Syntheses and Molecular Structures of Chromium(IV) Halides and Pseudohalides Bearing a Triamidoamine Ligand

Alexander C. Filippou,*[a] Sven Schneider,[a] and Burkhard Ziemer[a]

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A general method for the synthesis of chromium(IV) halides and pseudohalides of the general formula $[Cr(N_3N)X]$ (**2**: X = F; **3**: X = Cl; **4**: X = Br; **5**: X = I; **6**: X = CN) is presented. It involves the one-electron oxidation of the Cr^{III} triamidoamine complex $[Cr(N_3N)]$ $\{(N_3N)^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}\}$ (**1**) with silver(I) salts. The oxidation of **1** with one equivalent of $AgBF_4$ or $[Ag(CNtBu)_2](BF_4)$ (**7**) affords the chromium(IV) fluoride $[Cr(N_3N)F]$ (**2**), and treatment of **1** with AgX (X = Cl, Br, I, CN) gives the complexes **3**–**6**. Alternatively, the complexes **4** and **5** can be obtained by halogenation of **1** with 0.5 equivalents of X_2 (X = Br, I). The magnetic moments of **2**–**6** range from 2.7–3.0 μ_B at 297 K, indicating the presence of high spin d^2 chromium complexes, and their ^1H NMR spectra suggest an averaged C_{3v} symmetry in solution. X-ray crystallography shows that complexes **4** and **6** have a distorted trigonal-bipyramidal coordination geometry, with the halide(pseudohalide) ligand and the bridgehead amine nitrogen atom occupying the apical positions. The triamidoamine ligand is disposed, approximately with a three-fold symmetry about the chromium centre. The chromium centre is displaced out of the equatorial plane defined by the three amido nitrogen atoms towards the halide(pseudohalide) ligand, by 0.212 (**4**) and 0.191 Å (**6**). The molecular structures of **4** and **6** are compared with that of **3** and other chromium(IV) triamidoamine complexes and show a strong effect of the ligand X on the conformation of the N_3N ligand and the $Cr–N_{amine}$ bond length.

Introduction

The coordination and organometallic chemistry of chromium(IV) is much less developed than that of chromium in the oxidation states +II, +III, and +VI.[1] This can be traced back to the greater oxidising power of most chromium(IV) compounds and their inclination to valence disproportionation or reductive elimination.[2] Most of the isolable chromium(IV) complexes are stabilised by electronegative and strong σ- or π-donor ligands as exemplified by $[CrF_4]$,[3] the ionic fluorides $M^I[CrF_5]$, $M^I_2[CrF_6]$, and $M^{II}[CrF_6]$ (M^I = Li, K, Rb, Cs, Ag; M^{II} = Mg, Ca, Sr, Ba, Zn, Cd, Hg),[4] and the homoleptic chromium(IV) alkyls $[CrR_4]$ {R = CH_2SiMe_3, CH_2tBu, CH_2CMe_2Ph, CH_2CPh_3, 1-adamantylmethyl, *i*Pr, Cy (cyclohexyl), 2-adamantyl, *t*Bu, 1-camphyl, 1-norbornyl},[5] dialkylamides $[Cr(NRR')_4]$ (R, R′ = Et, Pr; R = Me, R′ = Bu; RR′ = C_5H_{10})[6] and alkoxides $[Cr(OR)_4]$ {R = C(H)(Me)*t*Bu, CH*t*Bu_2, *t*Bu, CMe_2Et, $CMeEt_2$, CEt_3, 1-adamantyl, $SiEt_3$}.[7]

Some chromium(IV) imido-,[8] oxo-,[9] peroxo-,[10] sulphido-,[11] pentamethylcyclopentadienyl-,[8c,9f,11a,12] and carbaborane complexes[13] are also known. Representative examples are the compounds $[Cr^{IV}Cl(NEt)(dmpe)_2]OTf$ {dmpe = 1,2-bis(dimethylphosphanyl)ethane, OTf = CF_3SO_3},[8a] $[Cr^{IV}(NAr)_2L_2]$ (Ar = C_6H_3-2,6-*i*Pr_2; L = PMe_3, PMe_2Ph),[8e] $[Cr^{IV}(O)(porphyrinato)]$,[9a−9e] $[Tp^{tBu,Me}Cr^{IV}(O)OPh]$ {$Tp^{tBu,Me}$ = hydridotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate},[9h] $[Cr^{IV}(O_2)_2(NH_3)_3]$,[10a] $[\{Cr^{IV}\text{-}(NRR')_2\}_2(\mu\text{-}S)_2]$ (R, R′ = Cy; R = 1-adamantyl, R′ = C_6H_3-3,5-Me_2)[11b] and $[(Cp^*Cr^{IV}Me_2)_2(\mu\text{-}O)]$ (Cp* = C_5Me_5).[9f] In comparison, chromium(IV) halides (halide = Cl, Br, I) and pseudohalides are rare and include the hydroxo derivatives $[\{Cr(OH)_2(X)_2(pyridine)\}_2]$ (X = Cl, Br, I),[14] the cyanochromate(IV) $K_2[Cr(CN)_4(O)(pyridine)]\cdot H_2O$,[15] and the Cr^{IV} iodide $[Cr(I)_2(NRAr_F)_2]$ {R = $C(CD_3)_2CH_3$, Ar_F = C_6H_3-2,5-F,Me}.[16]

Chromium(IV) halides are promising starting materials for the preparation of chromium(IV) alkyls. These compounds have attracted considerable interest since the recent reports of S. L. Scott et al. on the polymerization of α-olefins by silica-supported Cr^{IV} species,[17] and the theoretical studies of T. Ziegler et al. which predict that the chromium(IV) model compounds $[Cr(NR_2)_2R']^+$ (R = H, Me, SiH_3; R′ = Me Et) should be active ethylene polymerization catalysts.[18] Therefore, a general approach to stable chromium(IV) halides bearing amido ligands would be very valuable.

