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Chromium(VI) nitrido complexes: reactions with Brønsted acids and synthesis of organometallic derivatives

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Abstract—The chromium(VI) nitrido complex NCr(N-*i*-Pr$_2$)$_3$ was prepared in 67% yield by vanadium(III)-mediated deoxygenation of coordinated nitric oxide. The iodide complex NCr(I)(N-*i*-Pr$_2$)$_2$, prepared by treatment of NCr(N-*i*-Pr$_2$)$_3$ with lutidinium iodide, was converted to NCr(CH$_2$SiPhMe$_2$)(N-*i*-Pr$_2$)$_2$ upon treatment with Mg(CH$_2$SiPhMe$_2$)$_2$. NCr(N-*i*-Pr$_2$)$_3$ reacts with 1 equiv. of phenol or HOC(CF$_3$)$_2$Me to produce the mono-alkoxide complexes NCr(OPh)(N-*i*-Pr$_2$)$_2$ or NCr(OC(CF$_3$)$_2$Me)(N-*i*-Pr$_2$)$_2$ in respective yields of 89 and 77%. Spin saturation transfer measurements performed on NCr(OC(CF$_3$)$_2$Me)(N-*i*-Pr$_2$)$_2$ are indicative of Cr—N$_{amido}$ bond rotation with a first-order rate constant of ca 13 s^{-1}. Addition of an excess of HOC(CF$_3$)$_2$Me to NCr(N-*i*-Pr$_2$)$_3$ produced the mono-amido complex NCr(OC(CF$_3$)$_2$Me)$_2$(N-*i*-Pr$_2$) in 86% yield. Subjecting NCr(N-*i*-Pr$_2$)$_3$ to refluxing HS-*t*-Bu provided NCr(S-*t*-Bu)$_2$(N-*i*-Pr$_2$) in 73% yield. Black NCr(S-*t*-Bu)$_2$(N-*i*-Pr$_2$) evinces a monomeric structure in the solid state, according to single-crystal X-ray diffraction data, with a Cr—N$_{nitrido}$ distance of 1.543(6) Å. Bis-thiolate NCr(S-*t*-Bu)$_2$(N-*i*-Pr$_2$) forms an adduct with Cu(Et$_2$dtc), NCr(N-*i*-Pr$_2$)[(μ-S-*t*-Bu)$_2$Cu(Et$_2$dtc)], which was also characterized by X-ray diffraction. Reaction of NCr(N-*i*-Pr$_2$)$_3$ with two equiv. of phenol gave NCr(OPh)$_2$(N-*i*-Pr$_2$) in 81% yield. Dialkyl NCr(CH$_2$SiMe$_3$)$_2$(N-*i*-Pr$_2$) was obtained from NCr(OPh)$_2$(N-*i*-Pr$_2$) upon treatment with LiCH$_2$SiMe$_3$ in 57% yield. Insertion of *tert*-butylisonitrile was observed upon treatment of NCr(CH$_2$SiMe$_3$)$_2$(N-*i*-Pr$_2$) with excess *t*-BuNC to give NCr(C(=N-*t*-Bu)CH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)(N-*i*-Pr$_2$), which was isolated in 70% yield. The latter η^2-iminoacyl compound was characterized by X-ray diffraction, revealing a pseudo-square pyramidal ligand arrangement.

Keywords: chromium; nitrido; iminoacyl; protonolysis; amido; nitrosyl.

Recent developments in the activation of small molecules have led to the discovery of new routes to terminal nitrido complexes. For example, three-coordinate Mo(N[R]Ar)$_3$, where R is C(CD$_3$)$_2$(CH$_3$) and Ar is 3,5-C$_6$H$_3$Me$_2$, was found to react with dinitrogen to form NMo(N[R]Ar)$_3$ via a linear μ-dinitrogen dinuclear complex intermediate [1]. In addition, the cleavage of nitric oxide to nitride and oxo functionalities by two metal centers was achieved. Bradley's nitrosyl ONCr(N-*i*-Pr$_2$)$_3$ [2], in particular, was found to serve as an oxo donor to V(Mes)$_3$(THF) [3,4].

Much of the interest in reactions that produce terminal nitrido complexes stems from the possibility of producing useful chemical feedstocks like ammonia from strategic starting materials. Reactions that convert dinitrogen or NO$_x$ gases to nitrido complexes could represent a useful first step toward achieving this goal. Also important in this context is to elucidate the chemistry of the resulting nitrido complexes. In a study conducted by Chisholm and co-workers [5] reactions of NM(O-*t*-Bu)$_3$, where M = Mo and W, with excess *i*-PrOH were investigated. Treatment of NMo(O-*t*-Bu)$_3$ with isopropanol led to exclusive alkoxide substitution given NMo(O-*i*-Pr)$_3$. The tungsten derivative NW(O-*t*-Bu)$_3$, in contrast, was exhaustively attacked by isopropanol giving W(O-*i*-Pr)$_6$.

In addition to chemistry where the nitrido nitrogen is an active participant, there is also an extensive chemistry in which a nitrido nitrogen acts as a spectator ligand [6–8]. For example, molybdenum(VI) nitrides can be synthesized with soft ligands such as thiolates [9] or hard ligands such as amides [1,8,10].

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Molybdenum organometallic complexes also have been synthesized [11] including the σ organometallic complex NMo(neopentyl)$_3$ [7]. Chromium(VI) derivatives with this large variety of ligands offer an exciting new field of study [12].

RESULTS AND DISCUSSION

Synthesis of NCr(N-*i*-Pr$_2$)$_3$ (**3**) *and nitric oxide cleavage*

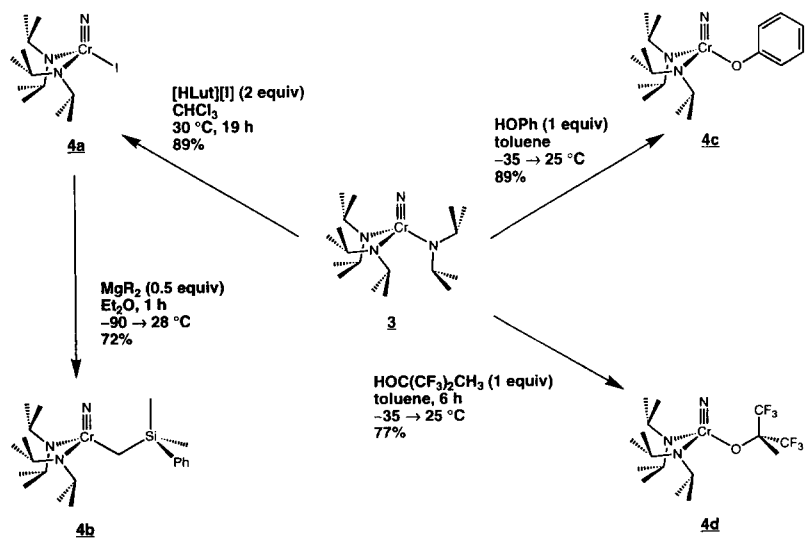
Bradley and co-workers synthesized Cr(N-*i*-Pr$_2$)$_3$ (**1**) by addition of 3 equiv. of LiN-*i*-Pr$_2$ to ethereal CrCl$_3$ [13]. Treatment of **1** with nitric oxide results in a rapid reaction to produce orange ONCr(N-*i*-Pr$_2$)$_3$ (**2**) [2]. The π acidic nitrosyl ligand induces a diamagnetic $\{ONCr\}^4$ low-spin electronic configuration, which results in a low N—O stretching frequency of 1643 cm^{-1}. Deoxygenation of **2** by two equiv. of V(mesityl)$_3$(THF)[3] gave rise to NCr(N-*i*-Pr$_2$)$_3$ (**3**) and OV(mesityl)$_3$, but the latter is trapped by an additional equiv. of V(mesityl)$_3$(THF) to form O[V(mesityl)$_3$]$_2$ [14]. The nitrido complex was easily separated from the vanadium(IV) μ-oxo species by pentane extraction [4].

The physical properties of beet-colored **3** are significantly different from those of **2** and **1**, consistent with the large difference in formal oxidation state. The solid state structure of **3** as determined by X-ray diffraction revealed an average Cr—N$_{amido}$ bond length that is ~0.3 Å shorter than found in **1**. The Cr—N$_{nitrido}$ distance of 1.544(3) Å in **3** is ~0.15 Å shorter than Cr—N$_{nitrosyl}$ bonds in ONCr[N(SiMe$_3$)$_2$]$_3$ and ONCr(I)(N[R]Ar$_F$)$_2$, where R = C(CH$_3$)(CD$_3$)$_2$ and Ar$_F$ = 2,5-C$_6$H$_3$FMe [15]. In addition, the ^{1}H NMR spectrum of **3** exhibits broad resonances for the amido ligands at room temperature. The broad nature of the peaks is attributed to hindered rotation around the Cr—N$_{amido}$ bonds and contrasts with the narrow line widths found in the ^{1}H NMR spectrum of ONCr(N-*i*-Pr$_2$)$_3$ (**2**).

Bis-amido chromium(VI) complexes (scheme 1)

(*i*) *Synthesis of* NCr(I)(N-*i*-Pr$_2$)$_2$(**4a**). Lutidinium iodide is conveniently synthesized in anhydrous form by the reaction of 2,6-lutidine, *tert*-butyl alcohol and ISiMe$_3$ in dry ether. Addition of 2.5 equiv. of lutidinium iodide to 1 equiv. of **3** initiated a color change of the reaction mixture to orange-red. Protolytic amido replacement was found to have occurred giving NCr(I)(N-*i*-Pr$_2$)$_2$ (**4a**) [16]. The lutidine by-product was easily separated by recrystallization. An attempt to produce NCr(I)$_2$(N-*i*-Pr$_2$) under forcing conditions only resulted in an intractable product and starting materials.

