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A bis(amido) ligand set that supports two-coordinate chromium in the +1, +2, and +3 oxidation states[†]

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Abstract

The amido ligand $-N(Si^iPr_3)DIPP$ (DIPP = 2,6-diisopropylphenyl) has been used to prepare two-coordinate complexes of Cr^I, Cr^{II}, and Cr^{III}. The two-coordinate Cr^{II} complex has also been used to prepare a three-coordinate Cr^{III} iodide complex, which can be used to access a stable Cr^{III} methyl species.

The first-row transition metals are unique in their ability to support very low coordination numbers over a wide range of d^n configurations. The interest in such compounds has largely been driven by attempts to understand structure and bonding for these unusual coordination geometries, and this has led to the isolation and characterization of fewer than one hundred two-coordinate, open-shell complexes.[1–11] Recently, the silyl(aryl)amido ligand $-N(SiMe_3)DIPP$ (DIPP = 2,6-diisopropylphenyl) has been shown to allow access to multiple oxidation states for two-coordinate nickel, iron and cobalt complexes.[4–7] Interestingly, this silylamido ligand cannot be used to support a strictly two-coordinate chromium complex; attempts to synthesize $Cr[N(SiMe_3)DIPP]_2$ led to C–H bond activation of the ligand and formation of a remarkable tetra-chromium complex containing bridging $-CH_2(SiMe_2)$ groups (**A**, Figure 1).[6] Also, although the silylamido ligand $-N(SiMe_2Ph)_2$ can be used to support a two-coordinate chromium complex in the solid state, the bis(THF) adduct of the complex is also isolated from the same reaction mixture (**B**, Figure 1).[8]

The stabilization of low-coordinate complexes is more challenging for the earlier first-row transition metals, due to their larger atomic radii and lower d^n counts. Notably, only two two-coordinate vanadium complexes have been reported and both require stabilization by extremely bulky terphenylamido ligands.[2] Similar requirements for exceptional steric bulk seem to hold for open-shell, two-coordinate chromium complexes, which have been obtained with bulky supporting borylamido,[12,13] arylamido,[3,14] thiolato,[15] and terphenyl[16–19] ligands.[1] Although the aforementioned $-N(SiMe_3)DIPP$ ligand cannot stabilize a two-coordinate Cr^{II} species, it seemed that an increase of the steric bulk for this type of ligand would allow for isolation of such a complex. Herein, we describe the

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synthesis and characterization of a two-coordinate Cr^{II} complex with the sterically demanding $-N(Si^iPr_3)DIPP$ ligand, which also allows access to low-coordinate complexes of Cr^I and Cr^{III}.

$Cr[N(Si^iPr_3)DIPP]_2$ (**1**) was synthesized by a salt metathesis reaction of $CrCl_2$ with 2 equiv of $K[N(Si^iPr_3)DIPP]$ in THF at ambient temperature. Workup of the red reaction mixture and recrystallization from pentane and hexamethyldisiloxane (HMDSO) afforded green crystals of **1** in 60% yield. The X-ray structure of **1** (Figure 2) reveals a linear geometry about chromium with a crystallographically imposed 180° N–Cr–N bond angle and a Cr–N bond length of 2.0026(1) Å, which falls within the 1.94–2.00 Å range of distances previously reported for two-coordinate chromium bis(amido) complexes.[1,8] The solid state structure also indicates a close interaction between the chromium atom and the *ipso* carbon of the adjacent aryl ring, with a Cr–N–C$_{ipso}$ angle of 81.59(8)° and a Cr–C$_{ipso}$ distance of 2.2709(1) Å. This distance is shorter than Cr-C$_{ipso}$ interactions observed for related chromium bis(amido) complexes, with $Cr[N(Ph)BMes_2]_2$ (Mes = C_6H_2-2,4,6-Me_3) having the shortest distance of 2.328(2) Å between the chromium atom and an *ipso* carbon from a –BMes$_2$ group.[1,13] The solution magnetic moment of **1**, determined by Evans' method,[20,21] is 4.9 μ_B and consistent with a high-spin d^4 configuration. Correspondingly, non-distinctive, broad, unintegrable signals are observed in the ^1H NMR spectrum of **1**, due to its paramagnetism.