We have recently described the synthesis and molecular structure of the triamidoamine complex $[Cr(N_3N)Cl]$ $\{(N_3N)^{3-} = [(SiMe_3NCH_2CH_2)_3N]^{3-}\}$ (**3**), which is a remarkably stable chromium(IV) chloride (m.p. 155−158

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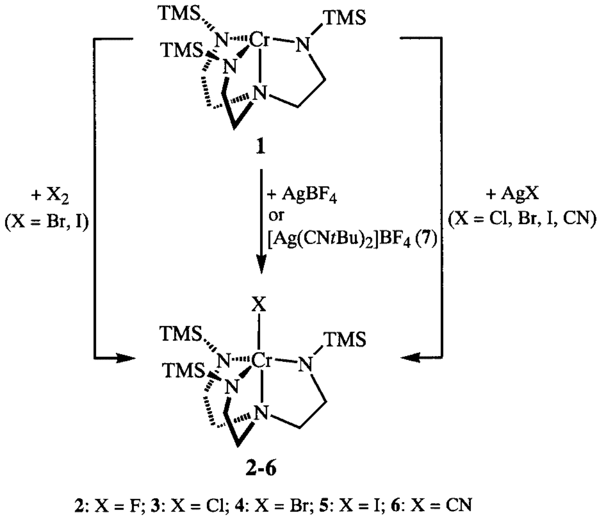
[a] Institut für Chemie, Humboldt-Universität zu Berlin,
Brook-Taylor Straße 2, 12489 Berlin, Germany
Fax: (internat.) +49−(0)30/2093 6939
E-mail: filippou@chemie.hu-berlin.de

°C),[19] considering the thermal instability of $CrCl_4$.[1a] In continuation of our studies in this field, here, we present a general method for the synthesis of chromium(IV) halides and pseudohalides of the general formula $[Cr(N_3N)X]$ (X = F, Br, I, CN) and describe their spectroscopic properties, as well as the molecular structures of the bromo and cyano derivatives.

Results and Discussion

Syntheses and Characterisation

The starting material for the reactions described below was the Cr^{III} triamidoamine complex $[Cr(N_3N)]$ (**1**), which was obtained from $CrCl_3(THF)_3$ and $Li_3(N_3N)$, as described recently.[19] Treatment of **1** with one equivalent of $AgBF_4$ in THF at −78 °C resulted in the rapid precipitation of elemental silver and a colour change from green to dark brown, indicating the fast oxidation of **1**. After evaporation of the solvent and extraction of the residue with pentane, the chromium(IV) fluoride $[Cr(N_3N)F]$ (**2**) was isolated as a dark brown/black crystalline solid in a 43% yield (Scheme 1).[20]



Scheme 1. Syntheses of $[Cr(N_3N)X]$ (X = F, Cl, Br, I, CN) (**2−6**) (TMS = $SiMe_3$)

The formation of **2** suggests that a cationic species $[Cr(N_3N)]^+$, which was expected as the primary product of the one-electron oxidation of **1** with Ag^+, is electrophilic enough (as other inorganic electrophiles[21]) to abstract a fluoride ion from BF_4^-. In an attempt to trap such a species with *t*BuNC, the oxidation of **1** with the silver(I) isocyanide complex $[Ag(CN\textit{t}Bu)_2](BF_4)$ (**7**) was investigated. Complex **7** was synthesised for this purpose by the reaction of $AgBF_4$ with two equivalents of *t*BuNC in CH_2Cl_2 and was isolated as a white solid in a 89% yield. It was characterised by elemental analysis and spectroscopic methods (vide infra). Treatment of **1** with **7** in THF at −78 °C also led to the rapid precipitation of elemental silver and a reddish-black solution indicating the fast oxidation of **1**, as in the case of $AgBF_4$. IR spectroscopic monitoring of the reaction revealed the fast replacement of the ν(C≡N) absorption of $[Ag(CN\textit{t}Bu)_2](BF_4)$ at 2212 cm^{-1} by that of uncoordinated *t*BuNC at 2134 cm^{-1}, and gave no evidence for the formation of any stable Cr^{IV} isocyanide complexes even at low temperatures. Workup of the reaction mixture afforded $[Cr(N_3N)F]$ (**2**) as the only pentane-soluble product in a 52% yield (Scheme 1, Table 1).

Table 1. Preparation of **2−6** by oxidation of $[Cr(N_3N)]$ (**1**)

Oxidant	Product	Yield (%)
$AgBF_4$	$[Cr(N_3N)F]$ (**2**)	43
$[Ag(CN\textit{t}Bu)_2](BF_4)$		52
AgCl	$[Cr(N_3N)Cl]$ (**3**)[a]	54
$CrCl_3(THF)_3$		50
$PhICl_2$		28
AgBr	$[Cr(N_3N)Br]$ (**4**)	64
Br_2		16
AgI	$[Cr(N_3N)I]$ (**5**)	71
I_2		29
AgCN	$[Cr(N_3N)CN]$ (**6**)	57

[a] Ref.[19]

Oxidation of **1** with Ag^I salts has proven to be a versatile route for obtaining chromium(IV) triamidoamine complexes as shown by the syntheses of $[Cr(N_3N)X]$ (**4**: X = Br; **5**: X = I; **6**: X = CN) via the reactions of **1** with AgX (X = Br, I, CN) in THF (Scheme 1). Complexes **4−6** were isolated after crystallisation from diethyl ether or pentane as black crystalline solids in good yields (Table 1). The chloro complex **3** was previously obtained using the same method (Scheme 1, Table 1).[19] Alternatively, the halides **4** and **5** can be prepared by halogenation of **1** with 0.5 equivalents of X_2 (X = Br, I) in THF, albeit in lower yields (Table 1). The chromium(IV) complexes **2−6** are moderately air-sensitive solids, and their melting points are 159 (**2**), 155−158 (**3**), 175 (**4**), 177 (**5**), and 166 °C (**6**). They are very soluble in pentane, diethyl ether, toluene, and THF, giving dark brown (**2**), dark red (**3**, **6**), reddish-black (**4**), and yellowish-black (**5**) solutions. The thermal stability of the halides **3**, **4**, and **5** is remarkable, given the very low thermodynamic stability of CrX_4 (X = Cl, Br).[1a] This can be attributed to the strong π-donating ability of the N_3N ligand.