The ^{1}H NMR spectrum of **4a** is indicative of hindered rotation [17,26] around the Cr—N$_{amido}$ bonds. Four doublets are observed in the spectrum. These correspond to the diastereotopic methyl hydrogens, which are differentiated further by being syn or anti with respect to the nitrido nitrogen. Two septets are also observed in the spectrum, septets which correspond to methine hydrogens located syn and anti with respect to the nitrido group. A dramatic slowing of the Cr—N$_{amido}$ rotation rate in **4a** versus **3** is explicable in terms of a qualitative molecular orbital picture for the two molecules [18]. In NCr(N-*i*-Pr$_2$)$_3$ (**3**), the chromium has a degenerate set of two orbitals available for π bonding to the three amido substituents. The three amido π donor orbitals must compete for



Scheme 1.

the two metal π acceptor orbitals, resulting in a bond order for the amido substituents of one and two-thirds. The iodide complex **4a** has only two amides to donate into the two metal orbitals with proper symmetry for π bonding. Therefore, the amido substituents in NCr(I)(N-*i*-Pr_2)$_2$ may form two double bonds (formally) to the chromium center. The hindered rotation observed for **4a** is even more dramatic in light of the steric difference between NCr(I)(N-*i*-Pr_2)$_2$ (**4a**) and NCr(N-*i*-Pr_2)$_3$ (**3**). The iodide complex **4a,** which presumably is less sterically congested, exhibits characteristics indicative of slower amido rotation.

(ii) Synthesis and thermal decomposition of NCr($CH_2SiPhMe_2$)(N-*i*-Pr_2)$_2$ (**4b**). A nitrido alkyl complex NCr($CH_2SiPhMe_2$)(N-*i*-Pr_2)$_2$ (**4b**) was produced by addition of Mg($CH_2SiPhMe_2$)$_2$ to a cold solution of **4a** in ether [16]. NCr($CH_2SiPhMe_2$)(N-*i*-Pr_2)$_2$ **4b** is a rare example of a chromium(VI) organometallic complex [19]. The σ alkyl complex **4b** also is a rare example of an alkyl nitrido complex [7,11]. Orange NCr($CH_2SiPhMe_2$)(N-*i*-Pr_2)$_2$ (**4b**) was isolated in 72% recrystallized yield and has a ^{1}H NMR spectrum with four doublets and two septets assignable to the amido hydrogens.

The alkyl-nitrido complex **4b** is stable in solution at room temperature for hours without appreciable decomposition, but the compound decomposes at 60°C with a first order rate constant of $(2.4 \pm 0.1) \times 10^{-4}$ s^{-1} [16]. The data for the decomposition are consistent with β-hydrogen abstraction [20] from one of the amido substituents by the departing alkyl. The products included $PhSiMe_3$ (GC/MS and ^{1}H NMR), the imine Me_2C=N-*i*-Pr (tentative ^{1}H NMR identification), and diisopropylamine (^{1}H NMR). We have not characterized a black solid (possibly CrN [21]) produced during the thermolysis.

(iii) Synthesis of NCr(OPh)(N-*i*-Pr_2)$_2$ (**4c**). Addition of one equiv. of phenol to **3** in toluene caused the solution to change color to orange over a few minutes. The phenoxide NCr(OPh)(N-*i*-Pr_2)$_2$ (**4c**) product, which was purified by recrystallization from ether, was isolated in 88% yield.

Phenoxide **4c** is stable for long durations in solution at room temperature, and exhibits slightly different NMR properties from **4a** and **4b**. The compound displays four peaks for the methyl hydrogens and two peaks for the methine hydrogens as in the previously discussed bis-amido compounds. However, the peaks in NCr(OPh)(N-*i*-Pr_2)$_2$ are significantly broadened which suggests faster rotation around the Cr—N_{amido} bonds than in NCr(I)(N-*i*-Pr_2)$_2$ and NCr($CH_2SiPhMe_2$)(N-*i*-Pr_2)$_2$. The less hindered rotation is indicative of the greater π donating ability of the phenoxide ligand relative to the alkyl or iodide ligands.

(iv) Synthesis of NCr($OC(CF_3)_2Me$)(N-*i*-Pr_2)$_2$ (**4d**) *and spin saturation transfer* Phenol and HOC(CF_3)$_2$Me are often compared due to their similar pK_a' [22] but dramatically different π basicity [23]. Addition of one equiv. of HOC(CF_3)$_2$Me to a stirring solution of **3** cleanly produced NCr($OC(CF_3)_2Me$)(N-*i*-Pr_2)$_2$ (**4d**), which was isolated in 77% yield.

The ^{1}H NMR spectrum has the four-doublets-two-septets pattern indicative of hindered rotation about the Cr—N_{amido} bonds. The compound **4d,** unlike phenoxide **4c,** has sharp peaks in its spectrum corresponding to the amido ligands. The more hindered rotation found for **4d** relative to **4c** can be attributed to decreased π donation by the fluorinated alkoxide ligand relative to phenoxide and to the larger steric demands of the alkoxide ligand.

Magnetization transfer between the two methine hydrogens in **4d** was measured using the method of Dahlquist, Longmuir and Du Vernet [24]. The experiment was performed in C_6D_6 at room temperature, and the data are plotted in Fig. 1. The data were fit to $A_0 e^{-Xt}$, where t is the delay time and A_0 is the intensity of the selectively-irradiated peak in the difference spectrum at t = 0. The difference curve fit converged at A_0 = 178 (0.77) and X = 13.99 (0.096) with R = 0.9997. The sum curve fit converged at A_0 = 187 (0.59) and X = 0.428 (0.016) with R = 0.983. From the values of X a rate constant for amido rotation equal to 13.5 (0.1) s^{-1} is obtained, which correlates to $\Delta G^{\ddagger}$ = 16 kcal/mol [25].

Mono-amido chromium(VI) nitrido complexes (scheme 2)

(i) Synthesis of NCr($OC(CF_3)_2Me$)$_2$(N-*i*-Pr_2) (**5a**) *and spin saturation transfer.* Addition of excess

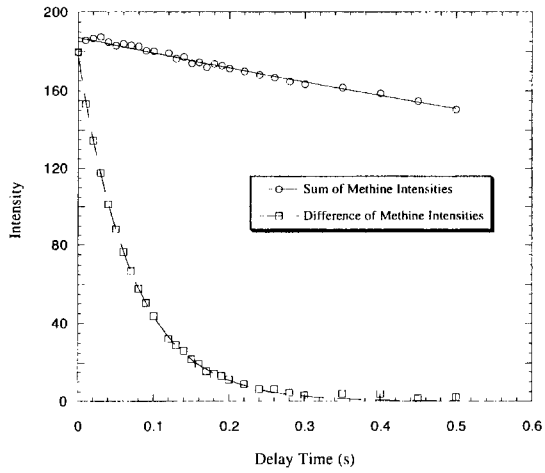
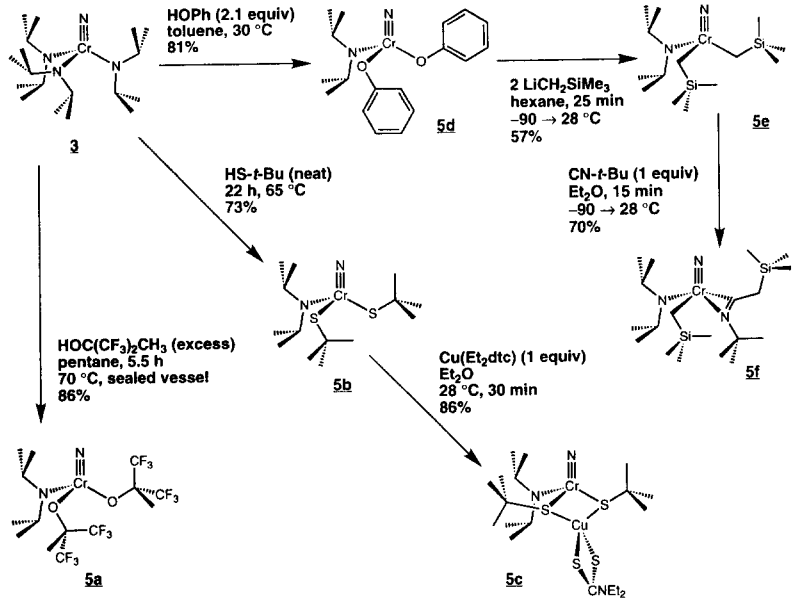


Fig. 1. Sum and difference in intensity plot for the two septets in NCr($OC(CF_3)_2Me$)(N-*i*-Pr_2)$_2$ (**4d**) in C_6D_6. The lines were fit to the equation $A_0 e^{-Xt}$, where A_0 is the initial intensity of the selectively pulsed peak and t is the delay time in seconds. X in the sum plot is equal to 1/T1. In the difference plot X is equal to 1/T1 + k(1) + k(−1). The sum curve fit converged at A_0 = 187(0.59) and X = 0.428(0.016) with R = 0.983. The difference curve fit converged at A_0 = 178 (0.77) and X = 13.99 (0.096) with R = 0.9997. The fits indicate a rate constant for the amido rotation of 13.5 (0.1) s^{-1} for k(1) + k(−1) which correlates to $\Delta G^{\ddagger}$ = 16 kcal/mol.



Scheme 2.

$HOC(CF_3)_2Me$ to **3** produced the bis-alkoxide complex $NCr(OC(CF_3)_2Me)_2(N\text{-}i\text{-}Pr_2)$ (**5a**). The reaction was quite slow and required heating at 70°C in a concentrated solution of the alcohol for 5 h. The production of **5a** was very clean and yielded 86% of the purified complex. This is in contrast to the reaction of **4a** with lutidinium iodide, which did not result in the clean production of $NCr(I)_2(N\text{-}i\text{-}Pr_2)$.

An alternative synthesis of **5a** involves heating $NCr(I)(N\text{-}i\text{-}Pr_2)_2$ in the neat alcohol for 12 h. Under these conditions $[H_2N\text{-}i\text{-}Pr_2]$ [I] precipitates from the solution, and **5a** is produced in 64% yield.

The ^1H NMR spectra of all of the mono-amido complexes exhibit two doublets for the methyl hydrogens and two septets for the methine hydrogens of the diisopropylamide. The inequivalence of the *iso*-propyl groups is attributed to syn and anti differentiation with respect to the nitrido functionality and is indicative of significant amido—chromium multiple bond character.