A previous report on the ability of the $-N(SiMe_3)DIPP$ ligand to stabilize multiple d^n configurations and oxidation states of nickel[5] prompted an investigation of **1** by cyclic voltammetry (CV). The cyclic voltammogram of **1** reveals reversible Cr(I/II) and Cr(II/III) couples at –2.04 V ($E_{1/2}$ vs Fc/Fc$^+$, ip$_a$/ip$_c$ = 0.95) and –0.38 V ($E_{1/2}$ vs Fc/Fc$^+$, ip$_a$/ip$_c$ = 1.09), respectively (see Supporting Information, SI). The reversibility of these redox events suggested that the analogous two-coordinate complexes of Cr^I and Cr^{III} would be stable and electrochemically accessible.

Reduction of **1** with 1.1 equivs of KC_8 in diethyl ether over 30 min at ambient temperature, followed by recrystallization from dimethoxyethane (DME) and pentane, afforded orange crystals which were dried under reduced pressure to provide [K(DME)$_n$]{$Cr[N(Si^iPr_3)DIPP]_2$} (**2a**) in 97% yield (Scheme 1, n = 1.5, determined by ^1H NMR integration against an internal standard). The X-ray structure of **2a** before desolvation under vacuum (Figure 3) reveals that the linear coordination environment of the complex is maintained, with a N–Cr–N bond angle of 175.02(1)° and Cr–N bond lengths of 2.054(3) and 2.061(3) Å, which are slightly longer than that of **1**, as expected. Interestingly, the *ipso* carbon of **2** interacts less strongly with Cr^I than with Cr^{II} (in **1**), with a Cr–C$_{ipso}$ distance greater than 2.8 Å and Cr–N–C$_{ipso}$ angles of 108.4(2)° and 108.5(2)° for **2a**. Additionally, unlike the analogous Ni^I species $K\{Ni[N(SiMe_3)DIPP]_2\}$,[5] the potassium is not coordinated to the aryl groups of the amido ligands and is instead complexed by four equivalents of DME to give the outer-sphere [K(DME)$_4$]$^+$ cation. The solution magnetic moment of **2a**, 5.2 μ_B (by Evans' method), is lower than the expected spin-only value of 5.9 μ_B but consistent with a high-spin d^5 configuration.

Compound **2a** reacted with tetrabutylammonium bromide to provide $[N^nBu_4]$ $\{Cr[N(Si^iPr_3)DIPP]_2\}$ (**2b**), which has a geometry consistent with that of **2a** (Scheme 1, ESI,[†] S8). The solution magnetic moment of **2b** is 5.7 μ_B, also consistent with a high-spin d^5 configuration. The UV-vis spectra of **2a** and **2b** in DME are consistent with each other; despite being high-spin, the Cr^I species displays several intense absorptions with molar absorptivities ranging from 5200 to 18000 mol^{-1} L cm^{-1}, likely corresponding to ligand-to-metal charge transfer.

Reaction of **1** with ferroceniumtetrakis(pentafluorophenyl)borate over 1 h at ambient temperature afforded dark red crystals of $\{Cr[N(Si^iPr_3)DIPP]_2\}[B(C_6F_5)_4]$ (**3**) from 1,2-difluorobenzene and HMDSO in 82% yield (Scheme 1). The complex co-crystallizes with 1,2-difluorobenzene and contains two crystallographically independent molecules of **3** within the unit cell. Both molecules are linear, having a N–Cr–N bond angle of 180.000(1)° (Figure 4, ESI,[†] S9). Due to a smaller atomic radius, the Cr–N bond lengths for each of the molecules of **3** are 1.872(2) and 1.869(2) Å, respectively, and notably shorter than comparable distances observed for **1**. Correspondingly, the Cr–C_{ipso} interaction is increased, such that relatively short Cr–C_{ipso} distances of 2.225(2) and 2.217(2) Å are observed. The solution magnetic moment of **3**, determined by Evans' method, is 3.8 μ_B and most consistent with a high-spin d^3 configuration. Assuming a $(d_{xy}, d_{x2-y2})^2(d_{xz}, d_{yz})^1(d_{z2})^0$ electronic configuration based on $D_{\infty h}$ symmetry, **3** might be expected to be anisotropic. However, despite being isoelectronic to the linear two-coordinate complex $V\{N(H)(C_6H_3$-2,6-$(C_6H_2$-2,4,6-$^iPr_2)_2)\}_2$,[2] **3** does not exhibit significant spin-orbit coupling. Calculations on a similar complex, $Fe[N(SiMe_3)DIPP]_2$, have shown that the nitrogen lone pairs can interact with the metal center, breaking degeneracy of the (d_{xz}, d_{yz}) pair and quenching orbital angular momentum.[22,23] In contrast to the isoelectronic vanadium complex, the cationic charge on **3** is expected to increase further the strength of the ligand field and such degeneracy-breaking interactions, such that isotropic magnetic properties would be observed for **3**.

