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Unusually Stable Chromium(IV) Alkyls Bearing a Triamidoamine Ligand

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*Summary: The chromium(IV) triamidoamine complex [Cr(N_3N)Cl] (**1**; $(N_3N)^{3-}$ = $((SiMe_3NCH_2CH_2)_3N)^{3-}$) reacts with LiR (R = Me, n-Bu) in THF to give selectively the remarkably stable, green chromium(IV) alkyls [Cr(N_3N)R] (**2**, R = Me; **3**, R = n-Bu), which have a d^2 high-spin electronic configuration and feature, according to ^1H and ^{13}C NMR spectroscopy, pseudo-C_{3v} symmetry in solution. Compounds **2** and **3** are the first methyl and n-butyl complexes of chromium(IV) to be characterized by single-crystal X-ray crystallography.*

Oxide-supported chromium catalysts are used worldwide in commercial processes to polymerize α-olefins, particularly ethylene.[1] In a search for homogeneous functional models for the industrially applied heterogeneous systems, various Cr^{II} and Cr^{III} alkyl complexes were prepared and their catalytic activity in α-olefin polymerization was studied.[2] In comparison, related studies on Cr^{IV} alkyls are quite rare.[3] This is not surprising, given the pronounced inclination of chromium(IV) complexes to decompose via bond homolysis, reductive elimination, or valence disproportionation.[4] Therefore, well-characterized chromium(IV) organometallic compounds are scarce, the homoleptic σ-organyls [CrR_4] representing by far the most common group.[5] Silica-supported Cr^{IV} species were recently shown to catalyze the polymerization of α-olefins,[3d−i] and a theoretical study led to the prediction that the chromium(IV) model compounds $[Cr^{IV}(NR_2)_2R']^+$ (R = H, Me, SiH_3; R′ = Me, Et) should be efficient ethylene polymerization catalysts.[6] These studies stimulated our interest in exploring the chemistry of organochromium(IV) compounds bearing amido ligands. Here we report the synthesis, properties, and structural characterization of chromium(IV) methyl and *n*-butyl complexes stabilized by a triamidoamine ligand.[7]

Treatment of [Cr(N_3N)Cl] (**1**; $(N_3N)^{3-}$ = $((SiMe_3NCH_2CH_2)_3N)^{3-}$)[8] with 1.05 equiv of LiMe in THF at −78 °C affords selectively the Cr^{IV} methyl complex [Cr(N_3N)Me] (**2**), which was isolated after crystallization from *n*-pentane as dark green needles in 92% yield.[9] Similarly, transmetalation of **1** with *n*-butyllithium leads to [Cr(N_3N)(*n*-Bu)] (**3**), which was purified by sublimation and isolated as a lime green, microcrystalline solid in 61% yield.[10] Chromium(IV) methyl and *n*-butyl complexes are very rare, the only other reported

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(9) **[Cr(N_3N)Me] (2)**: a dark red solution of **1** (0.34 g, 0.76 mmol) in 25 mL of THF was treated at −78 °C with a 1.6 M solution of LiMe in diethyl ether (0.50 mL, 0.80 mmol). Within a few minutes the color changed to dark green. After it was warmed to room temperature, the solution was stirred for 1.5 h and then evaporated to dryness in vacuo. The residue was extracted with 20 mL of *n*-pentane and the extract filtered from LiCl. The filtrate was concentrated to about 2 mL and stored overnight at −78 °C to afford dark green needles of **2**, which were separated from the supernatant solution, washed with a minimum amount of cold *n*-pentane at −78 °C, and dried under fine vacuum at room temperature for 1 h. Yield: 0.30 g (0.70 mmol, 92%). Mp: 123−125 °C. Anal. Calcd for $C_{16}H_{42}CrN_4Si_3$ (426.78): C, 45.03; H, 9.92; N, 13.13. Found: C, 44.93; H, 9.65; N, 12.81; Cl, <0.25. IR (Nujol mull): ν (cm^{-1}) 1401 vw, 1337 w, 1326 vw, 1299 vw, 1269 m, 1246 s, 1220 w, 1144 w, 1124 w, 1069 m, 1060 m, 1050 s, 1022 m, 939 vs, 912 s, 837 vs, 779 vs, 745 s, 726 m, 682 m, 672 m, 567 m, 558 m. ^1H NMR (300.1 MHz, C_6D_6, room temperature): δ 4.88 (s, $\Delta\nu_{1/2}$ = 220 Hz, 27H, 3 × $SiMe_3$), −29.3 (s, $\Delta\nu_{1/2}$ = 1200 Hz, 6H, 3 × NCH_2), −139 (s, $\Delta\nu_{1/2}$ = 5200 Hz, 6H, 3 × NCH_2). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, room temperature): δ 59.5 (s, $\Delta\nu_{1/2}$ = 130 Hz, $SiMe_3$), −131 (s, $\Delta\nu_{1/2}$ = 540 Hz, NCH_2) (no signals were detected for the other methylene groups and the chromium-bonded methyl group in the range of ±1000 ppm). $\mu_{eff} = 2.8\ \mu_B$.