Table 1. Selected bond distances (Å) and angles (°) for $NCr(S\text{-}t\text{-}Bu)_2(N\text{-}i\text{-}Pr_2)$ (**5b**)

Cr(1)—N(2)	1.543(6)
Cr(1)—N(1)	1.780(6)
Cr(1)—S(1)	2.217(3)
Cr(1)—S(2)	2.235(3)
N(2)—Cr(1)—N(1)	106.3(3)
N(2)—Cr(1)—S(1)	107.7(2)
N(2)—Cr(1)—S(2)	107.5(2)
N(1)—Cr(1)—S(1)	109.6(2)
N(1)—Cr(1)—S(2)	108.8(2)
C(11)—S(1)—Cr(1)	113.8(3)
C(21)—S(2)—Cr(1)	111.8(3)

Spin saturation transfer experiments carried out for $NCr(OC(CF_3)_2Me)_2(N\text{-}i\text{-}Pr_2)$ (**4a**) did not indicate magnetization transfer between the methyl hydrogens of the amido substituent even at 90°C. The lack of transfer suggests a rotation rate constant of less than $\sim 0.3\ s^{-1}$ at that elevated temperature, and the activation energy required for rotation can be estimated to be $\geqslant 22$ kcal/mol. The activation energies associated with Cr—N_{amido} rotation in **4d** and **5a** are comparable with some of the larger $M{=}ER_2$ (where E is carbon or nitrogen) bond rotation activation energies found in the literature. The $M_2(NR_2)_6$ complexes of molybdenum and tungsten, where R is methyl or ethyl, have activation energies for amido rotation of 11 to 14 ± 0.5 kcal/mol [26]. Schrock and co-workers have measured the activation energies required for alkylidene rotation in several tantalum complexes [27]. $Cp_2Ta(Cl)(CHC(CH_3)_3)$, $Cp_2Ta(CH_2Ph)(CHPh)$ and $Cp_2Ta(CH_3)(CH_2)$ are reported to have values of $\Delta G^{\ddagger}$ for Ta=C rotation of 16.8 ± 0.1, 19.3 ± 0.1 and $\geqslant 21.4$ kcal/mol, respectively.

(ii) Synthesis and X-ray crystal structure of $NCr(S\text{-}t\text{-}Bu)_2(N\text{-}i\text{-}Pr_2)$ (**5b**). Group 6 nitrides with soft ligands such as thiolates are rare [9]. The scarcity of reports involving high oxidation state nitrido thiolate complexes could be construed as indicative of instability in this class of compounds. The most common decomposition route for thiolate complexes is S—S bond formation giving reduction at the metal center [28]. This decomposition can occur by thiolate radical loss from the metal with subsequent S—S bond formation, by reductive elimination of two thiolates on the same metal center or by dimerization with

Table 2. Selected bond distances (Å) and angles (°) for NCr(N-*i*-Pr$_2$)[(μ-S-*t*-Bu)$_2$Cu(Et$_2$dtc)] (**5c**)

Cr—N(1)	1.805(13)
Cr—N(2)	1.547(13)
Cr—S(1)	2.240(6)
Cr—S(2)	2.247(6)
Cu—S(1)	2.277(5)
Cu—S(2)	2.250(5)
Cu—S(3)	2.395(5)
Cu—S(4)	2.370(5)
Cr—Cu	2.607(4)
N(2)—Cr—N(1)	107.0(6)
N(1)—Cr—S(1)	111.2(5)
N(2)—Cr—S(1)	108.9(5)
N(1)—Cr—S(2)	111.0(5)
N(2)—Cr—S(2)	109.5(5)
S(1)—Cr—S(2)	109.2(2)
N(1)—Cr—Cu	136.5(4)
N(2)—Cr—Cu	116.4(5)
S(1)—Cr—Cu	55.4(2)
S(2)—Cr—Cu	54.62(14)
S(2)—Cu—S(1)	107.8(2)
S(1)—Cu—S(4)	122.4(2)
S(2)—Cu—S(4)	120.0(2)
S(1)—Cu—S(3)	110.9(2)
S(2)—Cu—S(3)	116.2(2)
S(4)—Cu—S(3)	75.9(2)
S(1)—Cu—Cr	54.1(2)
S(2)—Cu—Cr	54.53(14)
S(3)—Cu—Cr	140.4(2)
S(4)—Cu—Cr	143.6(2)
Cr—S(1)—Cu	70.5(2)
Cr—S(2)—Cu	70.8(2)
C(11)—S(1)—Cr	115.8(6)
C(11)—S(1)—Cu	113.3(6)
C(21)—S(2)—Cr	115.1(6)
C(21)—S(2)—Cu	113.8(6)
C(1)—S(3)—Cu	83.3(6)
C(1)—S(4)—Cu	84.3(6)

Table 3. Selected bond distances (Å) and angles (°) for NCr(C(=N-*t*-Bu)CH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)(N-*i*-Pr$_2$) (**5f**)

Cr(1)—N(11)	1.77(2)
Cr(1)—N(12)	1.90(2)
Cr(1)—N(13)	1.59(2)
Cr(1)—C(11)	2.50(2)
Cr(1)—C(121)	1.67(2)
N(12)—C(121)	1.56(3)
N(12)—C(126)	1.55(3)
N(13)—Cr(1)—C(121)	103.9(10)
N(13)—Cr(1)—N(11)	110.6(9)
C(121)—Cr(1)—N(11)	120.9(10)
C(121)—Cr(1)—N(12)	51.4(8)
N(11)—Cr(1)—N(12)	133.7(9)
N(13)—Cr(1)—N(12)	115.5(10)
N(11)—Cr(1)—C(11)	95.3(8)
N(12)—Cr(1)—C(11)	66.6(8)
N(13)—Cr(1)—C(11)	108.4(9)
C(121)—Cr(1)—C(11)	117.6(9)
Si(11)—C(11)—Cr(1)	121.0(10)
C(121)—N(12)—Cr(1)	56.4(10)
C(126)—N(12)—C(121)	114(2)
C(126)—N(12)—Cr(1)	170(2)

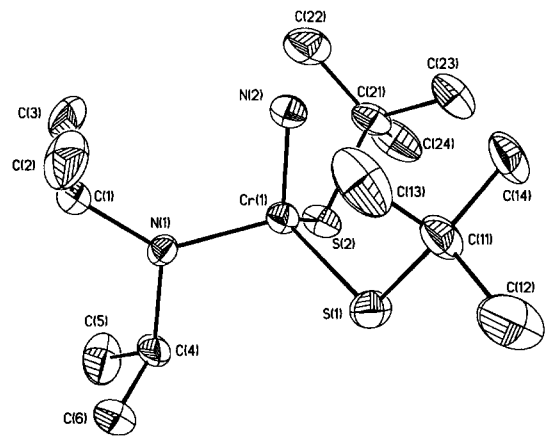


Fig. 2. ORTEP diagram of NCr(S-*t*-Bu)$_2$(N-*i*-Pr$_2$) (**5b**). The ellipsoids are at the 35% probability level.

reductive elimination from two metal centers. The decomposition mechanisms listed above allow the metal center to access its lower oxidation states and would seem to be favorable for a chromium(VI) thiolate complex. It was found, however, that refluxing *tert*-butylthiol will convert **3** to the quite stable thiolate complex NCr(S-*t*-Bu)$_2$(N-*i*-Pr$_2$) (**5b**) in 73% yield. The dark, highly crystalline product forms green or blue solutions depending on the solvent.

An X-ray diffraction study carried out on **5b** yielded a model exhibiting a monomeric structure in the solid state (Fig. 2). All of the structurally characterized chromium(VI) nitrido complexes are monomeric in the solid state, which contrasts with the polymeric structures of many molybdenum and tungsten nitrido compounds [29]. The nitrido nitrogen is surrounded closely by an isopropyl group from the amido substituent and the two *tert*-butyl groups of the thiolates. The structure exhibits a Cr—N(2) distance of 1.543(6) Å which is a typical Cr—$N_{nitrido}$ distance for this class of complexes [4,12,16]. The Cr(1)—N(1) distance in **5b** is ~0.09 Å shorter than the average Cr—N_{amido} distance in Cr(N-*i*-Pr$_2$)$_3$ and ~0.06 Å shorter than in NCr(N-*i*-Pr$_2$)$_3$. The shortening of the metal—N_{amido} bond is consistent with increased π bonding in the mono-amido Cr(VI) complex.

(iii) Synthesis and X-ray crystal structure of NCr(N-*i*-Pr$_2$)[(μ-S-*t*-Bu)$_2$Cu(Et$_2$dtc)] (**5c**). A blue ethereal solution of NCr(S-*t*-Bu)$_2$(N-*i*-Pr$_2$) (**5b**) gives an orange-brown reaction mixture when added to a slurry of Cu(Et$_2$dtc) [30]. The resultant complex NCr(N-*i*-Pr$_2$)[(μ-S-*t*-Bu)$_2$Cu(Et$_2$dtc)] (**5c**) has *tert*-butyl thiolate ligands bridging the chromium and cop-

Table 4. Summary of crystal data for $NCr(S\text{-}t\text{-}Bu)_2(N\text{-}i\text{-}Pr_2)$ (**5b**), $NCr(N\text{-}i\text{-}Pr_2)[(\mu\text{-}S\text{-}t\text{-}Bu)_2Cu(Et_2dtc)]$ (**5c**) and $NCr(C(=N\text{-}t\text{-}Bu)CH_2SiMe_3)(CH_2SiMe_3)(N\text{-}i\text{-}Pr_2)$ (**5f**)

