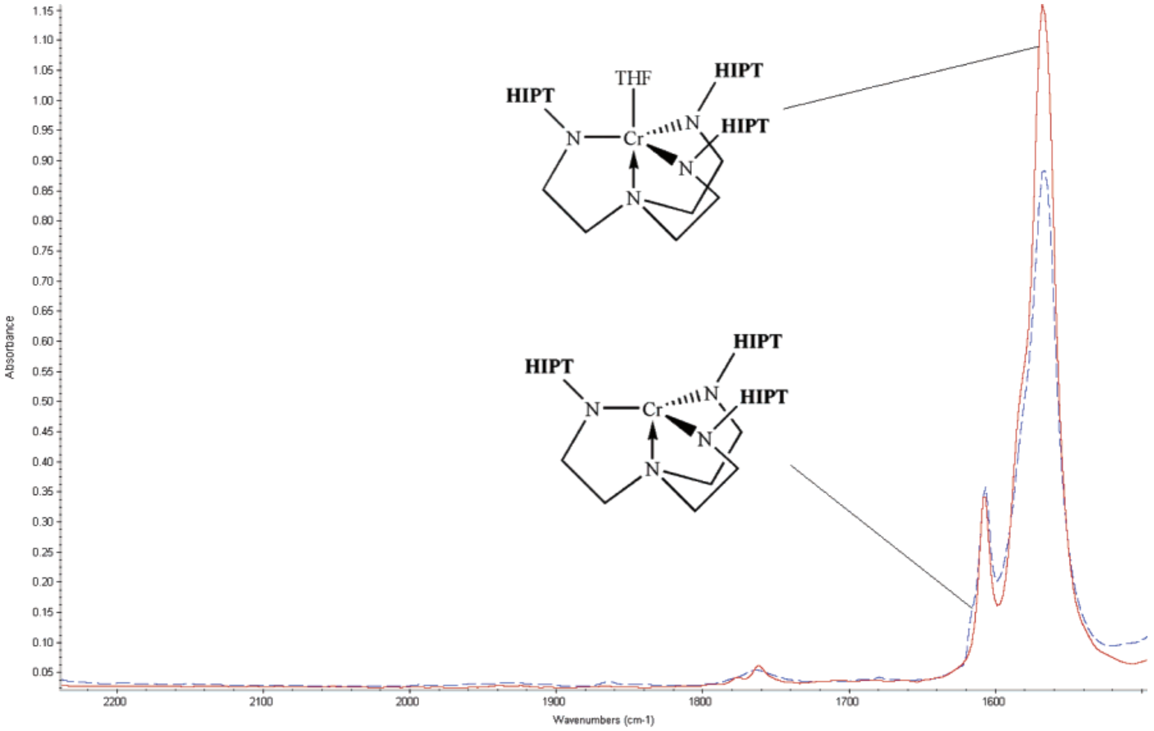

**Figure 3.** Solution (heptane) IR spectrum (solvent subtracted) of {**1**|**2**}.

**Scheme 1.** Reactions of **Cr** (**1**) or **Cr**(THF) (**2**) where **Cr** = [(HIPTNCH$_2$CH$_2$)$_3$N]Cr.

$$\begin{tikzcd}
\{\mathbf{Cr}\text{CO}\}\text{K }(\mathbf{5}) & \mathbf{Cr}\text{CO }(\mathbf{4}) \arrow[l, "\text{KC}_8"'] & \\
\mathbf{Cr}\text{K }(\mathbf{3}) \arrow[u, "\text{CO}"'] & \mathbf{1}\text{ or }\mathbf{2} \arrow[l, "\text{KC}_8"'] \arrow[u, "\text{CO}"'] \arrow[r, "\text{NO}"] \arrow[d, "\text{AgCl}"'] & \mathbf{Cr}\text{NO }(\mathbf{6}) \\
 & \mathbf{Cr}\text{Cl }(\mathbf{7}) \arrow[r, "n\text{-Bu}_4\text{NN}_3"] & \mathbf{Cr}\text{N }(\mathbf{8})
\end{tikzcd}$$

is only slightly soluble in pentane, which supports our formulation of **Cr**K as an anionic potassium salt. Unfortunately, attempts to obtain X-ray-quality crystals so far have yielded only powder. The formulation of **Cr**K is further supported by its reaction with CO, as discussed below.

Exposure of a degassed solution of {**1**|**2**} in pentane to an atmosphere of CO at room temperature yields a red solution, although the reaction requires several minutes to go to completion. IR spectra suggest that the product of this reaction is **Cr**CO (**4**). In heptane, $\nu_{\text{CO}}$ is found at 1951 cm$^{-1}$; in **Cr**($^{13}$CO), $\nu_{^{13}\text{CO}}$ is found at 1907 cm$^{-1}$ and $\nu_{^{13}\text{C}^{18}\text{O}}$ is found at 1862 cm$^{-1}$. **Cr**CO was further characterized in an X-ray study of a crystal obtained from heptane at room temperature. (All structural studies are discussed together in a separate section later.) It should be noted that the reaction between {**1**|**2**} and CO is not instantaneous, which raises the possibility that **1** and **2** are in high spin states and that a low-spin doublet is required to bind CO. The Evans method was employed to show that **Cr**CO is a low-spin species ($\mu_{\text{eff}}$ = 1.69 $\mu_{\text{B}}$). It should be noted that Cummins' chromium trisamide system does not bind CO.[16]

Reduction of red **Cr**CO in ether with potassium graphite quickly yields a green solution of [**Cr**CO]K (**5**). IR spectra are consistent with formulation of [**Cr**CO]K as a reduced carbonyl complex, according to a $\nu_{\text{CO}}$ stretch at 1711 cm$^{-1}$ and a $\nu_{^{13}\text{CO}}$ stretch at 1670 cm$^{-1}$. (In [**Mo**CO]Na, the $\nu_{\text{CO}}$ stretch is found at 1632 cm$^{-1}$.[17]) [**Cr**CO]K also may be prepared by treating **Cr**K with CO in pentane, consistent with the proposed formulations of each.