Complexes **2−6** have very similar IR spectra in nujol, indicating the structural similarity of these compounds. It is worth noting that the IR spectrum of **6** in nujol lacks an absorption for the ν(C≡N) vibration of the cyano ligand, as was previously observed for the analogous molybdenum and tungsten complexes $[M(N_3N)(CN)]$.[22] The Ag^I isocyanide complex **7** is stable in CH_2Cl_2 and THF solutions at ambient temperature, as shown by the IR spectra, which display only one intense absorption band for the ν(C≡N) vibrations of the isocyanide ligands at 2225 and 2212 cm^{-1}, respectively. This absorption is assigned to the Σ_u^+ mode and indicates a local $D_{\infty h}$ symmetry of the $Ag(C{\equiv}N{-}C)_2$ core in **7**.[23] In comparison, the IR spectrum of **7** in KBr shows two ν(C≡N) absorption bands at very different wavenumbers (2245 and 2185 cm^{-1}) from that in solution, which indicates that **7** reacts with the KBr matrix under pressure.[24] The opposite behaviour is shown by $[Ag(CN\mathit{t}Bu)_4](BF_4)$ (**8**), which is stable in pressed KBr discs but unstable in CH_2Cl_2 solution, in which it exists in a dissociation equilibrium with $[Ag(CN\mathit{t}Bu)_3](BF_4)$ (**9**) and *t*BuNC.[25] Thus, in KBr complex **8** gives rise to only one ν(C≡N) absorption band at 2184 cm^{-1}, which is assigned to the T_2 stretching mode and suggests a local T_d symmetry of the $Ag(C{\equiv}N{-}C)_4$ core of the cation.[23] However, in CH_2Cl_2 two ν(C≡N) absorption bands are observed at 2200 and 2140 cm^{-1}, in addition to the band at 2183 cm^{-1} assigned to **8**, which by comparison with authentic samples are assigned to **9** and *t*BuNC, respectively.[25]

The effective magnetic moments of **2−6** were determined in C_6D_6 solution at 297 K by the method of Evans (Table 2).[26,27] These range from 2.8−3.0 μ_B, and are similar to the spin-only value for a d^2 high-spin configuration (2.83 μ_B). The ^1H NMR spectra of **2−6** in C_6D_6 at 297 K display three very broad, strongly shifted signals due to the presence of the two unpaired electrons. On the basis of integration of these signals, two are assigned to the backbone methylene groups and one to the trimethylsilyl groups of the N_3N ligand. This suggests an averaged C_{3v} symmetry of these complexes in solution on the ^1H NMR spectroscopic time scale (Table 2).

Table 2. ^1H NMR spectroscopic data and magnetic moments of **2−6**

Compound[a]	δ(Si*Me*$_3$)[b]	δ(C*H*$_2$)[b]	δ(C*H*$_2$)[b]	μ_{eff} [μ_B]
$[Cr(N_3N)F]$ (**2**)	3.28 (190)	−33.1 (1400)	−208 (5100)	3.0
$[Cr(N_3N)Cl]$ (**3**)[c]	4.47 (220)	−40.8 (1300)	−211 (6000)	2.6
$[Cr(N_3N)Br]$ (**4**)	5.17 (250)	−47.4 (1000)	−185 (2700)	2.8
$[Cr(N_3N)I]$ (**5**)	5.88 (150)	−54.1 (950)	−145 (2100)	3.0
$[Cr(N_3N)CN]$ (**6**)	3.49 (220)	−39.0 (1400)	−188 (6900)	2.9

[a] ^1H NMR spectra and magnetic moments in C_6D_6 at 297 K. [b] Chemical shifts in ppm relative to the residual proton resonance of the deuterated solvent [$\delta(C_6D_5\mathit{H})$ = 7.15 ppm], $\Delta\nu_{1/2}$ [Hz] in parentheses. [c] Ref.[19]

Molecular Structures

The solid-state structures of **4** and **6** were determined by single-crystal X-ray diffraction.[28] Complex **6** is the first chromium(IV) cyano complex to be structurally characterised. DIAMOND plots of the molecular structures of **4** and **6** are shown in Figures 1 and 2, respectively, and selected bond lengths and angles are listed in Table 3. For comparative purposes, the corresponding bonding parameters of complex **3**[19] are also summarised in Table 3.