Compound	**5b**	**5c**	**5f**
Empirical formula	$C_{14}H_{32}CrN_2S_2$	$C_{19}H_{42}CrCuN_3S_4$	$C_{19}H_{45}CrN_3Si_2$
Space group	$P2_1/n$	$P2_1/n$	P1
a, Å	9.891(8)	13.501(8)	7.6178(10)
b, Å	12.334(8)	9.974(9)	10.1373(13)
c, Å	16.537(10)	20.97(2)	18.181(2)
α, degrees	90	90	89.358(2)
β, degrees	94.56(4)	98.16(7)	80.999(4)
γ, degrees	90	90	71.845(2)
Z	4	4	2
V, Å^3	2011(2)	2795(4)	1316.6(3)
ρ_{calcd}, g/cm^3	1.138	1.322	1.069
Cryst. dimens, mm	$0.40 \times 0.30 \times 0.10$	$0.45 \times 0.26 \times 0.09$	$0.71 \times 0.14 \times 0.12$
Cryst. color	black	black	yellow-green
R1(F)	0.0642	0.1148	0.0924
Rw(F^2)	0.1231	0.2905	0.1809
GOF ($I > 2\sigma I$)	1.289	1.152	1.125
ψ-scans max. trans.	0.1372	0.1685	0.7189
ψ-scans min. trans.	0.1125	0.1095	0.6096
temp., K	188(2)	130(2)	193(2)

per metal centers and is synthesized in 73% purified yield. The solid state structure of **5c** (Fig. 3) as determined by X-ray diffraction shows a $NCr(N\text{-}i\text{-}Pr_2)(S\text{-}t\text{-}Bu)_2$ fragment which is essentially unperturbed from the structure of **5b** (Fig. 2). The complex exhibits a pseudo-tetrahedral arrangement of sulfurs around the copper(I) metal center. The *tert*-butyl substituents enclose the nitrido nitrogen while the $Cu(Et_2dtc)$ fragment occupies a position on the opposite side of the S(1)—S(2)—N(1) plane [31].

(*iv*) *Synthesis of* $NCr(OPh)_2(N\text{-}i\text{-}Pr_2)$ (**5d**). Treatment of a toluene solution of **3** with two equiv. of phenol results in a rapid color change to dark orange and production of $NCr(OPh)_2(N\text{-}i\text{-}Pr_2)$ (**5d**). The reaction is complete in less than thirty min in dramatic contrast to the conditions for the synthesis of **5a**.

The bis-phenoxide complex **5d** is easily synthesized and isolated but is, however, somewhat thermally sensitive. The complex decomposes in solution at room temperature to yield an intractable solid. The nature of this decomposition, although currently unknown, is probably the result of Cr—O homolytic bond cleavage to reduce the oxidation state of the metal and produce phenoxide radical [32].

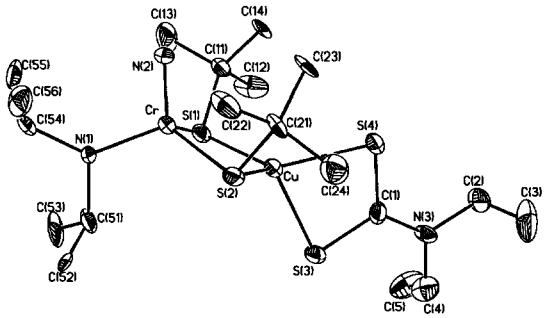


Fig. 3. ORTEP diagram of $NCr(N\text{-}i\text{-}Pr_2)[(\mu\text{-}S\text{-}t\text{-}Bu)_2Cu(Et_2dtc)]$ (**5c**). The ellipsoids are at the 35% probability level.

(*v*) *Synthesis and thermolysis of* $NCr(CH_2SiMe_3)_2(N\text{-}i\text{-}Pr_2)$ (**5e**). Addition of two equiv. of $LiCH_2SiMe_3$ to a cold solution of **5d** in pentane results in the formation of the chromium(VI) organometallic complex $NCr(CH_2SiMe_3)_2(N\text{-}i\text{-}Pr_2)$ (**5e**). The highly lipophilic compound was purified by recrystallization from hexamethyldisiloxane at -35°C in 57% yield.

The complex **5e** exhibits thermal stability similar to that found for **4b**. The compound can be stirred at room temperature overnight without substantial decomposition, but it decomposes rapidly at 60°C. The decomposition, though not as clean as found for **4b**, may proceed by a similar β-hydrogen abstraction mechanism. The ^1H NMR spectrum of the decomposition products revealed tetramethylsilane, $HN\text{-}i\text{-}Pr_2$ and the imine $Me_2C{=}N\text{-}i\text{-}Pr$ to be among the products. There is also a black solid produced during the thermolysis.

(*vi*) *Reactivity of* **5e** *with tert*-butyisonitrile. *The synthesis and X-ray crystal structure of* $NCr(C(=N\text{-}t\text{-}Bu)CH_2SiMe_3)(CH_2SiMe_3)(N\text{-}i\text{-}Pr_2)$ (**5f**). Addition of *t*-butyl isonitrile to an ethereal solution of **5e** produced a color change to yellow-green, forming the iminoacyl $NCr(C(=N\text{-}t\text{-}Bu)CH_2SiMe_3)(CH_2SiMe_3)(N\text{-}i\text{-}Pr_2)$ (**5f**). Only a single insertion reaction occurs even with 24 h exposure of the dialkyl to 10 equiv. of *t*-butyl isonitrile. The greater reactivity of $NCr(CH_2$

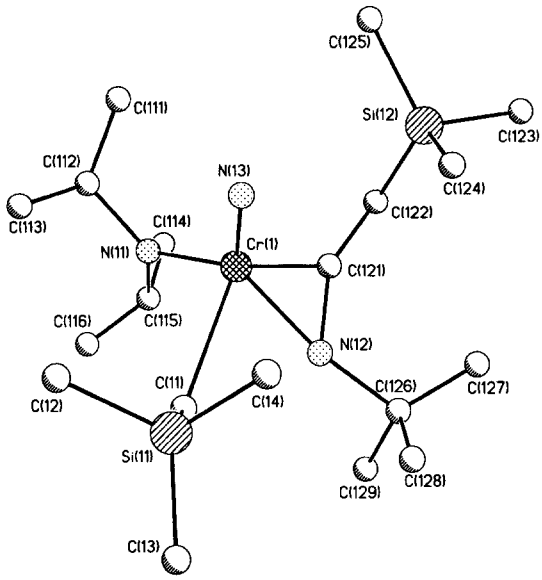


Fig. 4. PLUTO diagram of NCr(C(=N-*t*-Bu)CH_2 $SiMe_3$)(CH_2SiMe_3)(N-*i*-Pr_2) (**5f**). One of the two chemically equivalent molecules in the asymmetric unit is shown.

$SiMe_3)_2$(N-*i*-Pr_2) (**5e**) relative to NCr(C(=N-*t*-Bu)CH_2SiMe_3)(CH_2SiMe_3)(N-*i*-Pr_2) (**5f**) towards insertion can be attributed to electronic differences between the two complexes. The dialkyl can be described as a 14e complex with an available low energy orbital in the plane normal to the nitrido vector and passing through chromium. The iminoacyl complex **5f** has a 16e metal center and no low energy orbitals available, such that a second insertion reaction is unfavorable. Accordingly, treatment of the 16e monoalkyl complex **4b** with 10 equiv. of *t*-butyl isonitrile also gave no reaction even after 24 h reaction time.

An X-ray diffraction study (Fig. 4) carried out on **5f** clearly revealed the presence of an η^2-iminoacyl group. The four different ligands reside in a pseudo square pyramidal arrangement with the η^2-iminoacyl, amido and alkyl substituents residing in the basal plane and the nitrido nitrogen occupying the axial site.

Reactivity of the nitrido nitrogen in chromium(VI) nitrido complexes

(*i*) *Reaction of* 3 *with nucleophiles.* Nitrido complexes often react with nucleophiles to produce complexes with lower oxidation states for the central metal [8]. Nitrides react with phosphines to produce phosphiniminato complexes [33] or with sulfur to produce thionitrosyls [34]. Reactions of this type that effect a reduction of the metal center would seem favorable for chromium(VI). However, a clean addition reaction involving the nitrido nitrogen has not been observed. The microscopic reverse of the nitrosyl deoxygenation reaction does not occur on treatment of NCr(N-*i*-$Pr_2)_3$ (**3**) with 10 equiv. of pyridine-*N*-oxide or trimethylamine-*N*-oxide in CH_2Cl_2 over several d. Nitrido **3** does not react with a concentrated solution of S_8 in CS_2 even after two d. In addition, **3** does not react with neat triethylphosphine even with 24 h of reaction time. This lack of reactivity towards phosphines is especially intriguing due to the reactivity of NCr^{V}(TPP) with PMe_3 to produce $Me_3P{=}NCr^{III}$(TPP) [35].

(*ii*) *Reaction of* NCr(N-*i*-$Pr_2)_3$ *with water.* The nitrido functionality, although stable to a number of protic reagents, does react with water. Addition of 2 equiv. of water to a THF solution of **3** resulted in the precipitation of an insoluble black material, which has not been characterized. However, addition of a THF solution of **3** to an excess of water resulted in smooth hydrolysis of the nitrido nitrogen to form [H_2N-*i*-$Pr_2]_2[Cr_2O_7]$, which was isolated in 73% recrystallized yield.

EXPERIMENTAL

General considerations

All manipulations were carried out in a Vacuum Atmospheres dry box under a purified nitrogen atmosphere unless stated otherwise. Anhydrous ether was purchased from Mallinckrodt and freshly distilled from purple sodium benzophenone ketyl. Toluene was purchased from Mallinckrodt and purified by refluxing over molten sodium under nitrogen for at least two d. Pentane (EM Science) was distilled from purple sodium benzophenone ketyl. Distilled solvents were transferred under vacuum to glass vessels and stored in a Vacuum Atmospheres dry box prior to use. Nitric oxide (grade 5.0) was purchased from BOC corporation and used as supplied. *Tert*-butyl mercaptan was purchased from Aldrich, dried over activated 3 Å sieves for two d and then was distilled under nitrogen prior to use. *Tert*-butylisonitrile was purchased from Aldrich, degassed and stored over 3 Å sieves prior to use. Hexafluoro-2-methylisopropanol (hexafluoro-*tert*-butanol) purchased from PCR Chemical Company was degassed and dried over 3 Å sieves prior to use. (*N*,*N*-diethyldithiocarbaminato)copper(I) [30] and V(mesityl)$_3$(THF) [3] were made according to published procedures. All other solvents, including deuterated solvents, were degassed and stored over activated 3 Å sieves for at least 24 h before use. The sieves were activated by heating at approximately 200°C *in vacuo* overnight. Other chemicals were purchased from commercial sources and used as received. Cr(N-*i*-$Pr_2)_3$ [13], and (ON)Cr(N-*i*-$Pr_2)_3$ [2], were made according to literature methods. NCr(I)(N-*i*-$Pr_2)_2$ and NCr(CH_2SiMe_2Ph)(N-*i*-$Pr_2)_2$ were prepared as previously communicated [16].