The reaction between {**1**|**2**} and NO instantly gives a blood-red solution of **Cr**NO (**6**). **Cr**NO has an absorption at 1715 cm$^{-1}$ in its IR spectrum in heptane ascribable to $\nu_{\text{NO}}$ and has been further characterized in an X-ray diffraction study (see later). A $^1$H NMR spectrum of **Cr**NO (Figure 4) shows sharp resonances in the normal region typical of a diamagnetic compound. Therefore, **Cr**NO appears to have four electrons in the two orbitals that are employed for back-bonding to NO, namely $d_{xz}$ and $d_{yz}$ (if the $z$ axis is the 3-fold axis).[16] Unlike **Cr**CO, **Cr**NO is not susceptible to reduction by KC$_8$, which is consistent with NO acting as a reducing equivalent and chromium existing in the 2$^+$ oxidation state.

Compound {**1**|**2**} is oxidized by AgCl in ether at room temperature over a period of 3 days in the absence of light to give dark purple **Cr**Cl (**7**) and silver metal. **Cr**Cl may be crystallized from a saturated pentane solution. Isolated yields of **Cr**Cl vary between 40% and 65%. Although the yield appears to be higher, according to NMR spectra of solutions of the crude product, little **Cr**Cl can be isolated from what remains after one or two crops have been isolated. A magnetic measurement (Evans method) shows **Cr**Cl to have two unpaired electrons (2.55 $\mu_{\text{B}}$), consistent with what would be expected of high-spin Cr(IV) and what has been observed for the related [Me$_3$SiN$_3$N]CrCl complex (2.6 $\mu_{\text{B}}$).[11] Crystal-

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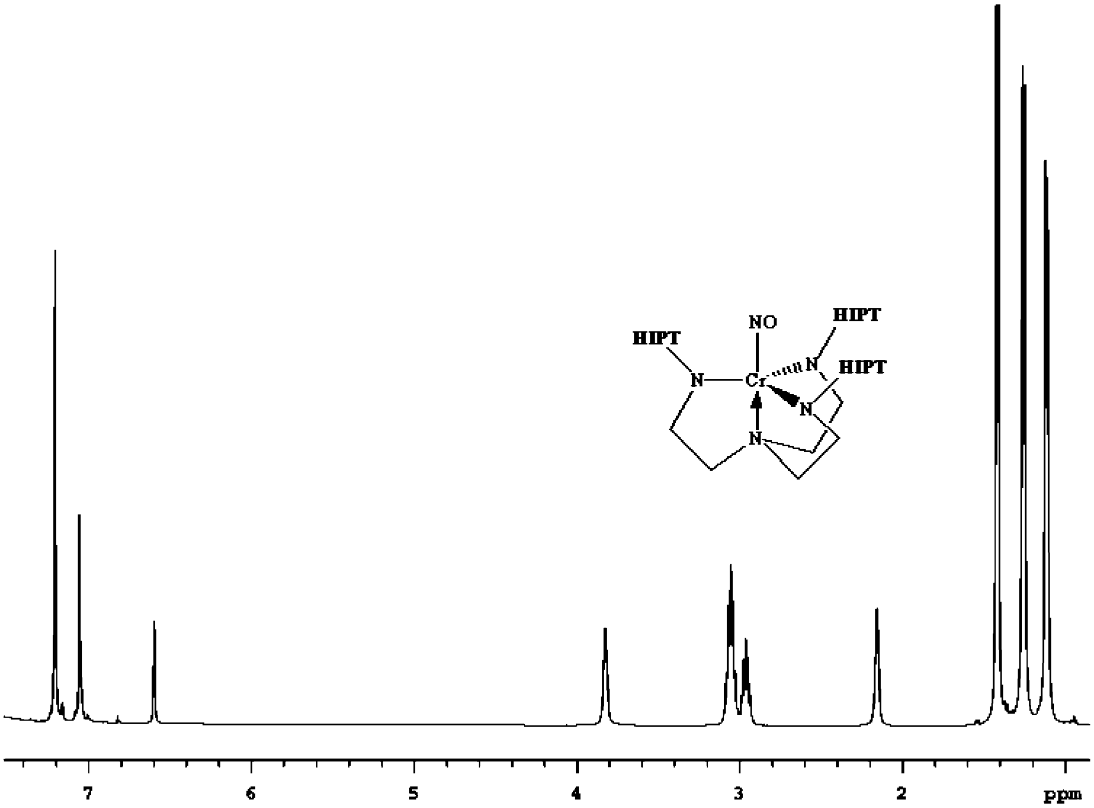

**Figure 4.** $^1$H NMR Spectrum of **Cr**NO in benzene-$d_6$.

lization of **Cr**Cl from heptane at room temperature yielded crystals suitable for an X-ray structure, as described in a later section.

