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Triamidoamine Complexes of Chromium(III) and Chromium(IV)

Sven Schneider and Alexander C. Filippou*

Fachinstitut für Anorganische und Allgemeine Chemie der Humboldt-Universität zu Berlin, Hessische Strasse 1-2, D-10115 Berlin, Germany

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Treatment of $[CrCl_3(THF)_3]$ with slightly more than 1 equiv of $Li_3(N_3N)$ $[(N_3N)^{3-} = ((Me_3SiNCH_2CH_2)_3N)^{3-}]$ affords the triamidoamine complex $[Cr(N_3N)]$ (**1**) in 75% yield. **1** is oxidized by $PhICl_2$, $CuCl_2$, or AgCl to give the chromium(IV) complex $[Cr(N_3N)Cl]$ (**2**) in moderate yields. Alternatively, complex **2** is obtained directly from $[CrCl_3(THF)_3]$ in 50% yield after treatment with 0.5 equiv of $Li_3(N_3N)$. Both compounds are high-spin complexes bearing three and two unpaired electrons, respectively. Their molecular structures are described revealing a trigonal monopyramidal and trigonal bipyramidal coordination geometry of the chromium center, respectively.

Introduction

Triamidoamine ligands of the type $[(RNCH_2CH_2)_3N]^{3-}$ (R $=$ Me_3Si, ${}^tBuMe_2Si$, C_6F_5) bind to various transition metals in a tetradentate manner to form relatively rigid distorted trigonal bipyramidal and trigonal monopyramidal complexes, which exhibit unusual reactivity.[1] This has been used in the case of molybdenum and tungsten to activate dinitrogen,[2] to form stable complexes with a metal−pnictogen triple bond,[3] and to prepare alkylidyne complexes either from alkyl complexes by α,α-dehydrogenation or from cyclopropyl and cyclobutyl complexes by C−C bond cleavage.[4] In comparison, studies on related chromium compounds are very rare. To the best of our knowledge only one triamidoamine complex of chromium, $[Cr(N_3N')]$ $\{(N_3N')^{3-} = [({}^tBuMe_2SiNCH_2CH_2)_3N]^{3-}\}$, has been prepared and characterized by ^1H NMR and IR spectroscopy.[5] This has initiated the following work describing the synthesis, molecular structures, and properties of the Cr^{III} and Cr^{IV} triamidoamine complexes $[Cr(N_3N)]$ (**1**) and $[Cr(N_3N)Cl]$ (**2**) $\{(N_3N)^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}\}$.

Experimental Section

General Details. All experiments were carried out under an atmosphere of argon using Schlenk and glovebox techniques.[6] The solvents were dried over CaH_2 (*n*-pentane) or Na/benzophenone (toluene and diethyl ether), distilled under argon, and deoxygenated prior to use. C_6D_6 and $SiMe_4$ were distilled from sodium and stored over 4 Å molecular sieves. $CrCl_3(THF)_3$,[7] $Li_3(N_3N)$,[8] $PhICl_2$,[9] and anhydrous $CuCl_2$[10] were prepared as reported in the literature. AgCl was dried in vacuo at 70 °C for 4 h under exclusion of light.

Elemental analyses were obtained from the Zentrale Analytische Gruppe des Instituts für Chemie der Humboldt Universität zu Berlin. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer in C_6D_6 at room temperature and were calibrated to the residual proton resonance of the solvent (δ 7.15). Magnetic moments were determined in C_6D_6 at room temperature using the Evans method as modified by Sur using the shift of the proton resonance of internal $SiMe_4$.[11,12] The diamagnetic correction was performed as described in ref 13. The melting point of **2** was determined using a Büchi 530 melting point apparatus and is corrected. The sample was sealed under vacuum in a capillary tube and heated at a rate of 3 K/min to a temperature that was lower by 10 K than the melting point of **2**. Heating was then continued slowly until the sample melted.