Infrared spectra were recorded on a Perkin Elmer

1600 Series FTIR or a Biorad FTS 135. ^{1}H, ^{13}C, ^{15}N and ^{19}F NMR spectra were recorded on Varian VXR-500, Varian XL-300, or Varian Unity-300 spectrometers. ^{1}H and ^{13}C chemical shifts are reported with reference to solvent resonances (residual C_6D_5H in C_6H_6 as 7.15 ppm; C_6D_6 as 128.0 ppm; $CHCl_3$ in $CDCl_3$ as 7.24 ppm; $CDCl_3$ as 77.0 ppm) and were recorded at room temperature unless otherwise stated. ^{19}F NMR chemical shifts are reported with reference to external $CFCl_3$ as 0.00 ppm. ^{15}N NMR chemical shifts are reported with respect to external nitromethane at 380.2 ppm (relative to liquid NH_3 at 0.00 ppm). Combustion analysis were performed by Oneida Research Services, Whitesboro, NY or by Microlytics, South Deerfield, MA. Melting points were obtained in sealed glass capillaries and are uncorrected.

Synthesis and reactivity studies

(*i*) *Synthesis of* $NCr(N\text{-}i\text{-}Pr_2)_3$ (**3**). $(ON)Cr(N\text{-}i\text{-}Pr_2)_3$ (1.094 g, 2.859 mmol, 1 equiv.), V(mesityl)$_3$(THF) (2.983 g, 6.207 mmol, 2.17 equiv.), 35 ml of toluene and a stir bar were loaded into a 300 ml glass vessel equipped with a side arm. The mixture was stirred in a 65°C oil bath for 60 min, during which the solution turned from brown to red. The volatiles were removed *in vacuo*, and the contents of the bomb were extracted with pentane. The resultant beet solution was filtered through a bed of Celite on a sintered glass frit. Extraction left a less soluble, highly pyrophoric black solid on the frit. The product was recrystallized from ether in 67% yield (0.701 g, 1.91 mmol). ^{1}H NMR ($CDCl_3$): δ 3.93 (v br s, 1H), 1.28 (v br s, 6H). ^{13}C NMR ($CDCl_3$): δ 54 (v br s), 27 (v br s), 23 (v br s). FTIR ($NCr(N\text{-}i\text{-}Pr_2)_3$, $CHCl_3$) 1054.0 cm^{-1}. FTIR ($^{15}NCr(N\text{-}i\text{-}Pr_2)_3$, $CHCl_3$) 1029.0 cm^{-1}. ^{15}N NMR ($^{15}NCr(N\text{-}i\text{-}Pr_2)_3$, C_6D_6) δ 979. M.p. ca 110°C (subl). EIMS (high res.) calc. 366.281435 (M^+); found 366.28109, error range 0.00071. Anal. calcd for $C_{18}H_{42}N_4Cr$: C, 58.98; H, 11.55; N, 15.28; Found: C, 59.11; H, 11.13; N, 15.26.

(*ii*) *Reaction of* **4a** *with lutidinium iodide.* Into a 120 ml glass bomb equipped with a stopcock was loaded lutidinium iodide (108 mg, 2.5 equiv., 0.459 mmol), **4a** (72.2 mg, 1 equiv., 0.184 mmol), 7 ml of $CHCl_3$ and 7 ml of THF. The solution was placed in a 75°C oil bath and stirred for 18 h. A small amount of green insoluble material formed, and the ^{1}H NMR spectrum in $CDCl_3$ exhibited peaks corresponding only to the starting materials.

(*iii*) *NMR tube thermolysis of* $NCr(CH_2SiPhMe_2)(N\text{-}i\text{-}Pr_2)_2$ (**4b**) In a sealable NMR tube was loaded 40 mg of **4b** and 995 mg of C_6D_6. The sealed tube was heated to 60°C in an oil bath and was checked periodically over 7 h. All starting material had been consumed by the 7 h mark according to ^{1}H NMR analysis. The spectrum showed $PhSiMe_3$ (s, 0.18 ppm; m, 7.19 ppm; m, 7.44) which was also seen in the GC/MS of the reaction products ($M^+ = 150$). Also observed in the ^{1}H NMR was $HN\text{-}i\text{-}Pr_2$ (d, 0.93 ppm; sept, 2.76 ppm) and peaks attributable to $Me_2C{=}N\text{-}i\text{-}Pr$ (d, 1.14 ppm; s, 1.35 ppm; s, 1.80 ppm; sept, 3.43 ppm). No other peaks were observed in the NMR spectrum. A black insoluble material was formed during the thermolysis.

(*iv*) *Preparation of* $NCr(N\text{-}i\text{-}Pr_2)_2(OPh)$ (**4c**). In a 125 ml Erlenmeyer flask was loaded $NCr(N\text{-}i\text{-}Pr_2)_3$ (750 mg, 2.05 mmol, 1 equiv.), 40 ml of toluene and a stir bar. The solution was frozen in a cold well at liquid nitrogen temperature and then removed to a stir plate. Once the solution could be stirred as a cold slurry, a −35°C solution of HOPh (193 mg, 2.04 mmol, 1 equiv.) in 20 ml of toluene was added dropwise. The solution was allowed to warm and stir for 30 min. and the reaction mixture changed from a beet color to dark orange. The product was recrystallized from ether in 89% yield (653 mg, 1.82 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (br app s, 6H, Pr-*i*-CH_3), 1.25 (br app s, 6H, *i*-PrCH_3), 1.43 (br app s, 6H, *i*-PrCH_3), 1.84 (br app s, *i*-PrCH_3), 3.75 (br app s, 2H, *i*-PrCH), 5.04 (br app s, 2H, *i*-PrCH), 6.76 (t, J_{HH} = 6.6 Hz, 1H, p-Ph), 6.95 (d, J_{HH} = 8.1 Hz, 2H, m-Ph), 7.15 (t, J_{HH} = 7.8 Hz, 4H, o-Ph). $^{13}C\{^{1}H\}$ NMR (300 MHz, $CDCl_3$ −20°C): δ = 21.207 (*i*-PrCH_3), 21.502 (*i*-PrCH_3), 30.240 (*i*-PrCH_3), 30.546 (*i*-PrCH_3), 55.440 (*i*-PrCH), 58.417 (*i*-PrCH), 166.838 (ipso-OPh), 128.997 (o-OPh), 119.090 (m-OPh), 117.720 (p-OPh). M.p. 64–65°C. EIMS (low res.): *m/z* (%): 359 (23.76) [$M^{+\bullet}$]. Anal. calcd for $C_{18}H_{33}N_3OCr$: C, 60.14; H, 9.25; N, 11.69. Found: C, 60.40; H, 9.55; N, 11.50.

(*v*) *Preparation of* $NCr(N\text{-}i\text{-}Pr_2)_2(OC(CH_3)(CF_3)_2)$ (**4d**). In a 20 ml scintillation vial $NCr(N\text{-}i\text{-}Pr_2)_3$ (286 mg, 0.764 mmol, 1 equiv.), 10 ml of toluene and a stirbar were cooled to −35°C. To the cool, stirring solution was added a −35°C solution of $HOC(CH_3)(CF_3)_2$ (139 mg, 0.764 mmol, 1 equiv.) in 6 ml of toluene dropwise over a few min. The mixture was warmed to room temp. and stirred for 6 h. The volatiles were removed under vacuum and the orange product was recrystallized from pentane in 77% yield (262 mg, 0.586 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.25 (m, 12H, *i*-PrCH_3), 1.45 (d, J_{HH} = 6.0 Hz, 6H, *i*-PrCH_3), 1.64 (s, 3H, *i*-PrCH_3), 1.78 (d, J_{HH} = 6.0 Hz, 6H, *i*-OPrCH_3), 3.71 (sept, J_{HH} = 6.0 Hz, 2H, *i*-PrCH), 4.94 (sept, J_{HH} = 6.0 Hz, 2H, *i*, PrCH). ^{19}F NMR (300 MHz, $CDCl_3$): δ = −78.51 ppm. $^{13}C\{^{1}H\}$ NMR (500 MHz, C_6D_6): δ = 20.2 (*i*-PrCH_3), 21.2 ($OC(CH_3)(CF_3)_2$), 29.79 (*i*-PrCH_3), 30.2 ($OC(CH_3)(CF_3)_2$), 55.7 (*i*-PrCH), 58.4 (*i*-PrCH), 79.9 ($OC(CH_3)(CF_3)_2$). M.p. 149–151°C. EIMS (low res.): *m/z* (%): 447(12.48) [$M^{+\bullet}$]. Anal. calcd for $C_{16}H_{31}N_3OF_6Cr$: C, 42.95; H, 6.98; N, 9.39. Found: C, 43.23; H, 7.15; N, 9.18.