Similar to what is observed for later first row transition metals supported by – $N(SiMe_3)DIPP$,[4,6] both **1** and **3** exhibit an eclipsed configuration of the two amido ligands, with C_{ipso}–NCrN–C_{ipso} dihedral angles of 180.0(1)° and 180.0(2)°, respectively. In contrast, the aryl groups on the ligands of **2a** and **2b** adopt a *syn* conformation and are approximately staggered, with C_{ipso}–NCrN–C_{ipso} dihedral angles of 44.1(3)° and 39.8(2)°, respectively.

To further explore the oxidation chemistry associated with **1**, 0.5 equivalents of I_2 were added to **1**, to afford dark red crystals of $(I)Cr[N(Si^iPr_3)DIPP]_2$ (**4**) from pentane in 76% yield (Scheme 1). Addition of the iodo ligand to **1** results in a trigonal planar geometry with a N–Cr–N bond angle of 138.49(7)° and shorter Cr–N bond lengths of 1.906(4) and 1.8889(4) Å (Figure 5). There is no significant interaction of the aryl *ipso* carbons with the chromium center, as indicated by Cr–N–C_{ipso} angles of 123.8(3) and 120.1(2)° for **4**. The solution magnetic moment of **4**, determined by Evans' method, is 3.35 μ_B and lower than the expected spin-only value of 3.87 μ_B but consistent with a d^3 configuration.

Given the long-standing interest in Cr^{III} alkyl complexes,[24–27] **4** was examined as a possible synthetic entry to such species. Addition of methylmagnesium chloride in THF to a dark red solution of **4** in diethyl ether resulted in a color change to red-orange after five minutes. Workup of the reaction mixture and recrystallization from pentane afforded red crystals of (Me)Cr[N(Si^{i}Pr$_3$)DIPP]$_2$ (**5**) in 71% yield (Scheme 1). Complex **5** crystallizes in a unit cell nearly identical to that of **4**. The N–Cr–N bond angle of 142.89(1)° is slightly wider than that for **4**, but comparable Cr–N bond lengths of 1.906(2) and 1.893(2) Å are observed (Figure 6). Similarly, there is no significant interaction of the *ipso* carbon with the chromium center, with Cr–N–C$_{ipso}$ angles of 122.71(2) and 118.75(2)°. The Cr–C$_{Me}$ bond length of 2.058(3) Å is comparable to the Cr-C$_{Me}$ distance of 2.081(3) Å observed in the β-ketiminate Cr^{II} methyl complex reported by Mindiola and coworkers, one of the few three-coordinate chromium alkyl complexes to be fully characterized.[28] The solution magnetic moment of **5** (3.57 μ$_B$, Evans' method) is consistent with a d^3 configuration.