The Cr(VI) nitride, **Cr**N (**8**), was prepared in 69% yield by heating a solution of $Bu_4NN_3$ and **Cr**Cl in benzene at ~80 °C for 1 week, followed by removing the $Bu_4NCl$ and excess $Bu_4NN_3$ and then heating the mixture of intermediate **Cr**$N_3$ and **Cr**N in toluene to ~110 °C for 10 days. **Cr**N is a diamagnetic species with a proton NMR spectrum similar to that of **Cr**NO; it appears to be somewhat stable in air. Crystallization (from heptane) of the product of a reaction that was carried out in benzene at 80 °C for 3 days was shown in an X-ray study be a 65:35 mixture of **Cr**Cl and **Cr**$N_3$ (see later), while the reaction between **Cr**Cl and $Bu_4NN_3$ in benzene at 100 °C for 5 days yielded a 50:50 mixture of **Cr**$N_3$ and **Cr**N, as shown in an X-ray study (see later). The reaction between **Cr**Cl and $Bu_4NN_3$ in toluene at 120 °C for 1 week gave a mixture of **Cr**Cl and **Cr**N, according to elemental analysis and IR spectra. We propose that $Bu_4NN_3$ decomposes slowly at 120 °C before it can react with **Cr**Cl to give first **Cr**$N_3$ and subsequently **Cr**N; this is the reason the synthesis must be carried out in two stages, as described above. There was little or no reaction between **Cr**Cl and $Me_3SiN_3$ in benzene at 80 °C or **Cr**Cl and $NaN_3$ in THF at room temperature. **Cr**N also could not be prepared by treating **Cr**NO with tris-mesityl vanadium, a method used by Cummins to prepare tris-amido chromium nitrides.[16]

A striking property of **Cr**N that complicated its identification is a variation of its color between green and purple in different solvents and at different temperatures. For example, at room temperature, a solution of **Cr**N in benzene is dark green, while at 80−90 °C it is dark purple. In contrast, a solution of **Cr**N in heptane at room temperature is dark purple but turns dark green upon cooling the solution to −35 °C. Upon warming, the solution turns purple again. These color changes are all reversible and adding benzene to a heptane solution of **Cr**N begins to change the color from dark purple to dark green. UV/vis spectra of **Cr**N in benzene and heptane have absorptions that are similar in shape but are at different positions in the two solvents. This solvent/temperature color dependence is illustrated in Figure 5. The origin of this behavior is not known. The only sensible explanation we can think of is that two isomers are present, e.g., the five-coordinate species whose structure has been determined and a *four*-coordinate species in which the central amine donor is not bound to the metal. Unfortunately, we also have not yet been able to think of a way of proving or disproving this proposal.

Some comments are called for concerning the magnetic moments obtained for **Cr** (3.03 $\mu_B$), **Cr**(THF) (2.46 $\mu_B$), and **Cr**K (3.74 $\mu_B$, average of two measurements). (Magnetic moments are reported to three significant figures, as is often the case in the literature, even though we recognize that two significant figures are perhaps more realistic.) These values are lower than the spin-only values (3.87 $\mu_B$ for **Cr** and **Cr**(THF) and 4.90 $\mu_B$ for **Cr**K). However, it should be noted that these complexes could not be recrystallized, in contrast to **Cr**Cl and **Cr**CO. Variations have been observed from sample to sample. For example, the magnetic moment of crude **Cr**CO was found to be 1.82 $\mu_B$ while the magnetic moment of purified **Cr**CO was found to be 1.69 $\mu_B$. A sample of **Cr**K that was prepared through addition of 2 equiv of

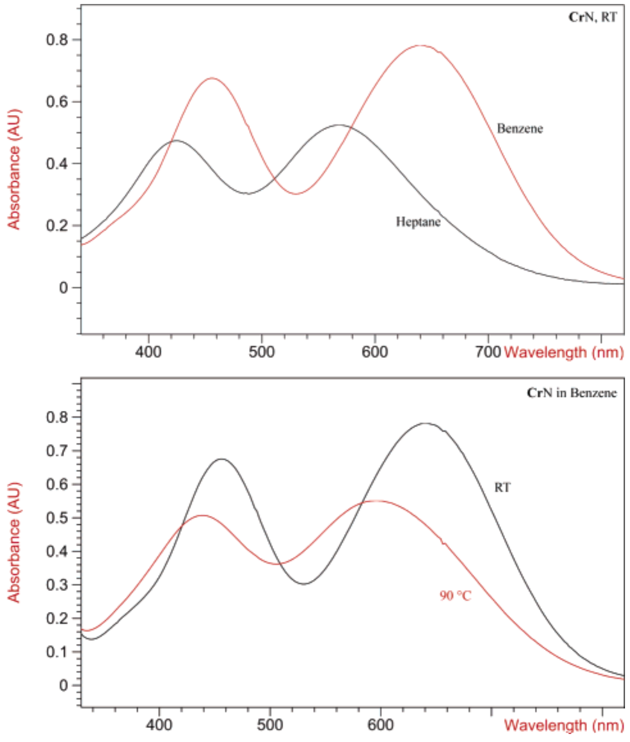

**Figure 5.** UV/vis spectra of **Cr**N.

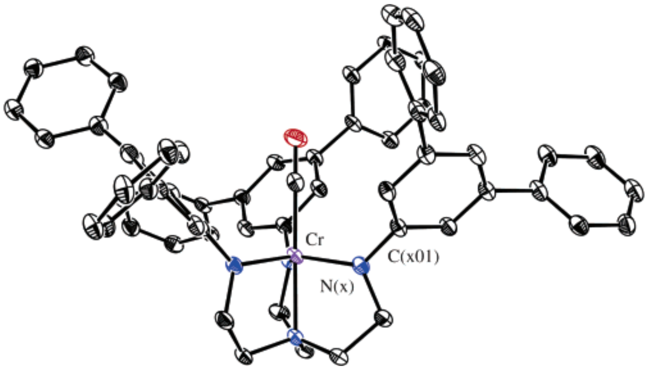

**Figure 6.** ORTEP diagram of **Cr**CO at 50% probability with isopropyl groups and the solvent heptane molecule removed for clarity.