(*vi*) *Spin saturation transfer experiments.* The magnetization transfer experiments were done by ^{1}H NMR using the method of Dahlquist, Longmuir and Du Vernet [24] in C_6D_6 at 294(1) K. In **4d,** mag-

netization transfer between the methine hydrogens of the amido substituents was examined. The technique involves a selective 180° pulse on one of the two methine peaks followed by a full spectrum 90° pulse. At zero delay time, the selectively-irradiated peak (P_1) appears inverted relative to the remainder of the spectrum. The delay time (t) between the selective and full spectrum pulses was varied. The peak heights of P_1 and the peak related to P_1 by rotation (P_2) vary with t if magnetization transfer occurs. The spectra are subtracted from the simple 90° pulse spectrum of the complex. At a delay time of zero P_1 displays twice the intensity in the difference spectrum, and all the other peaks (including P_2) are effectively eliminated in the subtraction. The sum of the intensities for P_1 and P_2 in the difference spectrum vary with the delay time as $A_0 e^{-(1/T1)t}$, where A_0 is the intensity of P_1 in the difference spectrum at $t = 0$ and T1 is the magnetization relaxation rate. A separate T1 determination gave the relaxation rates for P_1 and P_2 to be the same within the error of the experiment ($T1_{P1} = 1.667 \pm 0.01329$ s, $T1_{P2} = 1.664 \pm 0.01575$ s). The difference in the intensities of P_1 and P_2 in the difference spectra vary with t as $A_0 e^{-((1/T1)+k(1)+k(-1))t}$, where k(1) is the rate constant for the conversion of P_1 and P_2 and k(−1) is the rate constant for the conversion of P_2 to P_1. The sum and difference in the intensities for P_1 and P_2 are plotted and fit in Fig. 1. The fit was done to the equation $A_0 e^{-Xt}$. The difference in X for the sum and difference lines is the value k(1)+k(−1) and constitutes the rate constant for one full rotation. A_0 was refined and varies slightly in the sum and difference plots. The variation of A_0 is attributed to a small intensity value for P_2 in the $t = 0$ spectrum from incomplete quenching. The difference curve fit converged at $A_0 = 178$ (0.77) and $X = 13.99$ (0.096) with $R = 0.9997$. The sum curve fit converged at $A_0 = 187$ (0.59) and $X = 0.428$ (0.016) with $R = 0.983$. The fits indicate a value of 13.5 (0.1) s^{-1} for k(1)+k(−1) which correlates to $\Delta G^{\ddagger} = 16$ kcal/mol [25].

In **5a,** magnetization transfer between the methyl doublets was examined, but no transfer was observed. The lack of magnetization transfer is indicative of $k(1)+k(-1) \ll 1/T1$. The T1 values in s for the two doublets were found to be (2.365 ± 0.032883, 2.348 ± 0.02388) and (2.737 ± 0.2093, 2.783 ± 0.2198) by an inversion recovery experiment [37]. Therefore, placing the rate constant for the rotation at 0.3 s^{-1} is a conservative estimate, and the "real" activation energy could be much higher than 22 kcal/mol.

(*vii*) *Preparation of* NCr(N-*i*-Pr_2)(OC(CH_3)(CF_3)$_2$)$_2$ (**5a**). *Method A.* In a 20 ml scintillation vial was loaded NCr(N-*i*-Pr_2)$_3$ (0.571 g, 1.56 mmol, 1 equiv.), a stir bar and 5 ml of pentane. To the stirring solution was added HOC(CH_3)(CF_3)$_2$ (8 g, 440 mmol, 28 equiv.) dropwise. After a few min. of stirring the dark orange solution was transferred to a 120 ml glass bomb equipped with a stopcock. The solution was removed from the drybox and heated in an oil bath at 70°C with stirring. After heating $5\frac{1}{2}$ h the volatiles were removed *in vacuo* and the resulting orange solid was recrystallized from pentane to yield dark crystals of **5a** in 86% yield (0.704 g, 1.33 mmol).

Method B. In a 100 ml glass vessel equipped with a Teflon stopcock was loaded Cr(N)(I)(N-*i*-Pr_2)$_2$ (81 mg, 0.206 mmol, 1 equiv.), HOC(CH_3)(CF_3)$_2$ (3 g, 165 mmol, 800 equiv.) and a stir bar. The reaction mixture was heated at 74°C for 12 h to yield a colorless precipitate (likely [H_2N-*i*-Pr_2] [I]) and an orange solution. The volatiles were removed *in vacuo* and the resulting orange solid was extracted into a minimum of pentane and filtered. Cooling the solution gave the product as thin orange plates in 64% yield (57 mg, 0.132 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.15$ (d, $J_{HH} = 6.5$ Hz, 6H, *i*-PrCH_3), 1.82 (s, $J_{HH} = 6.5$ Hz, 6H, *t*-BuCH_3), 4.16 (sept, $J_{HH} = 6.5$ Hz, 1H, *i*-PrCH), 5.51 (sept, $J_{HH} = 6.5$ Hz, 1H, *i*-PrCH). ^{13}C{^{1}H} NMR (500 MHz, C_6D_6): $\delta = 18.88$ (*i*-Pr*C*H_3), 19.35 (*i*-Pr*C*H_3), 28.89 (OC(*C*H_3)(CF_3)$_2$), 64.96 (*i*-Pr*C*H), 65.19 (*i*-Pr*C*H), 81.70 (O*C*(CH_3)(CF_3)$_2$), 124.28 (OC(CH_3)(*C*F_3)$_2$). M.p. 112–113°C. Anal. calcd for $C_{12}H_{20}N_2O_2F_{12}Cr$: C, 31.83; H, 3.82; N, 5.30. Found: C, 32.05; H, 3.89; N, 5.17.

(*viii*) *Preparation of* NCr(N-*i*-Pr_2)(S-*t*-Bu)$_2$ (**5b**). A 300 ml two neck flask equipped with a gas adapter was loaded with NCr(N-*i*-Pr_2)$_3$ (352 mg, 0.960 mmol) and a stir bar. The remaining neck was stoppered with a septum and then the flask was removed from the dry box. Dry *t*-butylmercaptan (160 ml, 1.42 mol) was transferred to the reaction flask via canula. The septum was replaced under counterflow of nitrogen with a water cooled condenser and the solution was refluxed for 22 h. The volatiles were removed *in vacuo*. The black solid was extracted with pentane and filtered through a sintered glass frit using celite as a filtering agent. The pentane solution yielded black needle crystals in 73% yield (232 mg, 0.696 mmol) on concentrating and cooling. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.30$ (d, $J_{HH} = 6$ Hz, 6H, *i*-PrCH_3), 1.49 (d, $J_{HH} = 6$ Hz, 6H, *i*-PrCH_3), 1.70 (s, 18H, *t*-BuCH_3), 3.71 (sept, $J_{HH} = 6$ Hz, 1H, *i*-PrCH), 5.60 (sept, $J_{HH} = 6$ Hz, 1H, *i*-PrCH). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$): $\delta = 18.76$ (*i*-PrCH_3), 28.72 (*i*-PrCH_3), 35.37 (*t*-BuCH_3), 50.62 (*t*-BuC), 58.74 (*i*-PrCH), 59.48 (*i*-PrCH). ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 18.76$ (q, *i*-PrCH_3), 28.72 (q, *i*-PrCH_3), 35.37 (q, *t*-BuCH_3), 50.62 (s, *t*-BuC), 58.74 (d, *i*-PrCH), 59.48 (d, *i*-PrCH). EIMS (low res.): *m/z* (%): 344(24)[$M^{+\bullet}$]. Anal. calcd for $CrN_2S_2C_{14}H_{32}$: C, 48.80; H, 9.36; N, 8.13. Found: C, 49.05; H, 9.82; N, 8.22.

(*ix*) *Preparation of* NCr[(μ-S-*t*-Bu)$_2$Cu(Et_2dtc)](N-*i*-Pr_2) (**5c**). To a slurry of Cu(Et_2dtc) (0.129 g, 0.652 mmol, 1 equiv.) in 10 ml of ether was added a solution of **5b** (0.225 g, 0.652 mmol, 1 equiv.) in 5 ml of ether. During the addition, a rapid color change from the blue of **5b** to dark brown occurred. The solution was homogeneous a few min. after the addition was complete. The solution was allowed to stir for 30 min. before the volatiles were removed

under vacuum. The dark brown product was recrystallized from ether in 86% yield (0.304 g). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.691 (d, J_{HH} = 6 Hz, 6H, *i*-PrCH_3), 1.04 (t, J_{HH} = 7 Hz, 6H, EtCH_3), 1.59 (d, J_{HH} = 6 Hz, 6H, *i*-PrCH_3), 1.83 (s, 18H, *t*-BuCH_3), 3.17 (sept, J_{HH} = 6 Hz, 1H, *i*-PrCH), 3.70 (quar., J_{HH} = 7 Hz, 4H, EtCH_2) 3.77 (sept, J_{HH} = 6 Hz, 1H, *i*-PrCH). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): δ = 12.88 (*i*-PrCH_3), 19.56 (EtCH_3), 29.90 (*i*-PrCH_3), 34.63 (*t*-BuCH_3), 47.85 (EtCH_2), 54.08 (*t*-BuC), 57.24 (*i*-PrCH), 57.99 (*i*-PrCH). M.p. 99–102°C. Anal. calcd for $CrCuN_3S_4C_{19}H_{42}$: C, 41.02; H, 7.61; N, 7.55. Found: C, 40.81; H, 7.28; N, 7.53.