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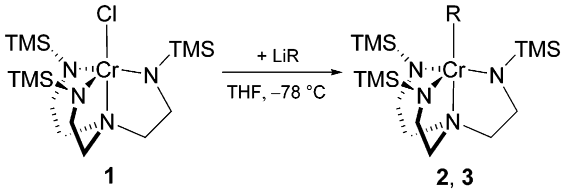

R = Me, *n*-Bu; TMS = SiMe$_3$

examples being [CrR$_4$] (R = Me, *n*-Bu)[11] and [(Cp*CrMe$_2$)$_2$(μ-O)].[12] The Cr^{IV} alkyls **2** and **3** are readily soluble in hydrocarbons, diethyl ether, and tetrahydrofuran and quite stable toward oxygen but rapidly hydrolyzed.[13] They are thermally quite robust, melting without decomposition at 123−125 and 132−134 °C, respectively. Their high thermal stability is best illustrated by comparison with [CrMe$_4$], which decomposes in solution above −78 °C.[5b] Furthermore, compounds **2** and **3** are volatile and can be sublimed without decomposition in vacuo (approximately 0.1 mbar and 100 °C).[14] The chromium(IV) alkyls **2** and **3** differ thereby from the corresponding tungsten compounds [W(N$_3$N)R], which decompose upon heating (R = Me) or decompose spontaneously (R = *n*-Bu) by α,α-dehydrogenation to give the carbyne complexes [(N$_3$N)-W≡CR′] (R′ = H, *n*-Pr).[15,16] Complex **2** does not react with methyl isocyanide or (trimethylsilyl)diazomethane but is oxidized from [Fe(η^5-C$_5$H$_5$)$_2$]PF$_6$ in toluene to give a mixture of products that cannot be identified thus far. Photolysis of **3** with a high-pressure mercury lamp (150 W) in pentane at −20 °C leads, after reductive cleavage of the Cr−C bond, to [Cr^{III}(N$_3$N)].

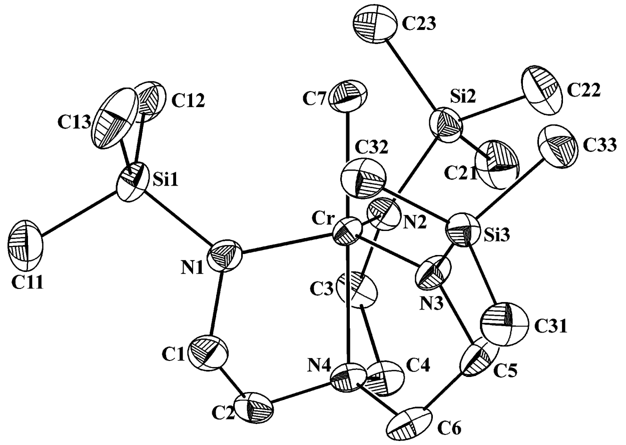

Figure 1. DIAMOND plot of the molecular structure of [Cr(N$_3$N)Me] (**2**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr−C7 = 2.078(2), Cr−N1 = 1.878(2), Cr−N2 = 1.878(2), Cr−N3 = 1.881(2), Cr−N4 = 2.250(2); N4−Cr−C7 = 179.43(8), N1−Cr−N4 = 82.12(7), N2−Cr−N4 = 82.55(7), N3−Cr−N4 = 82.01(7), Σ(∠N1) = 359.8, Σ(∠N2) = 360.0, Σ(∠N3) = 360.0.