potassium graphite to an ethereal solution or **Cr**Cl was found to have a moment of 4.16 $\mu_B$, while a sample prepared in THF was found to have a moment of 4.06 $\mu_B$. Samples prepared in heptane were found to have moments of 3.77 and 3.71 $\mu_B$. These values should be compared to the value of 5.1 $\mu_B$ reported for crystalline [Me$_3$SiN$_3$N]CrK(THF)$_2$.[15b] Although our results suggest that the magnetic moments for **Cr**, **Cr**(THF), and **Cr**K may be less than the spin-only value, we cannot conclude with a high degree of confidence that this is the case in the absence of further studies on recrystallized species, including SQUID studies, if recrystallized species in fact can be obtained. Nevertheless, it is clear that **Cr**CO is low spin, while it seems most likely that **Cr**, **Cr**(THF), and **Cr**K are high spin.

**X-ray Studies.** Five crystal structures have been determined (Table 1). Three studies involved pure compounds (**Cr**Cl, **Cr**CO, and **Cr**NO), while two studies involved mixtures of two co-crystallized compounds (**Cr**Cl and **Cr**N$_3$ (65:35) and **Cr**N$_3$ and **Cr**N (50:50)). All five compounds crystallize in the *Cc* space group and have almost identical structural parameters. The structures for the **Cr** core and the accompanying solvent molecule (heptane) are all identical, except in the case of the **Cr**Cl/**Cr**N$_3$ and **Cr**N$_3$/**Cr**N mixtures, which have some ligand disorder in the isopropyl groups. It is clear that separation of any of these compounds from one another through crystallization from heptane will not be possible. Details concerning the solutions of the structures of the compounds in mixtures may be found in the Experimental Section. A thermal ellipsoid drawing of one of the structures, **Cr**CO, is shown in Figure 6 (isopropyl groups have been removed for clarity).

The ligand core of the structures reported here were compared to the available **Mo** structures ([**Mo**N$_2$]MgBr(THF)$_3$,[4] **Mo**(N$_2$),[4] **Mo**≡N,[4] **Mo**−N═NH,[2] **Mo**(NH$_3$),[2] {**Mo**[2,6-lutidine]}$^+$,[2] [**Mo**═NNH$_2$]BAr′$_4$ (Ar′ = 3,5-(CF$_3$)$_2$-C$_6$H$_3$),[2] [**Mo**(NH$_3$)]BAr′$_4$,[4] [**Mo**═NH]BAr′$_4$,[2] **Mo**($\eta^2$-CH$_2$CH$_2$),[17] **Mo**(CH$_2$CH$_3$),[17] [**Mo**($\eta^2$-CH$_2$CH$_2$)]BAr′$_4$,[17] [**Mo**(THF)]BPh$_4$)[8] and **W** structures[9] ([**W**(N$_2$)]K, **W**(N$_2$), **W**−N═NH, [**W**═NNH$_2$]BAr′$_4$, and [**W**(NH$_3$)]BAr′$_4$). The displacement of the metal atom from the plane defined by the three ligand amido nitrogens was calculated by using the amido−M bond length and amido−M−donor angle and averaging the three results (Figure 7). Although the normality of the M−donor vector to this plane was assumed, the low standard deviations throughout each group of three calcula-

**Table 1.** X-ray Structure Solution Parameters

| | **Cr**Cl | **Cr**CO | **Cr**NO | **Cr**N$_3$/**Cr**Cl | **Cr**N$_3$/**Cr**N |
|---|---|---|---|---|---|
| formula | $C_{121}H_{175}ClCrN_4$ | $C_{122}H_{175}CrN_4O$ | $C_{121}H_{175}CrN_5O$ | $C_{121}H_{175}Cl_{0.66}CrN_5$ | $C_{121}H_{175}CrN_{5.99}$ |
| fw (g/mol) | 1773.10 | 1765.66 | 1767.66 | 1775.27 | 1765.46 |
| *T* (K) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| space group | *Cc* | *Cc* | *Cc* | *Cc* | *Cc* |
| *a* (Å) | 15.7588(8) | 15.7406(14) | 15.7440(6) | 15.7434(6) | 15.795(2) |
| *b* (Å) | 39.997(2) | 39.859(4) | 39.7549(16) | 39.9919(15) | 39.976(7) |
| *c* (Å) | 17.7963(10) | 17.7657(17) | 17.7703(6) | 17.7938(7) | 17.856(3) |
| α (°) | 90 | 90 | 90 | 90 | 90 |
| *β* (°) | 95.501(2) | 95.342(3) | 95.2400(10) | 95.2800(10) | 94.499(5) |
| *γ* (°) | 90 | 90 | 90 | 90 | 90 |
| GOF | 1.029 | 1.067 | 1.027 | 1.037 | 1.031 |
| *R* [$I > 2\sigma(I)$] (%) | R1 = 4.3, wR2 = 10.1 | R1 = 6.1, wR2 = 14.7 | R1 = 4.5, wR2 = 10.5 | R1 = 5.9, wR2 = 12.0 | R1 = 5.6, wR2 = 12.9 |
| *R* (all data) (%) | R1 = 5.5, wR2 = 10.8 | R1 = 8.3, wR2 = 16.3 | R1 = 5.5, wR2 = 11.0 | R1 = 8.4, wR2 = 13.1 | R1 = 7.1, wR2 = 13.6 |
| Cr−N(x), av (Å) | 1.886 | 1.878 | 1.876 | 1.885 | 1.887 |
| Cr−N(donor) (Å) | 2.123 | 2.109 | 2.132 | 2.129 | 2.234 |
| planar displacement, av (Å) | 0.24 | 0.22 | 0.25 | 0.24 | 0.29 |
| C(x01)−N(x)−Cr, av (°) | 129.6 | 129.8 | 128.8 | 129.3 | 127.7 |