(*x*) *Preparation of* NCr(N-*i*-Pr$_2$)(OPh)$_2$ (**5d**). Into a one neck 150 ml round bottom flask was loaded a stir bar, 20 ml of toluene and NCr(N-*i*-Pr$_2$)$_3$ (604 mg, 1.65 mmol, 1 equiv.). Into this stirring solution was added phenol (326 mg, 2.1 equiv., 3.47 mmol) in 13 ml of toluene dropwise via pipette. During addition the solution changed from beet to dark orange in color. After thirty min. of reaction time, the volatiles were removed under vacuum. The resultant black solid was recrystallized to give a black powder in 81% yield (458 mg, 1.33 mmol). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (d, J_{HH} = 6.6 Hz, 6H, *i*-PrCH_3), 1.78 (d, J_{HH} = 6.6 Hz, 6H, *i*-PrCH_3), 4.07 (sept, J_{HH} = 6.6 Hz, 1H, *i*-PrCH), 5.19 (sept, J_{HH} = 6.6 Hz, 1H, *i*-PrCH), 6.84 (t, J_{HH} = 7.2 Hz, 2H, p-Ph), 7.04 (d, J_{HH} = 7.8 Hz, 4H, m-Ph), 7.13 (app. q, J_{HH} = 7.2 Hz, 4H, o-Ph). ^{13}C{^{1}H} NMR (300 MHz, $CDCl_3$): δ = 20.53 (*i*-PrCH_3), 29.28 (*i*-PrCH_3), 63.77 (*i*-PrCH), 64.29 (*i*-PrCH), 116.97 (p-Ph), 122.33 (m-Ph), 129.29 (o-Ph), 167.33 (ipso-Ph). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 20.53 (q, J_{CH} = 128 Hz, *i*-PrCH_3), 29.28 (q, J_{CH} = 128 Hz, *i*-PrCH_3), 63.77 (d, J_{CH} = 128 Hz, *i*-PrCH), 64.29 (d, J_{CH} = 128 Hz, *i*-PrCH), 116.97 (d, J_{CH} = 167.3 Hz, p-Ph), 122.33 (d, J_{CH} = 158.9 Hz, m-Ph), 129.29 (d, J_{CH} = 159.7 Hz, o-Ph), 167.33 (s, ipso-Ph). EIMS (low res.): *m/z* (%): 352(27.67) [M$^+$]. Anal. calcd for $C_{18}H_{24}N_2O_2Cr$: C, 61.35; H, 6.86; N, 7.95. Found: C, 61.11; H, 6.91; N, 7.64.

(*xi*) *Preparation of* NCr(N-*i*-Pr$_2$)(CH$_2$SiMe$_3$)$_2$ (**5e**). NCr(N-*i*-Pr$_2$)(OPh)$_2$ (0.786 g, 2.23 mmol, 1 equiv.), a stir bar and 55 ml of hexane were loaded into a 250 ml round bottom flask. The flask was moved to a liquid nitrogen temperature cold well, and the solution was frozen. Once the solution was frozen the flask was removed to a stir plate to thaw. When the slurry could be stirred a near frozen solution of LiCH$_2$SiMe$_3$ (0.420 g, 4.46 mmol, 2 equiv.) in 55 ml of hexane was added dropwise over a few min. As the reaction mixture warmed the NCr(N-*i*-Pr$_2$)(OPh)$_2$ slowly went into solution and a colorless solid precipitated from the brown solution. The solution was allowed to stir for 5–10 min. after all the NCr(N-*i*-Pr$_2$)(OPh)$_2$ had dissolved (about 25 min. reaction time). The mixture was refrozen in the cold well and allowed to warm again until fluid. The cold solution was filtered into a chilled filter flask through a sintered glass frit using celite as a filtering agent. The filtered product was recrystallized from hexamethyldisiloxane giving light orange needles in 57% yield (432 mg, 1.27 mmol). The lipophilic purified material is thermally sensitive, but can be kept in solution at −35°C for long periods of time without noticeable decomposition. The material may also be kept in solution at room temperature overnight without substantial decomposition (<10%). M.p. 56–57°C. ^{1}H NMR (300 MHz, C_6D_6, 25°C): δ = −0.318 (d, J_{HH} = 10 Hz, 2H, CH_2), 0.347 (s, 18H, $SiMe_3$ CH_3), 0.870 (d, 6H, J_{HH} = 6.5 Hz, *i*-PrCH_3), 1.26 (d, 6H, J_{HH} = 6.5 Hz, *i*-PrCH_3), 2.12 (d, J_{HH} = 10 Hz, 2H, CH_2), 2.98 (sept, J_{HH} = 6.5 Hz, 1H, *i*-PrCH), 5.96 (sept, J_{HH} = 6.5 Hz, 1H, *i*-PrCH). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): d = 2.07 (s, SiCH_3), 21.1 (s, *i*-PrCH), 29.48 (s, *i*-PrCH), 56.47 (s, *i*-PrCH_3), 58.60 (s, *i*-PrCH_3), 69.16 (s, CH_2SiCH$_3$). ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = 2.07 (d, J_{CH} = 118 Hz, SiCH_3), 21.1 (s, J_{CH} = 133 Hz, *i*-PrCH), 29.48 (s, J_{CH} = 133 Hz, *i*-PrCH), 56.47 (s, J_{CH} = 117 Hz, *i*-PrCH_3), 58.60 (s, J_{CH} = 117 Hz, *i*-PrCH_3), 69.16 (s, J_{CH} = 116 Hz, CH_2SiCH$_3$). MS low res. EI: *m/z* (%): 340(0.42) [M$^+$]. Anal. calcd for $CrN_2Si_2C_{14}H_{36}$: c, 49.37; H, 10.65; N, 8.22. Found: C, 49.22; H, 11.11; N, 8.57.

(*xii*) *NMR tube thermolysis of* NCr(N-*i*-Pr$_2$)(CH$_2$SiMe$_3$)$_2$(**5e**). In a sealable NMR tube was loaded ~12 mg of **5e** and 700 mg of C_6D_6. The tube was partially evacuated then sealed. The solution was warmed to 60°C in an oil bath. The thermolysis was complete after 5 h as indicated by the ^{1}H NMR spectrum of the solution. The spectrum exhibited decomposition products which included $SiMe_4$ (s, 0.018 ppm), HN-*i*-Pr$_2$ (d, 0.935 ppm; sept, 2.76 ppm) and Me$_2$C=N-*i*-Pr (d, 1.14 ppm; s, 1.35 ppm; s, 1.80 ppm; sept, 3.34 ppm) in a molar ratio of 3.29:1.85:2.18.

(*xiii*) *Preparation of* NCr(C(=N-*t*-Bu)CH$_2$SiMe$_3$)(CH$_2$SiMe$_3$)(N-*i*-Pr$_2$) (**5f**). A solution of **5e** (32.3 mg, 1 equiv., 0.0948 mmol) and 3 ml of ether in a 20 ml scintillation vial was frozen in the box cold well. The solution was allowed to warm until stirring before a cold solution of *tert*-butylisonitrile (10 μl, 1.0 equiv., 0.0948 mmol) in 2 ml of ether was added. The solution rapidly changed color from orange to yellow-green. After 15 min. of reaction time the volatiles were removed *in vacuo* and the resulting solid was recrystallized from hexamethyldisiloxane. **5f** was isolated in 70% yield (28.2 mg). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.214 (s, 9H, SiCH_3), 0.711 (s, 9H, SiCH_3), 0.683 (d, 6H, J_{HH} = 6 Hz, *i*-PrCH_3), 0.713 (d, 6H, J_{HH} = 6 Hz, *i*-PrCH_3), 1.26 (d, J_{HH} = 11.7 Hz, H, CH_2), 1.38 (d, J_{HH} = 11.7 Hz, H, CH_2), 1.77 (d, J_{HH} = 6 Hz, H, CH_2), 1.81 (d, J_{HH} = 6 Hz, H, CH_2), 2.72 (d, J_{HH} = 11.7 Hz, H. CH_2), 2.86 (sept, J_{HH} = 6 Hz, 1H, *i*-PrCH), 3.31 (sept, J_{HH} = 6 Hz, 1H, *i*-PrCH). ^{13}C{^{1}H} NMR (300 MHz, C_6D_6): d = 2.07 (s, SiCH_3), 21.1 (s, *i*-PrCH), 29.48 (s, *i*-PrCH), 56.47 (s, *i*-PrCH_3), 58.60 (s, *i*-PrCH_3), 69.16 (s, CH_2SiCH$_3$). ^{13}C NMR (300 MHz, C_6D_6, 25°C): δ = (q, J_{CH} = 118 Hz, SiCH_3), (s, J_{CH} = 133 Hz, *i*-PrCH), (s, J_{CH} = 133 Hz, *i*-PrCH), (s, J_{CH} = 117 Hz, *i*-PrCH_3), (s, J_{CH} = 117 Hz, *i*-PrCH_3), (s, J_{CH} = 116 Hz, CH_2S-

iCH$_3$). MS low res. EI: m/z (%): 423(1.25) [M$^+$]. MS high res. EI: found: 423.25573 (0.00083) [M$^+$], calc.: 423.255715. M.p. 83–84°C. Anal. calcd for $CrN_3C_{19}H_{45}Si_2$: C, 53.85; H, 10.70; N, 9.92. Found: C, 54.64; H, 10.93; N, 9.96.

(*xiv*) *Reaction of* **3** *with excess water.* To a mixture of deoxygenated water (10 ml, ~1000 equiv.) and 12 ml of THF was added **3** (0.187 g, 0.510 mmol, 1 equiv.) as a solution in 20 ml of THF dropwise. The solution gradually took on an orange color as the addition was carried out. Once the addition was complete, the volatiles were removed *in vacuo*. The product [H$_2$N-*i*-Pr$_2$]$_2$[Cr$_2$O$_7$] was recrystallized from acetonitrile in 73% (0.153 g) yield. ^{1}H NMR (300 MHz, D$_2$O): δ = 1.28 (d, J_{HH} = 6 Hz, 24H, CH$_3$), 3.50 (sept, J_{HH} = 6 Hz, 4H, *i*-PrCH). Anal. calcd for $Cr_2N_2C_{12}H_{32}O_7$: C, 34.29; H, 7.67; N, 6.66. Found: C, 33.95; H, 7.51; N, 6.53.

(*xv*) *Extended Hückel calculations.* The calculations were done using the X-ray structural coordinates for NCr(N-*i*-Pr$_2$)$_3$ (**3**), monosubstituted NCr(N-*i*-Pr$_2$)$_2$(CH$_2$Si(Ph)Me$_2$) (**4b**), and disubstituted NCr(S-*t*-Bu)$_2$(N-*i*-Pr$_2$) (**5b**) as input for YAeHMOP ver 2 [38]. In each case the entire molecule was used in the calculation. The LUMO in each molecule was an orbital with metal-ligand π* character with respect to all of the π donors. The calculated energies for the LUMOs of **3**, **4b** and **5b** were −9.567, −9.816, and −9.384 eV, respectively.