Preparation of $[Cr(N_3N)]$ (1). A mixture of $[CrCl_3(THF)_3]$ (1.54 g, 4.11 mmol) and $Li_3(N_3N)$ (1.64 g, 4.31 mmol) was suspended in 50 mL of *n*-pentane at −78 °C, and the stirred suspension was allowed to warm to ambient temperature. The color of the solution started to change within approximately 15 min to dark green, and precipitation of a white solid (LiCl) was observed. After 4 h stirring at room temperature the solvent was removed in vacuo. The dark green oily residue was extracted three times with 20 mL of *n*-pentane, and the combined extracts were filtered through Celite. The filtrate was evaporated to dryness to give an oily residue containing according to ^1H NMR spectroscopy **1** and a small amount of **2** and $H_3(N_3N)$. The residue was distilled (80 °C, 10^{-2} mbar) to yield **1** as a dark green oil, which crystallizes upon storage in the freezer at −35 °C. Yield: 1.27 g (3.08 mmol, 75%). Anal. Calcd for $C_{15}H_{39}CrN_4Si_3$: C, 43.75; H, 9.55; N, 13.61. Found: C, 43.55; H, 9.42; N, 13.48. ^1H NMR: δ 42.3 (s, $\Delta\nu_{1/2} = 2000$ Hz, 6H, 3 × CH_2), 31.3 (s, $\Delta\nu_{1/2} = 590$ Hz, 27H, 3 × $SiMe_3$), −280 (s, $\Delta\nu_{1/2} = 5000$ Hz, 6H, 3 × CH_2). $\mu_{eff} = 3.8\ \mu_B$.

Preparation of $[Cr(N_3N)Cl]$ (2). Method a. A solution of **1** in 50 mL of *n*-pentane was prepared in situ from $[CrCl_3(THF)_3]$ (1.97 g, 5.26

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* Corresponding author. Fax: (internat.) +49 (0)30/20936939. E-mail: filippou@chemie.hu-berlin.de.

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mmol) and $Li_3(N_3N)$ (2.52 g, 6.62 mmol) as described above. $CuCl_2$ (0.88 g, 6.55 mmol) was added in one portion, and the suspension was stirred for 18 h at ambient temperature. During this time the color of the solution changed gradually from dark green to deep red. Afterward the solvent was removed in vacuo. The residue was extracted with 70 mL of *n*-pentane and the extract filtered through Celite. The filtrate was evaporated to dryness and the crude product crystallized from a diethyl ether/*n*-pentane mixture at −78 °C to afford **2** as dark red crystals in three crops. Yield: 1.26 g (2.82 mmol, 54% relative to $CrCl_3(THF)_3$). Oxidation of **1** with $PhICl_2$ or AgCl afforded **2** in 28 and 54% yields, respectively. Mp: 155−158 °C. Anal. Calcd for $C_{15}H_{39}ClCrN_4Si_3$: C, 40.29; H, 8.79; N, 12.53; Cl, 7.93. Found: C, 40.02; H, 8.43; N, 12.37; Cl, 7.88. ^{1}H NMR: δ 4.47 (s, $\Delta\nu_{1/2} = 220$ Hz, 27H, 3 × $SiMe_3$), −40.8 (s, $\Delta\nu_{1/2} = 1300$ Hz, 6H, 3 × CH_2), −211 (s, $\Delta\nu_{1/2} = 6000$ Hz, 6H, 3 × CH_2). $\mu_{eff} = 2.6\ \mu_B$.

Method b. A mixture of $Li_3(N_3N)$ (1.14 g, 3.00 mmol) and $[CrCl_3(THF)_3]$ (2.25 g, 6.01 mmol) was suspended in 40 mL of *n*-pentane at −50 °C. The solution instantly took on a light green color, which changed to mud brown and then to dark red upon warming the suspension to ambient temperature and stirring for 14 h. The solvent was then removed in vacuo. The residue was extracted with 30 mL of toluene, the extract filtered, and the filtrate evaporated to dryness. The crude product was recrystallized from a diethyl ether/*n*-pentane mixture at −78 °C to afford **2** as dark red crystals in one crop. Yield: 0.67 g (1.50 mmol, 50% relative to $Li_3(N_3N)$). Anal. Calcd for $C_{15}H_{39}ClCrN_4Si_3$: C, 40.29; H, 8.79; N, 12.53; Cl, 7.93. Found: C, 40.53; H, 8.64; N, 12.49; Cl, 7.94. $\mu_{eff} = 2.7\ \mu_B$. The product has an identical ^{1}H NMR spectrum with that obtained following method a.

Crystal Structure Determination of 1 and 2. Suitable single crystals of **1** were obtained as follows: A sample of **1** (50 mg) was sealed in a capillary (5 mm in diameter) under vacuum and warmed to 40 °C in a water bath. The resulting melt was slowly cooled to 4 °C to afford dark green cubes of **1**. Suitable single crystals of **2** were obtained when a saturated diethyl ether/*n*-pentane (1:1) solution was left for several weeks at room temperature.