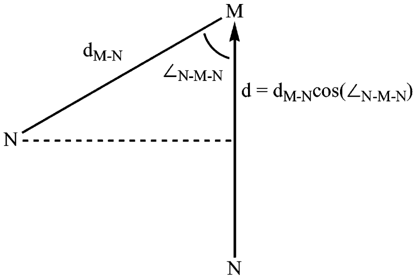

**Figure 7.** Calculation of metal displacement from the tris-amide plane.

tions show that this assumption is reasonable. Average displacements of 0.36 Å ($\sigma = 0.05$ Å) for **Mo** and 0.34 Å ($\sigma = 0.03$ Å) for **W** are not significantly different. **Cr** is slightly different, with parameters 0.25 Å ($\sigma = 0.03$ Å), which translates into chromium being on average ~0.1 Å deeper in the protected pocket. This pattern is emulated in the M−N(amido) bond lengths, with the **Mo** and **W** averages being identical at 1.98 Å ($\sigma = 0.02$ and 0.03 Å, respectively) and **Cr** being about 0.1 Å shorter at 1.88 Å ($\sigma = 0.01$ Å). The nitrogen-donor-to-metal bond shows no significant variation between **Cr** (2.16 Å, $\sigma = 0.05$ Å), **Mo** (2.23 Å, $\sigma = 0.07$ Å), and **W** (2.21 Å, $\sigma = 0.04$ Å). The average C(x01)−N(amido)−M angle provides some idea of the degree to which the ligand crowds upon the protective pocket; the average angle is the same for **Cr** (129°, $\sigma = 1°$), **Mo** (129°, $\sigma = 2°$), and **W** (129°, $\sigma = 2°$). From these parameters, it can be seen that the core structure of [HIPTN$_3$N]M complexes varies little upon going down the Group VI triad. The implication is that any difference in reactivity can be ascribed far more to electronic than to steric factors.

Some bond lengths and angles that involve the ligand in the binding pocket in the five structures are listed in Table 2. In the structure of **Cr**Cl, the Cr−Cl bond length is identical to than found in the related [Me$_3$SiN$_3$N]CrCl complex,[11] and in both cases the N(amine)−Cr−Cl angle is 180°. In both **Cr**CO and **Cr**NO, the N(amine)−Cr−A (A = C, N) and Cr−A−O angles are close to 180° and the Cr−NO bond in **Cr**NO is ~0.2 Å shorter than the Cr−CO bond in **Cr**CO, as might be expected. The Cr−NO and N−O bond lengths in **Cr**NO and [(Me$_3$Si)$_2$N]$_3$CrNO[18] are identical. The Cr−nitride bond length in **Cr**N (1.64 Å) is longer than it is in ($i$-Pr$_2$N)$_3$CrN (1.54 Å).[16] This slight lengthening is also exhibited when **Cr**N is compared to the other structurally characterized chromium (VI) nitrides.[19] However, since the nitride and α-nitrogen of the azide were difficult to separate during refinement of the **Cr**N/**Cr**N$_3$ mixture, this difference should be taken with caution.

**Attempts to Prepare an Ammonia Complex and to Reduce Dinitrogen.** Exposure of a degassed solution of {**1**|**2**} to an atmosphere of ammonia immediately yields a green solution. This solution turns brown after being stirred overnight. Removal of the solvent from either the green or brown solution yields a bright red solid that does not react with CO to yield **Cr**CO, does not react with AgCl to yield **Cr**Cl, and redissolves to yield a red solution. Therefore, this red solid cannot be **1**. However, attempts to crystallize the red solid from heptane over a period of days so far have led only to apparent decomposition and formation of a colorless solid. In short, it does not appear that **1** reacts with ammonia to give "**Cr**(NH$_3$)" as a stable and well-behaved species analogous to **Mo**(NH$_3$).

Three experiments were carried out in order to evaluate the viability of reducing dinitrogen to ammonia. A run carried out under conditions described for catalytic reduction of dinitrogen by **Mo** compounds with **Cr**N yielded 0.8 equiv of ammonia, which suggests that the nitride is reduced to ammonia, but no ammonia is formed from dinitrogen. If **Cr**N is worked up in a manner analogous to that after an attempted catalytic run, then only 0.1 equiv of ammonia is obtained. Therefore, much more of the nitride is converted into ammonia under the conditions of an catalytic run. Finally, a run with the 65:35 mixture of **Cr**Cl and **Cr**N$_3$ yielded 0.3 equiv of ammonia, consistent with stoichiometric reduction of the azide fraction to ammonia.

## Discussion and Conclusions

We conclude that dinitrogen is not reduced by **Cr** compounds under the conditions that are successful for **Mo** compounds. We propose that there are at least four problems. First, **Cr** is relatively high spin, and dinitrogen, a weakly binding two-electron $\sigma$-donor/$\pi$-acceptor ligand, cannot bind efficiently to a quartet in which there is one electron in each of the three frontier orbitals or promote conversion to a low-spin adduct. Even CO does not bind immediately, although NO, an odd-electron ligand, attacks the high-spin species readily. Second, Cr(III) is not as good a reducing agent as Mo(III), so any low-spin Cr(III) doublet would not be captured as efficiently by dinitrogen as the analogous Mo(III) doublet. Third, it is likely that the Cr(III) doublet is not as accessible energetically as the Mo(III) doublet, so little is available to bind dinitrogen. Fourth, it is easier to reduce Cr(III) than Mo(III), so **Cr** is reduced to {**Cr**}$^-$, and {**Cr**}$^-$ also does not react readily with dinitrogen. Almost certainly, there are other problems that prevent reduction of dinitrogen to ammonia, among them the lack of well-behaved chemistry that involves ammonia. Therefore, the prospect of reducing dinitrogen catalytically by [HIPTN$_3$N]Cr complexes appears slim. If the yield of ammonia from **Cr**N is taken at face value, even the stoichiometric reduction of **Cr**N in the presence of a reducing agent and protons is not as efficient as it is for **Mo**N.