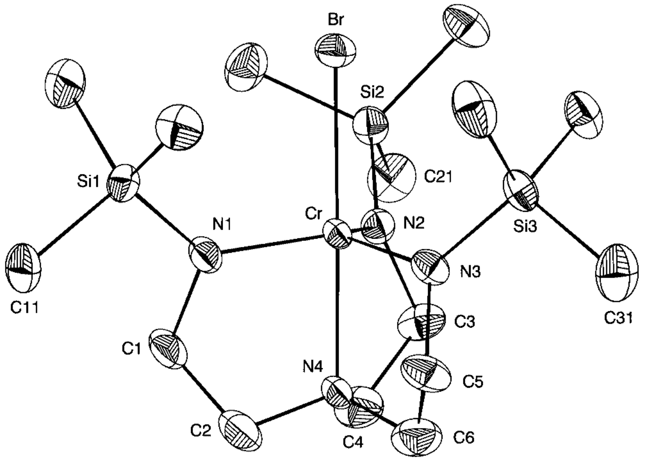


Figure 1. DIAMOND plot of the molecular structure of $[Cr(N_3N)Br]$ (**4**) with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity

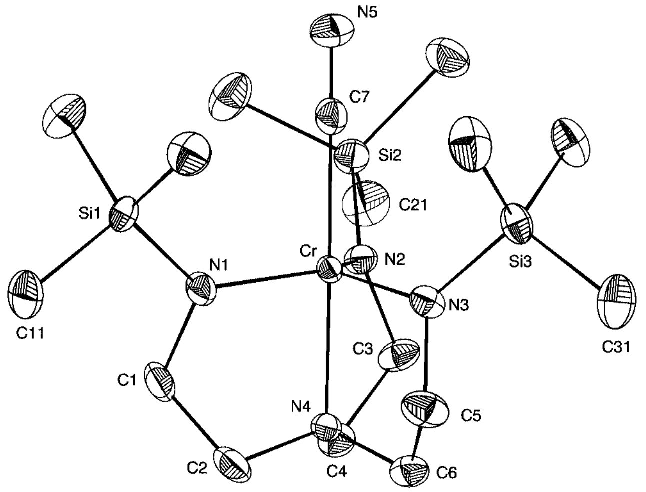


Figure 2. DIAMOND plot of the molecular structure of $[Cr(N_3N)CN]$ (**6**) with thermal ellipsoids drawn at the 50% probability level; hydrogen atoms are omitted for clarity

As for the case of **3**, both complexes are distorted trigonal-bipyramidal, with the bridgehead amine nitrogen atom N4 of the tetradentate N_3N ligand and the bromo (**4**) or cyano ligand (**6**) residing at the apexes of the trigonal bipyramid. Distortion arises as a result of the displacement of the chromium atom out of the equatorial plane defined by the three amido nitrogen atoms N1−N3, toward the halide (pseudohalide) ligand. The distance of the chromium atom from the equatorial plane is 0.212 (**4**) and 0.191 Å (**6**), larger than that in the chloro complex **3** (0.189 Å). This results in a slightly smaller mean $N_{amido}{-}Cr{-}N_{amine}$ bond angle of 83.5(2) (**4**) and 84.13(6)° (**6**), compared with that of **3** [84.2(2)°] (Table 3). In **4** and **6**, as in **3**, the amido groups approach an "upright" conformation, as shown by the torsion angles N4−Cr−N1−Si1, N4−Cr−N2−Si2 and N4−Cr−N3−Si3 (Table 3). The amido nitrogen atoms are sp^2 hybridised, as shown by the mean sum of the bond

Table 3. Selected bond lengths, bond angles and dihedral angles of complexes **4** and **6** (corresponding bonding parameters of **3** are also listed for comparative purposes).

	4	**6**	**3**[19]
Bond Lengths [Å]			
Cr−X	2.440(1)	2.062(2)	2.269(2)
Cr−N1	1.875(3)	1.869(2)	1.886(3)
Cr−N2	1.868(3)	1.870(2)	1.869(4)
Cr−N3	1.877(3)	1.876(2)	1.877(4)
Cr−N4	2.135(3)	2.140(2)	2.043(3)
Bond Angles [deg]			
N4−Cr−X	179.0(1)	179.06(7)	179.4(1)
N1−Cr−N4	83.8(2)	83.90(6)	84.2(2)
N2−Cr−N4	83.6(2)	84.53(6)	84.2(2)
N3−Cr−N4	83.1(2)	83.96(6)	84.3(2)
N1−Cr−N2	119.3(2)	119.15(7)	120.6(2)
N2−Cr−N3	118.2(2)	118.65(7)	117.9(2)
N1−Cr−N3	118.8(2)	119.10(7)	118.6(2)
Dihedral Angles [deg]			
N4−Cr−N1−Si1	158.8(3)	161.2(2)	164.0(3)
N4−Cr−N2−Si2	158.2(3)	160.3(2)	162.2(3)
N4−Cr−N3−Si3	156.4(2)	159.7(2)	163.8(3)

angles at the atoms N1−N3, which is 360.0° in both compounds (**3**: 359.1°). In addition, the Cr−N_{amido} bond lengths have an average value of 1.873(3) Å in the bromo complex **4** and 1.872(2) Å in the cyano complex **6**, which is similar to that of **3** [1.877(4) Å], but are considerably shorter than the Cr−N_{amine} bond lengths in these compounds, e.g. **4** [Cr−N_{amine} = 2.135(3) Å] (Table 3). All these structural features indicate extensive π-electron donation of the N_3N ligand to the chromium centre.

In complexes **4**, **6**, and **3** the tetradentate N_3N ligand is disposed with an approximate C_3 symmetry about the chromium centre. The nearly linear N_{amine}−Cr−X atom sequence corresponds to the principal axis. The $SiMe_3$ groups form a pocket in which the ligand X is located, as shown by the torsion angles Cr−N1−Si1−C11, Cr−N2−Si2−C21, and Cr−N3−Si3−C31 of −155.8(3), −164.6(3), and −160.2(2)° (**4**), and −156.5(2), −166.5(2), and −161.6(2)° (**6**), respectively. However, complexes **4** and **6** differ from **3** by the envelope conformation of the three five-membered chelate rings (Cr−N1−C1−C2−N4, Cr−N2−C3−C4−N4, and Cr−N3−C5−C6−N4) (Figure 3). In complexes **4** and **6** the N_{amido}-bonded methylene carbon atoms C1, C3, and C5 form the "flap" of the envelope, whereas in complex **3** the N_{amine}-bonded methylene carbon atoms C2, C4, and C6 are "tipped up" (Figure 3).