In summary, a series of two-coordinate chromium complexes has been isolated and characterized. The ability of the –N(Si^{i}Pr$_3$)DIPP ligand to support a monomeric Cr^{II} complex, in contrast to the less bulky –N(SiMe$_3$)DIPP ligand, highlights the role of sterics in maintaining linearity for two-coordinate complexes. Furthermore, isolation of these chromium species continues to demonstrate the ability of silyl(aryl)amido ligands to support two-coordinate species of first row transition metals in a variety of oxidation states. Studies further examining the reactivity of this chromium series are currently ongoing.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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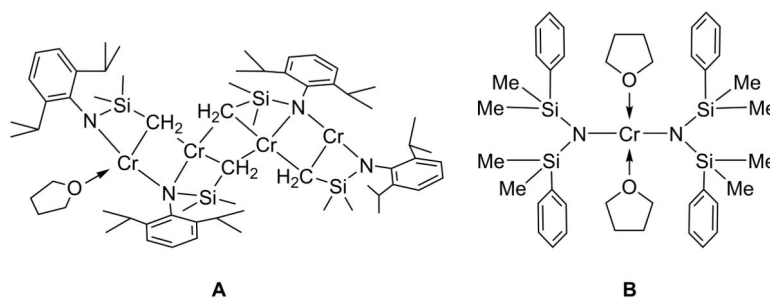
Fig. 1.
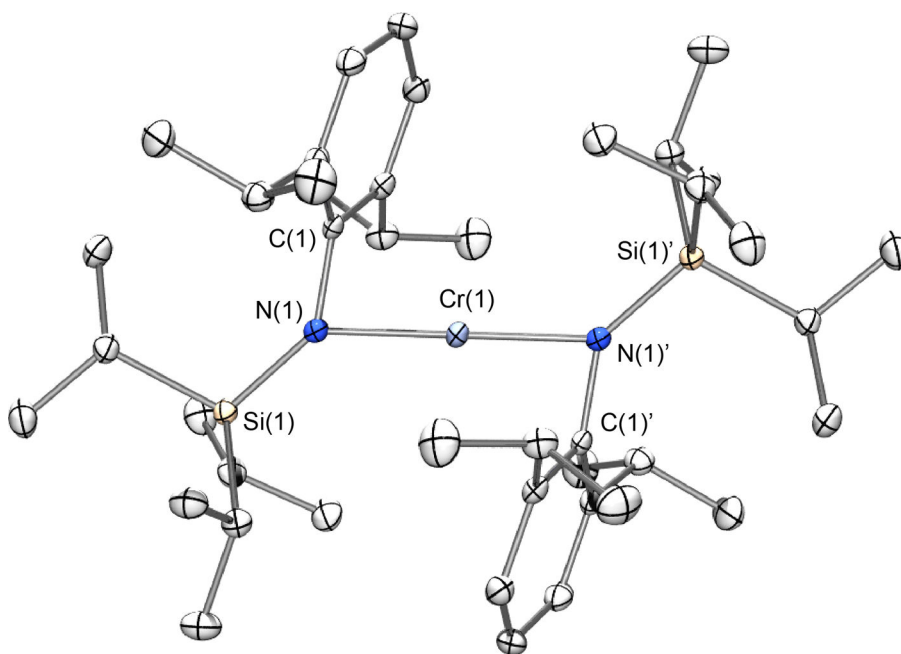Previous examples of chromium complexes supported by silylamido ligands, **A**[6] and **B**.[8]