We have invoked spin state as a significant problem with respect to binding of dinitrogen to **Cr** or {**Cr**}$^-$. Whether spin state can affect reactivity[20] is a question that has been discussed with greater frequency in the literature in the past

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**Table 2.** Selected Structural Data Relevant to the Apical Ligand

| | X = $Cl^-$ | X = CO | X = NO | X = $N^{3-}$ | X = $N_3^-$ |
|---|---|---|---|---|---|
| **Cr**−X (Å) | 2.2514(5) | 1.905(2) | 1.6759(13) | 1.635(11) | 1.717(12)<br>1.884(9) |
| $X_1$−$X_2$ (Å) | − | 1.142(3) | 1.1826(17) | − | 1.340(14)<br>1.20(3) |
| $X_2$−$X_3$ (Å) | − | − | − | − | 1.192(10)<br>1.176(7) |
| N(amine)−**Cr**−X (°) | 179.62(5) | 179.39(10) | 179.66(7) | 176.6(11) | 177.2(4)<br>177.6(10) |
| **Cr**−$X_1$−$X_2$ (°) | − | 179.3(2) | 179.58(15) | − | 135.0(9)<br>130(2) |
| $X_1$−$X_2$−$X_3$ (°) | − | − | − | − | 176.5(9)<br>175.3(15) |

10 years.[21−25] There seems to be agreement that spin state *can* affect reactivity, but the degree to which it does depends greatly upon the particular case being considered. As far as simple addition of an even-electron $\sigma$-donor/$\pi$-acceptor ligand to a metal is concerned, the more weakly binding the ligand (in terms of its combined $\sigma$-donor/$\pi$-acceptor ability) the more spin state can be a determining factor. Conversely, for an odd-electron ligand such as NO, the number of unpaired electrons on the metal probably is relatively unimportant. The results that we have found here are consistent with the general trends that one might expect.

## Experimental Section

**General.** All experiments were conducted under nitrogen in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Glassware was heated at ∼190 °C for a minimum of 12 h prior to use. Pentane was washed with $HNO_3/H_2SO_4$ (5:95 v/v), sodium bicarbonate, and water, dried with $CaCl_2$, and then sparged with nitrogen and passed through alumina columns followed by vacuum transfer from Na/benzophenone. Dry and deoxygenated benzene was purchased from Aldrich and passed through Q5 and alumina columns. Heptane, benzene-$d_6$ and toluene-$d_8$ were dried over Na/benzophenone then degassed (freeze−pump−thaw) and vacuum-transferred prior to use. All other solvents (diethyl ether, THF, toluene) were predried by passing them through an alumina column followed by storage over Na/benzophenone. They were degassed (freeze−pump−thaw) and vacuum-transferred prior to use. Once transferred, all solvents were stored over 4 Å molecular sieves in a drybox.

$CrCl_3$ (Strem), CO (Aldrich, passed through dry ice/acetone), NO (BOC gases), $NH_3$ (BOC, condensed onto Na sand), and $^{13}CO$ (Matheson, passed through dry ice/acetone) were purchased and used as received or purified as indicated. $H_3$[$HIPTN_3N$][4−6] and $CrCl_3(THF)_3$[26] were synthesized via literature procedures.

Proton NMR spectra were obtained on a Varian Mercury (300 MHz) or Inova (500 MHz) spectrometer and were referenced to the residual protio-solvent peak. Infrared spectra were obtained on an Nicolet Avatar 360 FT-IR spectrometer using a demountable cell (0.2 mm Teflon spacer and KBr plate). UV/vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer equipped with a Hewlett-Packard 89090A Peltier temperature control accessory with the solvent contribution manually subtracted using a standard background. Magnetic measurements (Evans method[27,28]) employed the shift of the toluene methyl group. The sample was dissolved in toluene-$d_8$, and a concentric sealed capillary filled with toluene was added. Elemental analyses were performed by H. Kolbe Microanalytics Laboratory, Mülheim an der Ruhr, Germany.

Structural data were collected at 100 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) using a Bruker-AXS Smart Apex CCD detector. The structures were solved using SHELXS[29] and refined against $F^2$ on all data by full-matrix least squares with SHELXL-97.[30] All non-hydrogen atoms were refined anisotropically, while hydrogen atoms were placed at calculated positions and refined using a riding model. ORTEP diagrams were created using ORTEP-3.[31] Any deviations from this procedure are noted below. Data for all five structures are available at http://www.reciprocalnet.org/ using the number that follows after each complex. **Cr**Cl (05105), **Cr**CO (05129), and **Cr**NO (05137) are isostructural with no disorder, including the solvent (heptane) molecule.