It is suggested that this conformational change results from the increased steric repulsion as the auxiliary ligand becomes more sterically demanding. This causes the $SiMe_3$ groups to twist out of the apical pocket, as shown by the mean torsion angle N_{amine}−Cr−N_{amido}−Si (**4**: 157.8°; **6**: 160.4°; **3**: 163.3°). Additional evidence for the influence of steric strain on the conformation of the N_3N ligand is also found in other chromium(IV) and related molybdenum(IV) triamidoamine complexes. For example, a similar conformation as in [Cr(N_3N)Cl] (**3**) is adopted by the N_3N ligand in [Cr(N_3N)H][29] containing the 'small' hydrido ligand, or in [Mo(N_3N)Cl],[30a] whereas the complexes [Cr(N_3N)Me],[29] [Mo(N_3N)CD_3],[30b] and [Mo(N_3N)OTf][30b] bearing "large" auxiliary ligands have the same N_3N ligand conformation as in **4** and **6**.

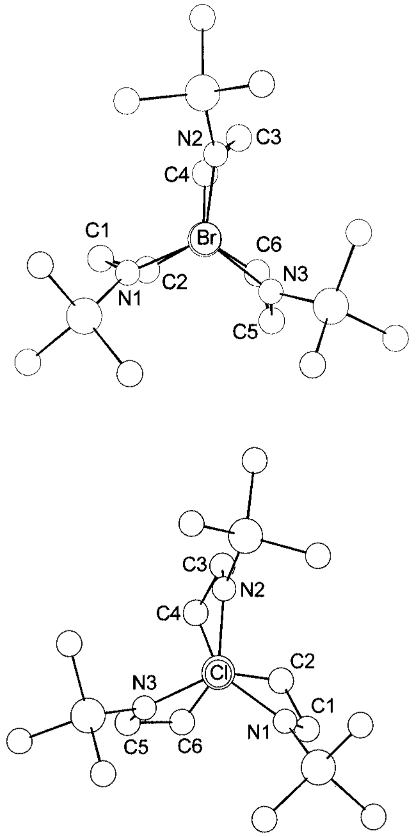


Figure 3. View of **4** (top) and of **3** (bottom) down the X−Cr−N4 axis showing the different conformation of the N_3N ligand in the two complexes

The Cr−Br distance of 2.440(1) Å in **4** is similar to that found in [$Cr^{IV}Br(\eta^5\text{-}Cp^*)(\mu\text{-}NCy)]_2$·toluene [Cr−Br = 2.470(2) Å],[8c] and the Cr−CN bond length of 2.063(2) Å in **6** is similar to those of six-coordinate Cr^{III} and Cr^{V} cyano complexes.[31] The Cr−N_{amine} bond length depends on the *trans*-influence[32] of the ligand X, as seen by the longer Cr−N_{amine} bond of [Cr(N_3N)Me] [Cr−N_{amine} = 2.250(2) Å][29] relative to that of **4** [Cr−N_{amine} = 2.135(3) Å] or **6** [Cr−N_{amine} = 2.140(2) Å], and the longer Cr−N_{amine} bond of [Cr(N_3N)H] [Cr−N_{amine} = 2.140(2) Å][29] relative to that of **3** [Cr−N_{amine} = 2.043(3) Å] (Table 3). The steric repulsion between the ligand X and the $SiMe_3$ groups, which is transmitted via the chelate backbone (see different conformations of **4** and **3** in Figure 3), also seems to affect the Cr−N_{amine} bond length, as indicated, for example, by the larger Cr−N_{amine} distance of **4** relative to that of **3** (Table 3).

Conclusion

The one-electron oxidation of the chromium(III) triamidoamine complex $[Cr(N_3N)]$ $\{(N_3N)^{3-} = [(Me_3SiNCH_2CH_2)_3N]^{3-}\}$ (**1**) with silver(I) salts is a very valuable method for the synthesis of rare, thermally stable chromium(IV) halides and pseudohalides of the general formula $[Cr(N_3N)X]$ (X = F, Cl, Br, I, CN). Their molecular structures, magnetic moments, and ^1H NMR spectra show the presence of distorted trigonal-bipyramidal, high-spin d^2 chromium complexes with threefold symmetry, in which the bridgehead amine nitrogen atom of the tetradendate N_3N ligand and the halide (pseudohalide) ligand occupy the apical positions. The strong π-donating ability of the N_3N ligand is expected to reduce the oxidising power of these compounds making them promising starting materials for the development of the organometallic chemistry of chromium(IV).

Experimental Section

General Remarks: All syntheses and sample manipulations were carried out under an atmosphere of argon using Schlenk and glovebox techniques.[33] The solvents were dried using standard methods (pentane with CaH_2 or sodium wire/benzophenone/tetraglyme, diethyl ether and THF with sodium wire/benzophenone and CH_2Cl_2 with Sicapent (Merck) and Na/Pb alloy), and freshly distilled and deoxygenated prior to use. Complex **1** was prepared as described recently.[19] AgBr and AgI were dried under exclusion of light in vacuo for 4 h at 70 °C. Br_2 was dried with concentrated sulphuric acid and distilled. $SiMe_4$ was dried with sodium, trap-to-trap distilled in vacuo and stored over 4 Å molecular sieves. All other commercially available chemicals were used as purchased. Elemental analyses were obtained from the Central Analytical Group of the Chemistry Department of the Humboldt-Universität zu Berlin. The IR spectra of the compounds were recorded on a Bruker IFS-55 spectrometer either in solution using a cell of NaCl plates, as dispersions in pressed KBr discs or as nujol mulls between KBr plates (**6** - between NaCl plates). The following abbreviations are used for the intensities and the shape of the absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, br = broad, sh = shoulder. The ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded on a Bruker AM-300 spectrometer in dry deoxygenated C_6D_6 and CD_2Cl_2. The ^1H and $^{13}C\{^1H\}$ NMR spectra were calibrated against the internal residual proton resonance and the natural abundance ^{13}C resonance of the solvent, respectively (C_6D_6, $\delta_H = 7.15$ and $\delta_C = 128.0$ ppm; CD_2Cl_2, $\delta_H = 5.32$ and $\delta_C = 53.8$ ppm). The ^{19}F NMR spectra were calibrated against external $CFCl_3$. Magnetic moments were determined in C_6D_6 at 297 K by the Evans method as modified by Sur[26,27] using the shift of the proton resonance of internal $SiMe_4$. The diamagnetic correction was performed using Pacault's method.[34] Melting points were determined using a Büchi 530 melting point apparatus and are corrected. The samples were sealed under vacuum in capillary tubes and heated slowly until the compounds melted.