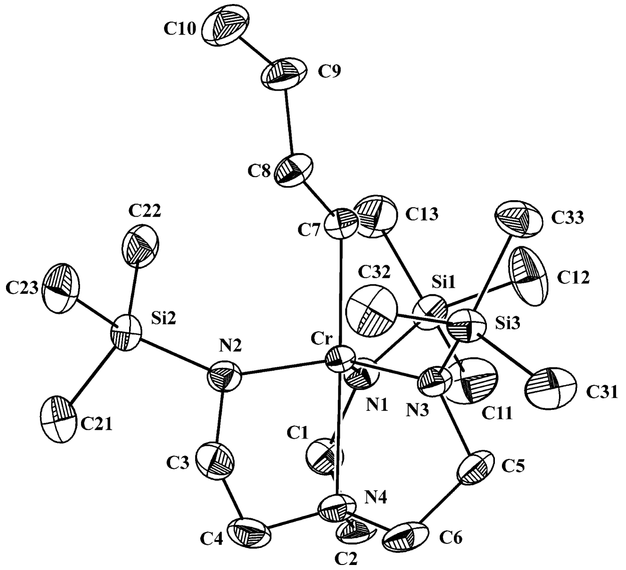

Figure 2. DIAMOND plot of the molecular structure of [Cr(N$_3$N)(*n*-Bu)] (**3**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cr−C7 = 2.074(4), Cr−N1 = 1.870(3), Cr−N2 = 1.884(3), Cr−N3 = 1.884(3), Cr−N4 = 2.288(3); N4−Cr−C7 = 178.4(2), N1−Cr−N4 = 81.7(2), N2−Cr−N4 = 81.0(2), N3−Cr−N4 = 81.4(2), Σ(∠N1) = 359.3, Σ(∠N2) = 356.6, Σ(∠N3) = 359.3.

Compounds **2** and **3** were characterized by IR and NMR spectroscopy[9,10] and single-crystal X-ray crystallography (Figures 1 and 2, Supporting Information).[17] They display similar IR spectra in Nujol, as one might expect for isostructural complexes. The effective magnetic moments μ_{eff} of **2** and **3** were determined in C$_6$D$_6$ at 24 °C by the Evans method[18] as modified by Sur[19] and were corrected for diamagnetic contribution by the method of Tillieu and Guy.[20] The experimental values (2.9 μ_B (**2**) and 2.8 μ_B (**3**)) are close to the expected spin-only value (2.83 μ_B) for two unpaired electrons. This agrees with the results of DFT calculations at the BP-86/6-311G** level of theory, which show that the d^2 complex [Cr(N$_3$N)H] adopts a triplet ground state con-

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(10) **[Cr(N$_3$N)(*n*-Bu)] (3)**: to a dark red solution of **1** (0.115 g, 0.26 mmol) in 30 mL of THF was added at −78 °C a 1.6 M solution of *n*-butyllithium in a mixture of hexanes (0.16 mL, 0.26 mmol) and the reaction solution worked up as described for **2** (vide supra). The pentane extract containing complex **3** was evaporated to dryness to leave a dark green sticky solid, which was sublimed at approximately 100 °C and 0.1 mbar to afford lime green microcrystals of **3**. Yield: 0.073 g (0.16 mmol, 62%). Mp: 132−134 °C. Anal. Calcd for C$_{19}$H$_{48}$-CrN$_4$Si$_3$ (468.87): C, 48.67; H, 10.32; N, 11.95. Found: C, 48.11; H, 10.03; N, 11.84; Cl, <0.15. IR (Nujol mull): ν (cm^{-1}) 1447 m, 1401 vw, 1335 w, 1299 vw, 1271 m, 1262 m, 1243 s, 1217 w, 1149 w, 1118 w, 1068 m, 1055 m, 1041 s, 1016 m, 936 vs, 906 s, 900 s, 837 vs br, 782 vs, 774 vs, 739 s, 724 m, 679 m, 563 m. ^{1}H NMR (300.1 MHz, C$_6$D$_6$, room temperature): δ 5.12 (sh), 4.68 (s, $\Delta\nu_{1/2}$ = 340 Hz) (both signals: 30H, *n*-Bu and 3 × Si*Me*$_3$), −25.6 (s, $\Delta\nu_{1/2}$ = 1600 Hz, 6H, 3 × NC*H*$_2$), −52.7 (s, $\Delta\nu_{1/2}$ = 2200 Hz, 2H, *n*-Bu), −123 (s, $\Delta\nu_{1/2}$ = 7400 Hz, 6H, 3 × NC*H*$_2$). μ_{eff} = 2.9 μ_B.