The unit cell of **Cr**Cl/**Cr**$N_3$ (05131) is very similar to that of **Cr**Cl. Indeed, **Cr**Cl/**Cr**N is perfectly isostructural to **Cr**Cl (and also to **Cr**CO) and is a mixed crystal, refined as a disorder. It is problematic to refine the 34% nitrogen next to the relatively high electron density of the 67% chlorine. Therefore, SIMU and DELU are used for the five critical atoms and ISOR for the nitrogen bound directly to the Cr. Another consequence of the disorder is that the empirical formula has a noninteger value for Cl. This is not true for N, as one-third of azide corresponds to one nitrogen atom. However, this is a coincidence and the relative occupancy has been refined freely with the help of a free variable.

The crystal of **Cr**N/**Cr**$N_3$ (05167) is a 50:50 mixture (within error of FVAR). The two Cr(1)−N(5) bond distances were refined as a disorder with the help of a free variable and rigid bond restraints.

**[$HIPTN_3N$]Cr (1).** $H_3$[$HIPTN_3N$] (2 g, 1.26 mmol) and LiN(TMS)$_2$ (632 mg, 3.78 mmol) were dissolved in ether, and the solution was stirred at room temperature. In ∼1 h, solid began to form. $CrCl_3$ (199 mg, 1.26 mmol) was added to this solution, and the mixture was allowed to stir for 2 days. The resulting red-black mixture was filtered and the solvent was removed in vacuo at ∼40 °C to give a dark solid: $^1H$ NMR ($C_6D_6$) $\delta$ −13.05 (br s). $\mu_{eff} = 3.03\ \mu_B$. Anal. Calcd for $C_{114}H_{159}N_4Cr$: C, 83.62; H, 9.79; N, 3.42;

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Cl, 0.00. Found: C, 83.47, 83.52; H, 9.66, 9.68; N, 3.34, 3.37; Cl, 0.00.

**[HIPTN$_3$N]Cr(THF) (2).** H$_3$[HIPTN$_3$N] (6 g, 3.78 mmol) and CrCl$_3$(THF)$_3$ (1.42 g, 3.78 mmol) were dissolved in THF, and the mixture was stirred for an hour at room temperature to give a violet-colored solution. LiN(TMS)$_2$ (1.96 g, 11.7 mmol) was added quickly, which caused the color to change to green-black. After another hour, the solvent was removed in vacuo at ~40 °C. The resultant solid was dissolved in pentane, and the solution was filtered. The solvent was removed from the filtrate in vacuo at ~40 °C to give green-black powder: $\mu_{\mathrm{eff}} = 2.46\ \mu_{\mathrm{B}}$. Anal. Calcd for $C_{118}H_{167}N_4OCr$: C, 82.90; H, 9.85, N, 3.28. Found: C, 83.08, 83.12; H, 9.95, 9.98; N, 3.25, 3.21.

**[HIPTN$_3$N]CrK (3).** **Cr**(THF) (500 mg, 0.29 mmol) was dissolved in ether in a 20 mL vial. A glass-coated stir bar was added along with KC$_8$ (47 mg, 0.35 mmol). The mixture was stirred for ~12 h and then filtered. The solvent was removed in vacuo to yield a yellow-orange powder. The same results were obtained using **Cr**: $\mu_{\mathrm{eff}} = 3.77$ and 3.71, average = 3.74 $\mu_{\mathrm{B}}$. Anal. Calcd for $C_{114}H_{159}N_4CrK$: C, 81.67; H, 9.56; N, 3.34. Found: C, 81.57, 81.51; H, 9.46, 9.40; N, 3.30, 3.26.

**[HIPTN$_3$N]CrCO (4).** **Cr**(THF) (500 mg, 0.29 mmol) was dissolved in ~20 mL of pentane, and the solution was added to a 50 mL solvent bulb which was then attached to a gas-transfer bridge. The solution was cooled in liquid nitrogen, and the atmosphere removed. The stainless steel tubing connecting the lecture bottle to the bridge was shaped into a coil that was immersed in CO$_2$/acetone. The bulb was pressurized to slightly less than 1 atm with CO and warmed to room temperature. The bulb was closed, and the solution was stirred. Within 5−10 min, the color turned red. The solvent was removed in vacuo to give a red solid. X-ray-quality crystals were obtained from a saturated heptane solution at room temperature. **Cr** can be substituted for **Cr**(THF) with the same results. The procedure for preparing the $^{13}$CO analogue was the same, but on a smaller scale: IR cm$^{-1}$ 1951 ($\nu_{\mathrm{CO}}$), 1907 cm$^{-1}$ ($\nu_{\mathrm{13CO}}$), 1862 ($\nu_{\mathrm{13C18O}}$). $\mu_{\mathrm{eff}} = 1.69\ \mu_{\mathrm{B}}$.

{**[HIPTN$_3$N]CrCO**}**K (5).** [HIPTN$_3$N]CrCO was reduced as described for the synthesis of **Cr**K. Alternatively, **Cr**K was exposed to CO. Both methods yield this green pentane-soluble complex quantitatively: $^1$H NMR (toluene-$d_8$, 18-crown-6 adduct) $\delta$ 7.63 (s, 6H), 7.17 (s, 12H), 6.35 (s, 3H), 4.09 (br s, 6H), 3.46 (br s, 12H), 2.91 (br s, 30H), 1.60 (br s, 6H), 1.39 (d, $J_{\mathrm{HH}} = 6.4$ Hz, 36H), 1.29 (d, $J_{\mathrm{HH}} = 5.8$ Hz, 36H), 1.17 (d, $J_{\mathrm{HH}} = 4.3$ Hz, 36H). IR cm$^{-1}$ 1711 ($\nu_{\mathrm{CO}}$), 1671 ($\nu_{\mathrm{13CO}}$). Anal. Calcd for $C_{115}H_{159}N_4OCrK$: C, 83.76; H, 9.63; N, 3.37. Found: C, 83.66, 83.70; H, 9.51, 9.57; N, 3.44, 3.41.