Preparation of $[Cr(N_3N)F]$ (2) by Oxidation of 1 with $AgBF_4$: A precooled solution (−78 °C) of $[Cr(N_3N)]$ (**1**) (0.356 g, 0.86 mmol) in 25 mL of THF was rapidly added, via a double ended needle, to a stirred solution of $AgBF_4$ (0.168 g, 0.86 mmol) in 20 mL of THF that was kept in the dark at −78 °C. The green solution of **1** quickly turned dark brown and elemental silver precipitated out of the solution. The reaction mixture was allowed to warm to ambient temperature and stirred in the dark for 15 h. The solvent was evaporated to dryness and the residue extracted twice with 25 mL of pentane. The red-brown extracts were filtered through a filter cannula and the filtrate was evaporated to dryness leaving 180 mg of a dark brown microcrystalline residue. The residue was recrystallised from pentane at −78 °C affording **2** as a black crystalline solid. Yield 0.16 g (43%). $C_{15}H_{39}CrFN_4Si_3$ (430.75): calcd. C 41.83, H 9.13, N 13.01; found C 42.39, H 9.15, N 12.63. The product was shown by ^1H NMR spectroscopy to be identical to that obtained from oxidation of **1** with **7** (vide infra).

Preparation of $[Cr(N_3N)F]$ (2) by Oxidation of 1 with 7: Under exclusion of light, a solution of $[Ag(CNtBu)_2](BF_4)$ (**7**) (0.36 g, 1.00 mmol) in 50 mL of THF was slowly added, via a double ended needle, to a stirred solution of $[Cr(N_3N)]$ (**1**) (0.42 g, 1.02 mmol) in 50 mL of THF, at −78 °C. The green solution of **1** rapidly turned reddish-black and elemental silver started to precipitate. The suspension was stirred at −78 °C for 0.5 h and then allowed to warm to ambient temperature in the dark. IR spectra of the reaction solution were recorded in the region of 2300−1500 cm^{-1} to monitor the progress of the reaction. These revealed the fast replacement of the ν(C≡N) absorption of $[Ag(CNtBu)_2](BF_4)$ at 2212 cm^{-1} by that of uncoordinated *t*BuNC at 2134 cm^{-1}. In addition, a weak ν(C≡N) absorption band of an intermediate was observed at 2203 cm^{-1}, which disappeared after stirring the reaction mixture for ca. 3.5 h at ambient temperature. All volatiles were removed after 4 h in vacuo. The residue was extracted twice with 40 mL of pentane and the extract filtered through a filter cannula. The filtrate was evaporated to dryness and the residue was washed with a minimum amount of pentane at −78 °C affording **2** as a dark brown microcrystalline solid (0.17 g). A second crop of **2** was obtained from the wash solution on crystallisation at −78 °C (0.06 g). Overall yield 0.23 g (52% relative to **1**), m.p. 159 °C. IR (nujol mull): $\tilde{\nu}$ [cm^{-1}] = 2726 vw, 2655 vw, 1458 m, 1450 m, 1421 w, 1408 vw, 1400 vw, 1344 w, 1331 w, 1310 vw, 1286 w, 1259 sh, 1245 sh, 1238 s, 1210 vw, 1180 vw, 1151 vw, 1131 w, 1090 m, 1077 m, 1062 m, 1025 w, 958 s, 944 s, 922 s, 887 m, 840 vs br, 793 s br, 756 m, 748 sh, 724 sh, 685 sh, 679 m, 632 w, 593 s, 577 m, 535 w, 493 m. ^1H NMR (300.1 MHz, C_6D_6, 297 K): δ [ppm] = 3.28 [s, $\Delta\nu_{1/2}$ = 190 Hz, 27 H, 3 × $Si(CH_3)_3$], −33.1 (s, $\Delta\nu_{1/2}$ = 1400 Hz, 6 H, 3 × CH_2), −208 (s, $\Delta\nu_{1/2}$ = 5100 Hz, 6 H, 3 × CH_2). $\mu_{eff} = 3.0\ \mu_B$. $C_{15}H_{39}CrFN_4Si_3$ (430.75): calcd. C 41.83, H 9.13, N 13.01; found C 41.47, H 8.85, N 13.13.