Fig. 2.
ORTEP diagram of **1**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity.
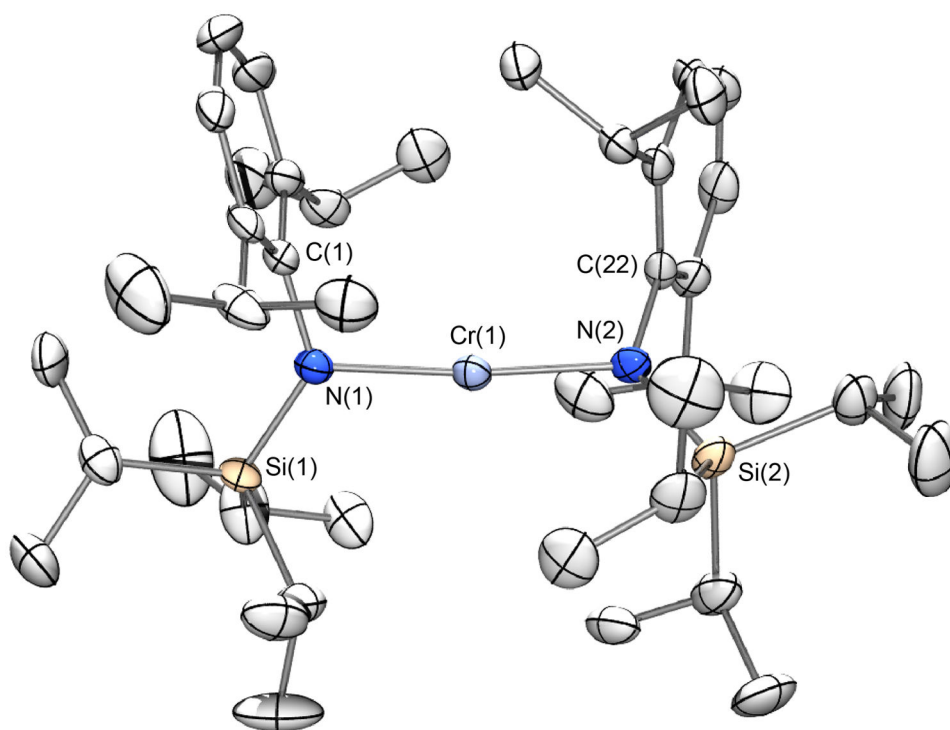
Fig. 3.
ORTEP diagram of **2a**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms, cations, and solvent are omitted for clarity.
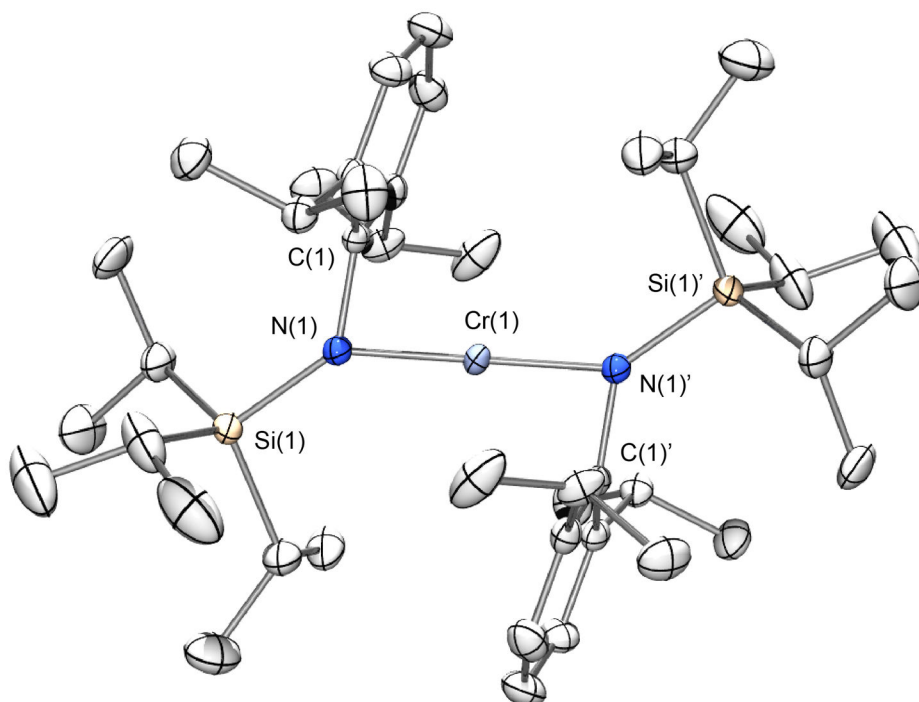
Fig. 4.
ORTEP diagram of **3**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms, anions, and solvent are omitted for clarity. The second crystallographically independent molecule of **3** has been omitted.