Data collection was performed with an imaging plate diffraction system (IPDS, Stoe & Cie.). Measurements were carried out at 180 K (Cryostream, Oxford Cryosystems) using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters were determined from least-squares analyses of 5000 reflections (5.1° < 2θ < 50.2°) (**1**) and of 5000 reflections (4.2° < 2θ < 52.2°) (**2**). Intensities were measured by φ-oscillation scans and corrected for polarization, Lorentz, and absorption effects.[14] The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system.[15] The H atoms were included isotropically as riding on the bound carbon atoms. Geometrical calculations were performed with PLATON[16] and illustrations with DIAMOND.[17]

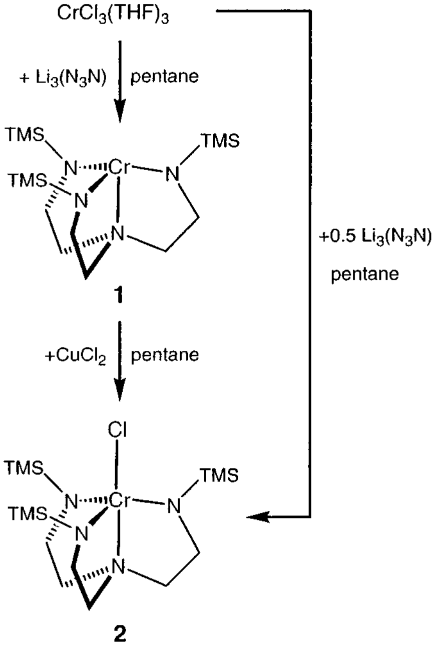
A summary of the crystal data, data collection, and structure refinement is given in Table 1.

Table 1. Crystallographic Data of the Compounds **1** and **2**

	1	2
empirical formula	$C_{15}H_{39}CrN_4Si_3$	$C_{15}H_{39}ClCrN_4Si_3$
fw	411.77	447.22
cryst color	dark green	dark red
cryst size/mm	0.36 × 0.32 × 0.28	0.22 × 0.11 × 0.04
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
a/Å	9.127(2)	9.762(3)
b/Å	16.219(3)	15.877(3)
c/Å	16.814(4)	16.170(4)
β/deg	93.22(3)	101.75(3)
V/Å^3	2485.0(8)	2453.5(10)
Z	4	4
D_{calc}/g cm^{-3}	1.101	1.221
T/K	180(2)	180(2)
μ/mm^{-1}	0.609	0.714
max θ/deg	25.25	26.26
$h/k/l$ ranges	−10,10/−19,19/−20/20	−12,12/−17,19/−19,20
no. of reflns collected	15 177	17 921
no. of unique reflns, n	4480	4854
R_{int} [$I > 2\sigma(I)$]	0.0382	0.1088
params, p	208	217
refinement method	full-matrix on F^2	full-matrix on F^2
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0483, 0.1291	0.0536, 0.1155
R_1, wR_2 (all data)	0.0718, 0.1385	0.1310, 0.1414
GoF[c]	1.042	0.828
largest peak/hole (e Å^{-3})	0.782 and −0.352	0.304 and −0.618

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] GoF $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$.

Scheme 1. Synthesis of Complexes **1** and **2**



Results and Discussion

Treatment of $[CrCl_3(THF)_3]$ with 1.05 equiv of $Li_3(N_3N)$ in pentane affords the chromium(III) triamidoamine complex **1** (Scheme 1). ^{1}H NMR spectra in C_6D_6 of the crude products, which were obtained in several runs after filtration of LiCl and evaporation of the solvent, revealed the formation of two byproducts in small amounts, which by comparison with authentic samples were identified to be $H_3(N_3N)$ and the chromium(IV) triamidoamine complex **2** (Scheme 1). Attempts to separate the major product **1** from **2** upon recrystallization from *n*-pentane at low temperature resulted in the isolation of the less soluble chloro complex **2**. However, complex **1** could be purified by vacuum distillation and isolated in 75% yield as a green, air-sensitive oil, which crystallizes upon storage in the freezer at −35 °C. The crystalline material melts at ambient temperature, is very soluble in pentane and diethyl ether, and turns rapidly brown when it is exposed to air. The product ratio **1**/**2** is strongly dependent on the stoichiometry of the above-mentioned reaction and decreases when the molar ratio of $[CrCl_3(THF)_3]$ to $Li_3(N_3N)$ is increased. This suggests that $[CrCl_3(THF)_3]$ behaves as a chlorinating agent toward **1,** oxidizing it to the chloro complex **2**. Taking advantage of this, a direct route to **2** was found, which involves treatment of $[CrCl_3(THF)_3]$ with 0.5 equiv of $Li_3(N_3N)$ in pentane (Scheme