Preparation of $[Cr(N_3N)Br]$ (4) by Oxidation of 1 with AgBr: $[Cr(N_3N)]$ (**1**) (0.42 g, 1.02 mmol) was dissolved in 40 mL of THF, the solution was cooled to −60 °C and transferred via a double ended needle to a Schlenk tube, which was charged with AgBr (0.192 g, 1.02 mmol) and cooled to −60 °C. The suspension was allowed to warm to ambient temperature and stirred in the dark for 16 h. During this time the colour of the solution turned from green to reddish-black and a black precipitate of elemental silver was formed. The volatiles were removed in vacuo and the residue was extracted with 30 mL of diethyl ether. The extract was filtered through a filter cannula and the filtrate was concentrated to approximately 5 mL. Crystallisation was completed by storing the solution at −35 °C, affording **4** as a brown-black microcrystalline solid. Yield 0.32 g (64%), m.p. 175 °C. IR (nujol mull): $\tilde{\nu}$ [cm^{-1}] = 2724 vw, 2642 vw, 1448 m, 1400 vw, 1366 w, 1335 w, 1325 w, 1302 vw br, 1262 m, 1245 s, 1212 vw, 1181 vw, 1150 vw, 1132 w, 1119 sh, 1066 m, 1052 s, 1030 w, 942 s, 919 s, 905 m, 841 vs br, 796 m, 777 s, 753 s, 742 m, 689 w, 671 m, 632 w, 602 m, 575 m, 563 w, 545 vw, 482 w. ^{1}H NMR (300.1 MHz, C_6D_6, 297 K): δ [ppm] = 5.17 [s, $\Delta\nu_{1/2}$ = 250 Hz, 27 H, 3 × $\mathrm{Si(C}H_3)_3$], −47.4 (s, $\Delta\nu_{1/2}$ = 1000 Hz, 6 H, 3 × $\mathrm{C}H_2$), −185 (s, $\Delta\nu_{1/2}$ = 2700 Hz, 6 H, 3 × $\mathrm{C}H_2$). μ_{eff} = 2.8 μ_B. $C_{15}H_{39}BrCrN_4Si_3$ (491.66): calcd. C 36.64, H 8.00, Br 16.25, N 11.40; found C 36.66, H 7.65, Br 16.32, N 11.28.

Preparation of [Cr(N_3N)Br] (4) by Oxidation of 1 with Br_2: A solution of [Cr(N_3N)] (**1**) (0.26 g, 0.63 mmol) in 50 mL of pentane was treated at −78 °C with a solution of Br_2 (0.016 mL, 0.31 mmol) in 1 mL of pentane. The colour of the reaction solution instantly turned black. After stirring for 2.5 h at ambient temperature, the solution was concentrated in vacuo to half of its volume and filtered from a black solid through a glass frit. The brownish-red filtrate was evaporated to dryness to yield 0.16 g of an oily residue. Crystallisation of the crude product from diethyl ether at −78 °C afforded **4** as black cubes. A second crop of **4** could be obtained after evaporation of the mother liquor to dryness and crystallisation of the residue from pentane at −78 °C. Overall yield 0.05 g (16%). The product was shown by ^{1}H NMR spectroscopy to be identical to that obtained from oxidation of **1** with AgBr.

Preparation of [Cr(N_3N)I] (5) by Oxidation of 1 with AgI: A mixture of [Cr(N_3N)] (**1**) (0.41 g, 1.00 mmol) and AgI (0.24 g, 1.02 mmol) was treated in the dark with 40 mL of THF at −78 °C. On warming to room temperature, the green solution of **1** turned yellowish-black and elemental silver precipitated out of the solution. After stirring for 16 h at room temperature in the dark, the solvent was removed in vacuo and insoluble material was removed by extraction of the residue with 40 mL of diethyl ether and filtration. The filtrate was concentrated to approximately 5 mL, then 10 mL of pentane was added and the volume of the solution was reduced in vacuo again to approximately 5 mL. Crystallisation of the product was completed by storing the solution overnight at −78 °C, thus providing **5** as black crystals, which were found by ^{1}H NMR spectroscopy to be more than 95% pure. Yield: 0.46 g (86%). Analytically pure **5** was obtained after recrystallisation of the crude product from diethyl ether and washing of the obtained crystals with pentane at −78 °C. Yield 0.38 g (71%), m.p. 177 °C. IR (nujol mull): $\tilde{\nu}$ [cm^{-1}] = 2635 w, 2080 w br, 2014 w, 1992 vw, 1925 w br, 1871 w br, 1447 m, 1401 w, 1366 vw, 1358 w, 1331 w, 1321 w, 1304 w, 1261 s, 1246 vs, 1211 w, 1136 m, 1115 w, 1069 m, 1050 sh, 1044 vs, 1024 m, 938 vs, 912 vs, 840 vs br, 781 vs br, 753 s, 740 s, 689 m, 674 m, 630 w, 574 s. ^{1}H NMR (300.1 MHz, C_6D_6, 297 K): δ [ppm] = 5.88 [s, $\Delta\nu_{1/2}$ = 140 Hz, 27 H, 3 × $\mathrm{Si(C}H_3)_3$], −54.1 (s, $\Delta\nu_{1/2}$ = 950 Hz, 6 H, 3 × $\mathrm{C}H_2$), −145 (s, $\Delta\nu_{1/2}$ = 2100 Hz, 6 H, 3 × $\mathrm{C}H_2$). μ_{eff} = 3.0 μ_B. $C_{15}H_{39}CrIN_4Si_3$ (538.66): calcd. C 33.45, H 7.30, I 23.56, N 10.40; found C 33.16, H 7.36, I 23.32, N 10.25.

Preparation of [Cr(N_3N)I] (5) by Oxidation of 1 with I_2: A solution of I_2 (0.127 g, 0.50 mmol) in 30 mL of THF was added dropwise to a solution of **1** (0.42 g, 1.02 mmol) in 50 mL of THF at −78 °C. The colour of the solution instantly changed to yellowish-black. The resulting reaction mixture was stirred at room temperature for 15 h. The volatiles were removed in vacuo and the residue was extracted with 40 mL of pentane and then with 10 mL of diethyl ether. The extracts were filtered and evaporated to dryness in vacuo providing 0.48 g of a brown-black sticky solid. This was crystallised from 10 mL of diethyl ether at −78 °C affording black crystals of **5**. Yield: 0.16 g (29% relative to **1**). $C_{15}H_{39}CrIN_4Si_3$ (538.66): calcd. C 33.45, H 7.30, I 23.56, N 10.40; found C 32.21, H 7.17, I 23.88, N 10.37. The product was shown by ^{1}H NMR spectroscopy to be identical to that obtained from the oxidation of **1** with AgI.