Crystallographic studies

X-ray diffraction data were collected using a Siemens Diffractometer. The detector includes a Mo Kα sensitive phosphor behind a Beryllium window which is 6 cm from the sample. The phosphor, which is activated by the crystal's X-ray diffraction, sends a signal via a fiber optic taper to a Charge Coupled Device (CCD). The CCD is cooled to ca. −55°C to reduce thermal noise. The CCD is read and the data collection controlled by a computer with a Pentium processor. The software for data collection, Siemens Molecular Analysis Research Tool (SMART v4.050), was developed by Siemens Industrial Automation, Inc. The data collection was done using a Siemens Platform three circle goniometer (χ set to 54.78°) and a water cooled Mo X-ray tube (λ = 0.71073 Å) operating at 50 kV/40 mA. A single crystal graphite monochromator was used. Prior to sample exposure the X-rays were columnated to 0.8 or 0.5 mm. The instrument is equipped with a Molecular Structure Corp. low temperature controller with a liquid nitrogen cooled inner stream and a heated dry N$_2$ outer stream. The temperatures were determined by a thermistor located within the low temperature device near the exit port and are uncorrected.

An initial unit cell determination was done using ω scans. Three sets of fifteen frames were collected with a −0.3° scan width. The starting positions for the first, second and third runs were (2θ = 337.02°, ω = 337.02°, φ = 0°), (2θ = 337.02°, ω = 337.02°, φ = 90°), and (2θ = 22.98°, ω = 22.98°, φ = 0°), respectively. From this frame data, a set of intense reflections were chosen and an initial cell was found through repeated least squares and Bravais lattice analysis.

The data were collected using ω scans in four separate runs using a −0.3° scan width. The first through fourth starting positions and number of frames collected were (2θ = −25°, ω = −26°, φ = 0°, no. frames = 606), (2θ = −25°, ω = −21°, φ = 88°, no. frames = 435), (2θ = −25°, ω = −23°, φ = 180°, no. frames = 230), and (2θ = −25°, ω = −23°, φ = 180°, no. frames = 50), respectively. The data collected constitute approximately a hemisphere plus an additional 40% of the Ewald sphere. The fourth run duplicates the first 50 frames of the initial run, and the data are corrected for crystal degradation by analyzing the intensity differences in reflections measured in these redundant frames. The data collections were done using 10 s correlated frames (2 × 5 s frames analyzed for anomalous intensity) with a 7 s total read out time. The total data collection time is approximately 6.5 h. Data storage, reduction and structure solution were done on a Silicon Graphics Indy equipped with a MIPS R5000 processor running at 180 MHz and 3 Gigabytes of a total disk space. Using the initial cell, the frame data were integrated to hkl/intensity data using the Siemens program package SAINT v4.050. The final unit cell was determined by SAINT using all the observed data.

The structures were solved and refined using SHELXTL Version 5.03, a program developed by G. M. Sheldrick and Siemens Industrial Automation, Inc. For absorption of a semi-empirical ψ-scan absorption correction was used, which includes all of the data as the basis set.

NCr(S-*t*-Bu)$_2$(N-*i*-Pr$_2$) (**5b**). Crystals grown from a concentrated ether solution at −35°C were quickly moved from a scintillation vial to a microscope slide containing Paratone N (an Exxon product). Under the microscope a black plate was selected and mounted on a glass fiber using wax. A total of 5293 reflections were collected ($-10 \leqslant h \leqslant 8$, $-13 \leqslant k \leqslant 13$, $-18 \leqslant l \leqslant 18$) in the θ range of 2.06 to 20.00° of which 1861 were unique (R_{int} = 0.0605). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated (d_{C-H} = 0.96 Å) positions. The largest peak and hole in the difference map were 0.254 and −0.315 e/Å^3, respectively. The least squares refinement converged normally.

NCr[(μ-S-*t*-Bu)$_2$Cu(Et$_2$dtc)](N-*i*-Pr$_2$) (**5c**). Crystals grown from a concentrated ether solution at −35°C were quickly moved from a scintillation vial to a microscope slide containing Paratone N. Under the microscope a black plate was selected and mounted on a glass fiber. A total of 7473 reflections were collected

($-12 \leqslant h \leqslant 14$, $-11 \leqslant k \leqslant 9$, $-23 \leqslant l \leqslant 19$) in the θ range of 1.69 to 20.00° of which 2590 were unique ($R_{int} = 0.0899$). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions. The largest peak and hole in the difference map were 2.813 and -0.810 e/Å^3, respectively. The residual electron density resides near the S, Cu and Cr atoms. The least squares refinement converged normally.

NCr(C(=N-*t*-Bu)CH_2SiMe_3)(CH_2SiMe_3)(N-*i*-Pr_2) (**5f**). Crystals grown from a concentrated hexamethyldisiloxane solution at −35°C were quickly moved from a scintillation vial to a microscope slide containing Paratone N. Under the microscope a yellow plate was selected and mounted on a glass fiber. A total of 3916 reflections were collected ($-7 \leqslant h \leqslant 8$, $-11 \leqslant k \leqslant 11$, $-20 \leqslant l \leqslant 20$) in the θ range of 2.12 to 20.00 giving 2999 independent reflections ($R_{int} = 0.0449$). The structure was solved by direct methods in conjunction with standard difference Fourier techniques. The structure suffers from pseudo-symmetry problems. The two molecules in the asymmetric unit sit on either side of a pseudo-inversion center which tries to relate the alkyl and iminoacyl ligands on the two molecules. The pseudo-inversion center creates a pseudo-mirror plane in the molecule in P(−1) which runs through the $N_{iminoacyl}$—$N_{nitrido}$—N_{amido} atoms. Attempts to refine the structure in P(−1) as a disorder problem were less successful than refinement of models in P(1) with no inversion center between molecules. The Cr(1)---C(11) distance was restrained to be within a 3 σ range of 2.3 Å with σ of 0.05 Å. Only the Cr and Si atoms were refined anisotropically. Hydrogen atoms were placed in calculated ($d_{C-H} = 0.96$ Å) positions. The largest peak and hole in the difference map were 0.573 and -1.034 e/Å^3, respectively.

CONCLUDING REMARKS

Chromium(VI) nitrido compounds are available through nitric oxide cleavage using Cr(N-*i*-Pr_2)$_3$ and V(mesityl)$_3$(THF). The nitrido functionality displays remarkable kinetic stability towards a variety of acidic reagents. Among the products available by protolytic removal of one amido substituent were found to be NCr(I)(N-*i*-Pr_2)$_2$ (**4a**), NCr(OPh)(N-*i*-Pr_2)$_2$ (**4c**) and NCr(OC(CF_3)$_2$Me)(N-*i*-Pr_2)$_2$ (**4d**). The monoalkyl complex NCr(N-*i*-Pr_2)$_2$($CH_2Si(Ph)Me_2$) (**4b**) was synthesized from the reaction of **4a** with Mg($CH_2SiPhMe_2$)$_2$. The products available by protolytic removal of two amido substituents were NCr(OC(CF_3)$_2$Me)$_2$(N-*i*-Pr_2) (**5a**), NCr(S-*t*-Bu)$_2$(N-*i*-Pr_2) (**5b**) and NCr(OPh)$_2$(N-*i*-Pr_2) (**5d**). Thiolate **5b** coordinates $Cu(Et_2dtc)$ to produce the bridging thiolate complex NCr(N-*i*-Pr_2)[(μ-S-*t*-Bu)$_2$Cu(Et_2dtc)] (**5c**). The reaction of **5d** with 2 equiv. of $LiCH_2SiMe_3$ produces NCr(N-*i*-Pr_2)(CH_2SiMe_3)$_2$ (**5e**). The chromium(VI) alkyl complexes **5e** and **4b** were found to decompose thermally with products indicative of β-hydrogen abstraction from the amido ligands. The 14e alkyl **5e** reacts with *tert*-butyl isonitrile to give an iminoacyl alkyl complex. The nitrido nitrogen is stable to some harsh acidic conditions, i.e. refluxing HS-*t*-Bu, but does undergo hydrolysis upon treatment with excess water.

Our results for the protolytic replacement of the amido substituents in nonpolar media on the complex NCr(N-*i*-Pr_2)$_3$ (**3**) are suggestive of two important kinetic factors which affect the viability of an amido protonation. The first is sterics. In a nonpolar environment, a mechanism involving the prior coordination of the incoming protic reagent with concomitant or subsequent proton transfer should be favored. Prior coordination of the protic reagent (e.g. an oxygen or sulfur lone pair) reduces the amount of charge separation in the intermediate or transition state vis-á-vis simple proton transfer followed by attack of the conjugate base. For such a mechanism, steric constraints at the metal center and at the incoming protic reagent could be exceedingly important but difficult to assess. The Lewis acidity of the metal center may play a role in the ease of coordination of an incoming Brønsted acid. Extended Hückel calculations incorporating the X-ray crystal structure coordinates of NCr(N-*i*-Pr_2)$_3$ (**3**), NCr(N-*i*-Pr_2)$_2$($CH_2Si(Ph)Me_2$) (**4b**), and NCr(S-*t*-Bu)$_2$(N-*i*-Pr_2) (**5b**) suggest that the LUMO energies decrease in the order **5b** > **3** > **4b**. This trend is consistent with the observation that **5b** is inert to excess HS-*t*-Bu, whereas **3** is attacked readily by the same reagent. Thus, we may propose that the greater the Lewis acidity of the chromium nitrido amido in question, the more readily will alcoholysis or thiolysis proceed.

In more polar media, the reactions may proceed by mechanisms involving greater charge separation in the transition states or intermediates. Accordingly, reaction of an almost 1:1 solution of THF/water with **3** provided [H_2N-*i*-Pr_2]$_2$[Cr_2O_7] in high yield.

Chromium(VI) nitrido complexes are now available for comparison with their molybdenum and tungsten analogs. Further investigation into the chemistry of these new complexes will serve to substantiate trends in nitrido chemistry of group 6. In addition, pseudo-tetrahedral high oxidation state chromium compounds comprise a new area of study in the already active area of chromium(VI) chemistry [36].

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