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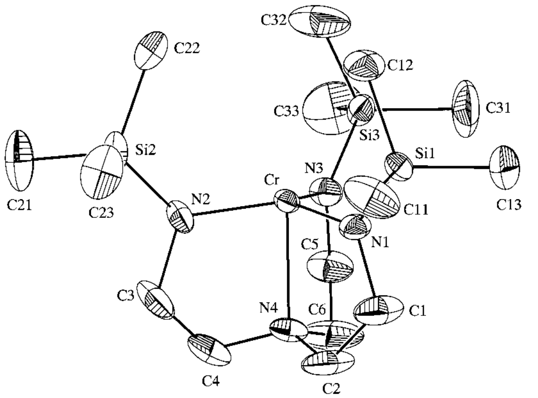

Figure 1. DIAMOND plot of the molecular structure of $[Cr(N_3N)]$ (**1**) with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms are omitted for clarity reasons.

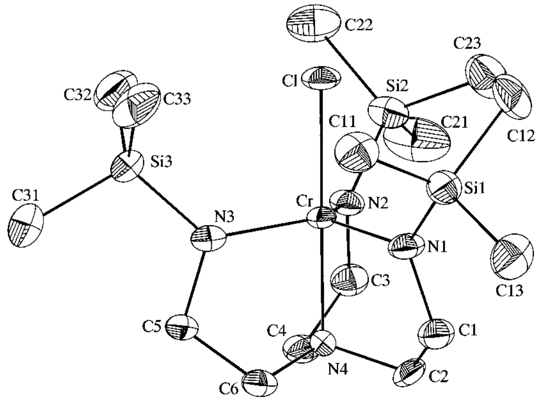

Figure 2. DIAMOND plot of the molecular structure of $[Cr(N_3N)Cl]$ (**2**) with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity reasons.

1). Complex **2** was thereby obtained as a red, crystalline solid in 50% yield. It is moderately air-sensitive, soluble in pentane and diethyl ether, and melts at 155−158 °C. An alternative method for the synthesis of **2** involves the in situ preparation of **1** from $[CrCl_3(THF)_3]$ and $Li_3(N_3N)$, followed by oxidation with $CuCl_2$, AgCl, or $PhICl_2$ (Scheme 1). $CuCl_2$ and AgCl proved in several runs to be more selective chlorinating agents leading to **2** in an overall yield of 54%. The magnetic moments (μ_{eff}) of **1** and **2** were determined at 23 °C using the Evans method and were found to be 3.8 and 2.7 μ_B, respectively. These are close to the spin-only μ_{eff} values expected for a high-spin d^3 and d^2 metal complex, respectively. The ^1H NMR spectra of **1** and **2** in C_6D_6 display three, strongly broadened and shifted singlets, one for the $SiMe_3$ groups and two for the backbone methylene protons of the $(N_3N)^{3-}$ ligand, indicating that both compounds are C_{3v} symmetric on the NMR time scale.

Table 2. Selected Bond Lengths and Bond Angles of **1** and **2**

	1	2
Bond Lengths (Å)		
Cr−Cl		2.269 (2)
Cr−N1	1.870 (3)	1.886 (3)
Cr−N2	1.886 (3)	1.869 (4)
Cr−N3	1.874 (3)	1.877 (4)
Cr−N4	2.243 (3)	2.043 (3)
Bond Angles (deg)		
N4−Cr−Cl		179.4 (1)
N1−Cr−N4	83.8 (2)	84.2 (2)
N2−Cr−N4	84.5 (2)	84.2 (2)
N3−Cr−N4	84.4 (2)	84.3 (2)
N1−Cr−N2	118.8 (2)	120.6 (2)
N2−Cr−N3	119.6 (2)	117.9 (2)
N1−Cr−N3	118.6 (2)	118.6 (2)