(11) The thermally unstable compounds [CrMe$_4$] and [Cr(*n*-Bu)$_4$] were prepared in situ from [Cr(O-*t*-Bu)$_4$] and the corresponding alkyllithium compounds and characterized in solution by ESR spectroscopy.[5b,d]

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(13) In this respect **2** and **3** show chemical behavior opposite to that of [CrR$_4$] (R = *i*-Pr, CH$_2$CMe$_3$, CH$_2$SiMe$_3$), which are not affected by water but ignite in air.[5b,d,f,l]

(14) The sublimed samples of **2** and **3** were studied by ^{1}H NMR spectroscopy and did not contain any [Cr(N$_3$N)],[8] [CrCH$_2$SiMe$_2$N(CH$_2$-CH$_2$NSiMe$_3$)$_2$], or [Cr(N$_3$N)H], the last compound being the product of β-hydride elimination and olefin loss from **3**: Schneider, S.; Filippou, A. C. *XXth International Conference on Organometallic Chemistry*, Corfu, Greece, July 7−12, 2002; Book of Abstracts, p 206.

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(16) We attribute the high thermal stability of **2** and **3** to a combination of steric and electronic effects, including the sterically crowded environment of the chromium center, the large HOMO−LUMO gap resulting from the strong σ- and π-bonding interactions of the N$_3$N ligand with the chromium center, and the high spin-pairing energy. These disfavor intermolecular decomposition pathways as well as intramolecular α- or β-hydride abstraction processes.