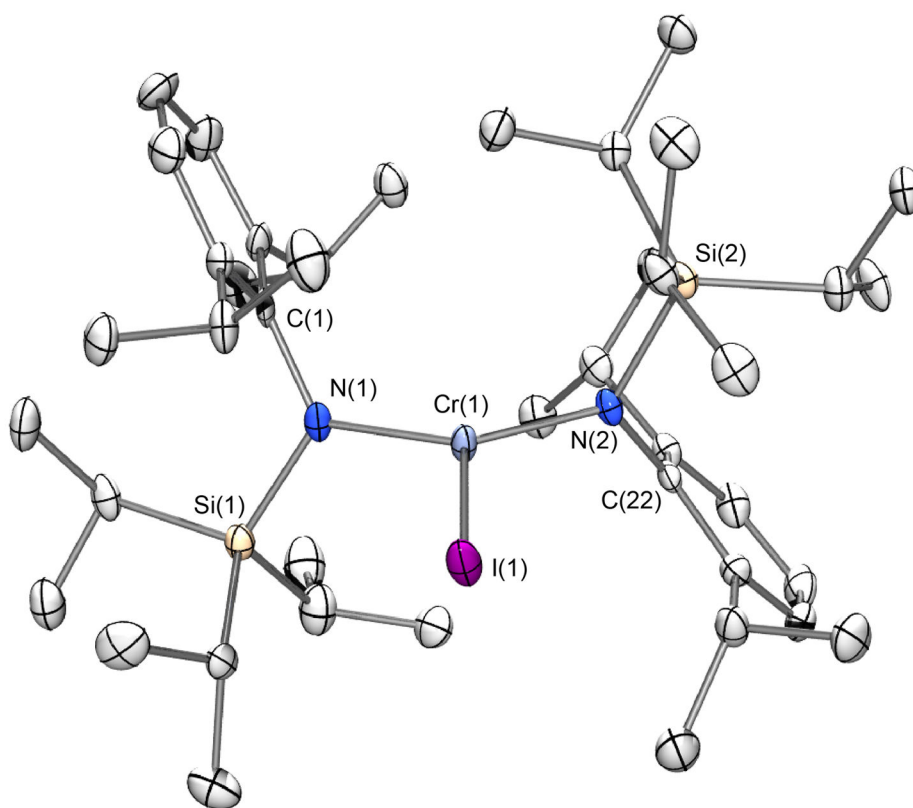
Fig. 5.
ORTEP diagram of **4**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity.
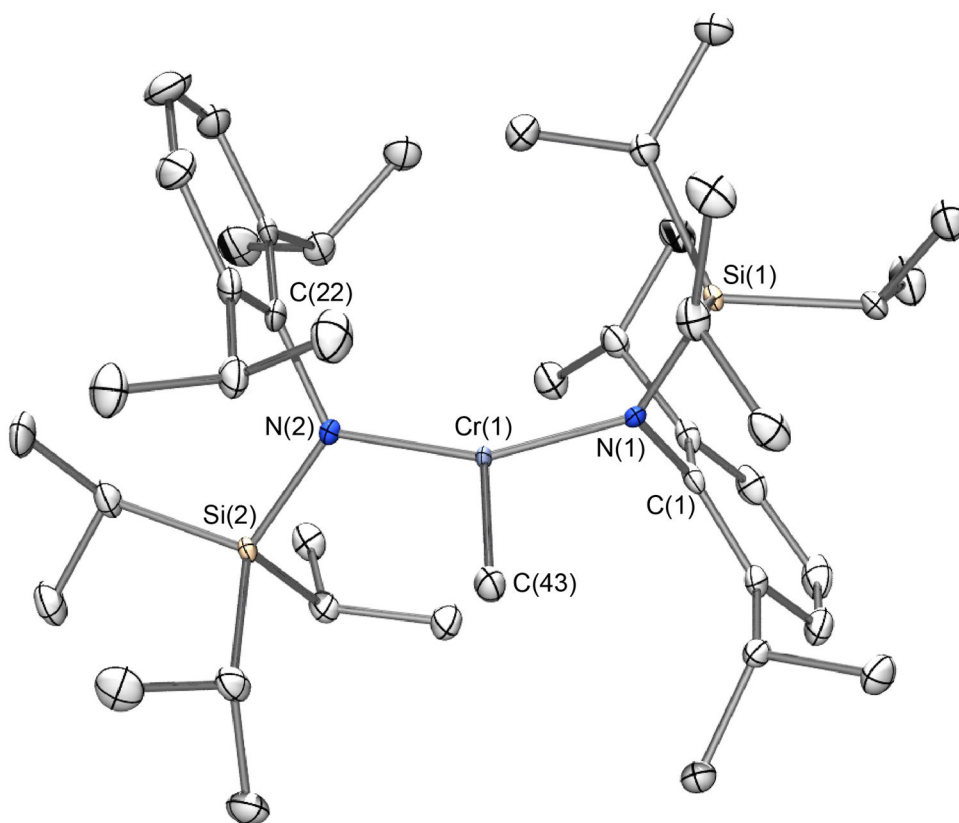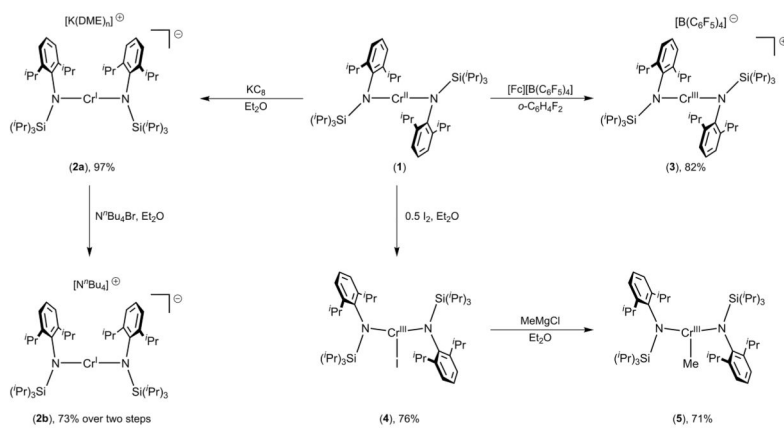
Fig. 6.
ORTEP diagram of **5**. Thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity. Disordered chromium and silicon atoms have been excluded.

Scheme 1.
Reactions of chromium bis(amido) complexes.