The molecular structures of **1** and **2** were determined by single-crystal X-ray diffraction studies and are depicted in Figures 1 and 2, respectively. Selected bond lengths and bond angles are listed in Table 2. Complex **1** reveals a trigonal monopyramidal coordination geometry with the bridgehead amine nitrogen atom N4 residing at the apex of the pyramid. Complex **2** shows a trigonal bipyradimal coordination geometry with the chloro ligand and the amine nitrogen atom N4 occupying the apical positions. The core of the triamidoamine ligand approaches in both compounds C_3 symmetry. Similar coordination geometries were found in other trivalent and tetravalent transition metal complexes of this ligand.[1a] The chromium atom is displaced by 0.189 Å from the equatorial plane defined by the amido nitrogen atoms N1−N3 toward the open coordination site (**1**) and the chloro ligand (**2**), respectively. This results in an average $N_{amido}-Cr-N_{amine}$ bond angle of 84.2(2)° in both complexes. The amido groups of the N_3N ligand are almost planar, as shown by the sums of the bond angles of the amido nitrogen atoms, which range from 358.2(2)° to 359.9(2)° in **1** and from 358.7(3)° to 359.3(3)° in **2**, and adopt approximately an upright conformation. This is evidenced by the dihedral angles between the equatorial plane (atoms N1−N3) and the three amido group planes defined by the atoms Si1, N1, and C1; Si2, N2, and C3; and Si3, N3, and C5, which are 86.9°, 89.7°, and 84.3° in complex **1** and 81.2°, 82.3°, and 81.1° in complex **2**, respectively. Complexes **1** and **2** differ in the conformation adopted by the $SiMe_3$ groups. In **2** the TMS groups form a pocket, in which the chloro ligand is sited, the torsional angles Cr−N1−Si1−C13, Cr−N2−Si2−C21, and Cr−N3−Si3−C31 being −168.6(3)°, −171.0(3)°, and −169.4(3)°, respectively. In comparison, in complex **1** one of the methyl groups (C12) points toward the vacant coordination site (Cr−N1−Si1−C12 = 4.1(3)°) and two other methyl groups (C22 and C32) are slightly twisted out of this position (Cr−N2−Si2−C22 = 25.2(3)°/Cr−N3−Si3−C32 = −24.3(4)°), thereby providing steric protection to the metal center. The $Cr-N_{amide}$ bond lengths of **1** have an average value of 1.877(3) Å, which is identical to that of **2** and close to that of trigonal planar chromium(III) amides, such as $Cr(N^iPr_2)_3$ (1.87 Å),[18] $Cr[N(SiMe_3)_2]_3 \cdot 0.5\ Si_2Me_6$ (1.889(2) Å),[19] $Cr(NCy_2)_3$ (1.858(5) Å),[20] and $Cr(NArR)_3$ (Ar = $C_6H_3Me_2$-3,5; R = 1-adamantyl) (1.868(2) Å).[21] The $Cr-N_{amine}$ bond of **1** is, at 2.243(3) Å, noticably longer than that of **2** ($Cr-N_{amine}$ = 2.043(3) Å) (Table 2). This cannot be explained by the difference of the ionic radii of Cr^{3+} and of Cr^{4+}, which is only 0.065 Å.[22] In addition, the reverse trend has been observed in the related vanadium complexes $[V(N_3N')]$ ($V-N_{amine}$ = 2.083 Å)[5] and $[V(N_3N)Cl]$ ($V-N_{amine}$ = 2.238(6) Å),[23] and in this case the elongation of the $V-N_{amine}$ bond of $[V(N_3N)Cl]$ has been attributed to the *trans* influence of the chloro ligand. An explanation for the long $Cr-N_{amine}$ bond of **1** can be given by a simplified frontier orbital scheme, which involves two degenerate metal-centered π orbitals (approximately d_{xz} and d_{yz}) at lower energy and one σ

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orbital (approximately d_{z^2}) at slightly higher energy (the Cr−N4 connecting line is taken to be the z axis).[1a] All three orbitals are occupied with one electron in **1**. Given the antibonding contribution of the d_{z^2} orbital to the Cr−N_{amine} bond, occupation of this orbital with one electron should cause an elongation of the Cr−N_{amine} bond.

To the best of our knowledge compounds **1** and **2** are the first examples of structurally characterized chromium triamidoamine complexes. Preliminary reactivity studies show that oxidation of **1** with silver(I) salts provides a general route to chromium(IV) halides and pseudohalides of the general formula $[Cr(N_3N)X]$ (X = F, Br, I, CN).

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1** and **2**. This material is free of charge via the Internet at http://pubs.acs.org.

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