figuration with the two unpaired electrons occupying two almost degenerate, metal-based d orbitals of π symmetry (d_{xz} and d_{yz}, if the Cr−R bond is taken as the z axis of the Cartesian coordinate system).[21] The ^{1}H NMR spectra of **2** and **3** in C_6D_6 at room temperature are those of the halides [Cr(N_3N)X] (X = F, Cl, Br, I),[4] with three broadened, strongly shifted resonances, one for the $SiMe_3$ and two for the methylene backbone groups of the N_3N ligand, indicating that the paramagnetic complexes have pseudo-C_{3v} symmetry on the NMR time scale.[9,10] This is confirmed by the $^{13}C\{^1H\}$ NMR spectrum of **2**, which displays at ±1000 ppm one broad signal for the $SiMe_3$ groups at +59.5 ppm and one of the two expected methylene carbon signals at −131 ppm. Furthermore, two resonances were found in the ^{1}H NMR spectrum of **3** at +5.12 and −52.7 ppm for the remote protons of the *n*-butyl group, whereas no signals could be detected for the α-protons of the alkyl group in **2** and **3**, as in the corresponding molybdenum compounds.[22] Both complexes adopt in the solid state a distorted-trigonal-bipyramidal coordination geometry with the alkyl group and the bridgehead amine nitrogen atom N4 of the tetradentate N_3N ligand occupying the apical positions (Figures 1 and 2). The chromium atom is displaced from the equatorial plane of the three amide nitrogen atoms N1−N3 toward the alkyl ligand. The distance of chromium to the equatorial plane (**2**, 0.254 Å; **3**, 0.283 Å) is greater than in [Cr(N_3N)Cl] (0.189 Å) and [Cr(N_3N)Br] (0.212 Å).[4,8] The N_3N ligand creates in both complexes a roughly C_3-symmetric cavity around the Cr−R moiety, the nearly linear N_{amine}−Cr−C_{alkyl} atom sequence (**2**, 179.43(8)°; **3**, 178.4(2)°) corresponding to the principal axis. Deviation from C_3 symmetry is greater in complex **3**, due to the presence of the *n*-butyl chain, which is extended over the N2−Cr−N3 plane lying closer to the N2 atom. In both complexes the $SiMe_3$ groups are twisted out of the apical pocket to reduce the steric repulsion by the alkyl ligand. This is evidenced by the mean torsion angles N_{amine}−Cr−N_{amide}−Si of 153.4° (**2**) and 138.6° (**3**), which generally decrease with increasing size of the auxiliary ligand X in [Cr(N_3N)X] (176.6° (X = H); 164.7° (X = F); 163.3° (X = Cl); 157.8° (X = Br)).[4,21] The three CrN_2C_2 rings adopt an "envelope" conformation with the N_{amide}-bonded methylene carbon atoms C1, C3, and C5 forming the "flap" of the envelope. The same conformation was previously observed in the complexes [Cr(N_3N)X] (X = Br, CN) as a consequence of the steric bulk of the ligand X.[4] Significant N_{amide}→Cr pπ−dπ bonding is suggested by the trigonal-planar-coordinated amide nitrogen atoms and the short Cr−N_{amide} bonds, which have an average length of 1.879 Å in both complexes.[8] The Cr−N_{amine} distances of 2.250(2) Å (**2**) and 2.288(3) Å (**3**) are considerably longer than in [Cr(N_3N)Br] (2.135(3) Å), as a result of the strong trans influence of the alkyl ligands,[4] and the Cr−C_{alkyl} bond lengths of 2.078(2) Å (**2**) and 2.074(4) Å (**3**) lie in the range of distances (2.04−2.18 Å) found for methyl complexes of chromium in the oxidation states +III and +V.[2c−f,12,23] Compounds **2** and **3** are the first structurally characterized chromium(IV) methyl and butyl complexes.

The chromium triamidoamine σ-organyls do not exhibit any reactivity toward ethylene. The homoleptic chromium(IV) alkyls also do not react with ethylene.[5d] Ongoing studies are focused on the synthesis and reactivity of chromium(IV) alkyls bearing sterically less demanding triamidoamine and related ligands.

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Supporting Information Available: Tables of X-ray crystallographic data for the structure determinations of **2** and **3**; these data are also available in electronic form as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for **2** and **3** have also been deposited with the Cambridge Crystallographic Data Centre under the file numbers CCDC-207837 and CCDC-207838, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax (+44)1223−336033, e-mail deposit@ccdc.cam.ac.uk).

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(17) Suitable single crystals of **2** were grown upon slow evaporation of the solvent from a saturated pentane solution at room temperature in a glovebox. Single crystals of **3** were grown upon slow cooling of a pentane solution from room temperature to −78 °C. Data were collected on a STOE IPDS (**2**) or STOE STADI4 (**3**) diffractometer at 180 K. Crystal data for $C_{16}H_{42}CrN_4Si_3$ (**2**): monoclinic, space group *Cc*, a = 17.337(5) Å, b = 9.7178(19) Å, c = 15.636(5) Å, β = 109.54(3)°, V = 2482.5(11) Å^3 (Z = 4); R1 = 0.0236 and wR2 = 0.0566 ($I > 2\sigma(I)$); R1 = 0.0264 and wR2 = 0.0575 (for all data). Crystal data for $C_{19}H_{48}CrN_4Si_3$ (**3**): monoclinic, space group $P2_1$, a = 10.294(2) Å, b = 12.522(9) Å, c = 10.703(5) Å, β = 92.93(3)°, V = 1377.9(12) Å^3 (Z = 2); R1 = 0.0298 and wR2 = 0.0671 ($I > 2\sigma(I)$); R1 = 0.0353 and wR2 = 0.0708 (for all data). The structures were refined by full-matrix least squares on F^2. Hydrogen atoms were included isotropically using a riding model.

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