**[HIPTN$_3$N]CrNO (6).** Compound **1** (300 mg, 0.18 mmol) was added to a 50 mL solvent bulb, and ~20 mL of pentane was added. NO was added as described for the synthesis of **Cr**CO. The color of the solution turned blood red as soon as it thawed under an atmosphere of NO. The solvent was removed in vacuo to give a red solid. X-ray-quality crystals were obtained from a supersaturated heptane solution at room temperature. **Cr** can be substituted for **Cr**(THF) with the same results: $^1$H NMR (C$_6$D$_6$) $\delta$ 7.21 (s, 12H), 7.06 (s, 6H), 6.60 (s, 3H), 3.83 (br t, 6H), 3.05 (sept, $J_{\mathrm{HH}} = 6.7$ Hz, 12H), 2.96 (sept, $J_{\mathrm{HH}} = 6.8$ Hz, 6H), 2.16 (br t, 6H), 1.42 (d, $J_{\mathrm{HH}} = 6.9$ Hz, 36H), 1.26 (d, $J_{\mathrm{HH}} = 6.8$ Hz, 36H), 1.11 (d, $J_{\mathrm{HH}} = 6.7$ Hz, 36H). IR cm$^{-1}$ 1715 ($\nu_{\mathrm{NO}}$). Anal. Calcd for $C_{114}H_{159}N_5OCr$: C, 82.11; H, 9.61; N, 4.20. Found: C, 82.05, 82.00; H, 9.65, 9.69; N, 4.28, 4.25.

**[HIPTN$_3$N]CrCl (7).** To a 100 mL round-bottom flask covered in electrical tape was added **Cr**(THF) (3.00 g, 1.75 mmol) and ~60 mL of ether. AgCl (251 mg, 1.75 mmol) was added in the dark. The flask was stoppered and covered in electrical tape. The mixture was stirred for 3 days and filtered to give a purple solution. The solvent was removed in vacuo at ~50 °C to give a dark purple solid which could be purified through crystallization from cold pentane. X-ray-quality crystals were obtained from a saturated heptane solution at room temperature. The same results are obtained when **Cr** is used instead of **Cr**(THF): $^1$H NMR (toluene-$d_8$) $\delta$ 25.58 (br s). UV/vis $\lambda_{\max}$(nm), $\epsilon$ (M$^{-1}$ cm$^{-1}$) heptane (280, 2.7 × 10$^4$; 372, 1.9 × 10$^4$; 566, 1.3 × 10$^4$); benzene (286, 2.0 × 10$^4$; 382, 1.5 × 10$^4$; 472, 7.1 × 10$^3$; 578, 1.1 × 10$^4$). $\mu_{\mathrm{eff}} = 2.55\ \mu_{\mathrm{B}}$. Anal. Calcd for $C_{114}H_{159}N_4CrCl$: C, 81.84; H, 9.58; N, 3.35; Cl, 2.12. Found: C, 81.75, 81.72; H, 9.51, 9.48; N, 3.22, 3.25; Cl, 2.19, 2.16.

**[HIPTN$_3$N]CrN (8).** CrCl (0.974 g, 0.58 mmol) was added to a 100 mL flask with a Teflon valve followed by Bu$_4$NN$_3$ (221 mg, 0.78 mmol), a Teflon-coated stir bar, and ~50 mL of benzene, making sure all solid was washed into the flask. The reaction mixture was then heated at 80 °C for 1 week with an additional equivalent of Bu$_4$NN$_3$ added halfway through. Solvent was removed from the resulting mixture (purplish at 80 °C, green at room temperature), and the resulting solid residue was extracted with pentane. The mixture was filtered through Celite in order to remove Bu$_4$NCl and excess Bu$_4$NN$_3$. The solvent was removed from the filtrate in vacuo, the residue was taken up in toluene (~50 mL), and the solution was then heated at 110 °C for 10 days. The solvent was removed in vacuo, and the residue was crystallized from saturated pentane solution at −35 to −40 °C to yield a dark purple microcrystalline solid (660 mg, 69%): $^1$H NMR (C$_6$D$_6$) $\delta$ 7.97 (br s, 6H), 7.19 (s, 12H), 6.56 (s, 3H), 3.77 (br t, 6H), 3.09 (sept, $J_{\mathrm{HH}} = 6.9$ Hz, 12H), 2.92 (sept, $J_{\mathrm{HH}} = 6.9$ Hz, 6H), 1.94 (br t, 6H), 1.36 (d, $J_{\mathrm{HH}} = 6.9$ Hz, 36H), 1.21 (d, $J_{\mathrm{HH}} = 6.9$ Hz, 36H), 1.05 (br d, $J_{\mathrm{HH}} = 6.6$ Hz, 36H). UV/vis $\lambda_{\max}$(nm), $\epsilon$ (M$^{-1}$ cm$^{-1}$): heptane (268, 2.9 × 10$^4$; 424, 1.6 × 10$^4$; 570, 1.8 × 10$^4$); benzene (284, 2.7 × 10$^4$; 456, 1.9 × 10$^4$; 638, 2.2 × 10$^4$). Anal. Calcd for $C_{114}H_{159}N_5Cr$: C, 82.91; H, 9.70; N, 4.24; Cl, 0.0. Found: C, 82.78, 82.90; H, 9.76, 9.80; N, 4.23, 4.23; Cl, 0.0, 0.0.

**Acknowledgment.** R.R.S. is grateful to the National Institutes of Health (GM 31978) for research support.

**Supporting Information Available:** Crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and anisotropic displacement parameters for all crystallographically characterized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

IC060549K