Preparation of [Cr(N_3N)CN] (6): A solution of **1** (0.59 g, 1.43 mmol) in 30 mL of THF was added to a suspension of AgCN (0.22 g, 1.64 mmol) in 30 mL of THF at −50 °C. The reaction mixture was allowed to warm to ambient temperature under the exclusion of light. The colour of the solution slowly changed to red, and a black precipitate of elemental silver was formed. The suspension was stirred overnight at room temperature in the dark. The volatiles were removed in vacuo and the residue was extracted with 70 mL of diethyl ether. The blood-red extract was filtered, the filtrate was concentrated to approximately 15 mL and stored overnight at −78 °C to complete crystallisation of the product. After decanting the supernatant solution, the black crystals were washed with a minimum amount of diethyl ether at −78 °C and dried in vacuo. Yield: 0.36 g (57%), m.p. 166 °C. IR (nujol mull): $\tilde{\nu}$ [cm^{-1}] = 2642 vw, 1929 vw, 1871 vw, 1402 m, 1367 m, 1335 w, 1323 m, 1309 w, 1265 m, 1259 m, 1246 s, 1211 w, 1180 vw, 1169 vw, 1150 vw, 1132 m, 1118 sh, 1069 sh, 1051 s, 1029 m, 1015 sh, 941 vs, 919 vs, 841 vs br, 778 vs br, 750 s, 743 s, 732 sh, 687 m, 676 m, 633 m, 629 w, 601 m, 575 s, 562 m, 490 m, 466 m, 444 w, 417 m. ^{1}H NMR (300.1 MHz, C_6D_6, 297 K): δ [ppm] = 3.49 (s, $\Delta\nu_{1/2}$ = 220 Hz, 27 H, 3 × $\mathrm{Si(C}H_3)_3$], −39.0 (s, $\Delta\nu_{1/2}$ = 1400 Hz, 6 H, 3 × $\mathrm{C}H_2$), −188 (s, $\Delta\nu_{1/2}$ = 6900 Hz, 6 H, 3 × $\mathrm{C}H_2$). μ_{eff} = 2.9 μ_B. $C_{16}H_{39}CrN_5Si_3$ (437.77): calcd. C 43.90, H 8.98, N 16.00; found C 44.14, H 9.06, N 15.75.

Preparation of [Ag(CN*t*Bu)$_2$](BF$_4$) (7): A suspension of AgBF$_4$ (0.625 g, 3.21 mmol) in 15 mL of CH_2Cl_2 was treated in the dark with *t*BuNC (0.72 mL, 6.37 mmol) and the reaction mixture was stirred at room temperature. After 5 min, an IR spectrum of the solution was recorded in the region of 2300−1500 cm^{-1} to follow the progress of the reaction. This showed two strong ν(C≡N) absorptions at 2225 and 2200 cm^{-1}, indicating the formation of the cations [Ag(CN*t*Bu)$_2$]$^+$ and [Ag(CN*t*Bu)$_3$]$^+$. After stirring for 30 min at ambient temperature, the IR spectrum of the reaction solution revealed that the ν(C≡N) absorption of [Ag(CN*t*Bu)$_3$]$^+$ at 2200 cm^{-1} had disappeared. The solution was then filtered and the filtrate was concentrated in vacuo to a few millilitres and pentane was added to precipitate complex **7**. The supernatant solution was discarded and the precipitate washed once with pentane and dried in vacuo to afford **7** as a white solid. Yield 1.03 g (89%). IR (CH_2Cl_2): $\tilde{\nu}$ [cm^{-1}] = 2225 vs [ν(*t*BuN≡C)]. IR (THF): $\tilde{\nu}$ [cm^{-1}] = 2212 vs [ν(*t*BuN≡C)]. IR spectra in KBr showed extensive decomposition of **7** due to reaction with the matrix. ^{1}H NMR (300.1 MHz, CD_2Cl_2, 248 K): δ [ppm] = 1.52 (s, 18 H, 2 × $\mathrm{C}Me_3$). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, 222 K): δ [ppm] = 29.3 (s, 2 × $\mathrm{C}Me_3$), 58.6 (s, 2 × $C\mathrm{Me}_3$), 132.7 (s, 2 × $C\mathrm{NCMe}_3$). ^{19}F NMR (282.4 MHz, CD_2Cl_2, 248 K): δ [ppm] = −152.65 (s, $^{11}\mathrm{B}F_4$), −152.60 (s, $^{10}\mathrm{B}F_4$). $C_{10}H_{18}AgBF_4N_2$ (360.94): calcd. C 33.28, H 5.03, N 7.76; found C 33.24, H 4.99, N 7.59.

X-ray Crystallographic Study: Suitable single crystals of **4** and **6** were grown by slow cooling of a saturated pentane (**4**) or diethyl ether (**6**) solution from ambient temperature to −35 °C. A summary of the crystal data, data collection and refinement is given in Table 4.

Data collection was performed on a STOE IPDS diffractometer (area detector) equipped with a low- temperature device (Cryostream, Oxford Cryosystems) using graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Unit cell parameters of **4** and **6** were determined from least-squares analyses using 5000 reflections (5.6° < 2θ < 50.0°). Intensities were measured by φ-oscillation scans and corrected for background, polarisation and Lorentz effects. DIFABS was applied for absorption correction of the data set of **4**.[35] The structures were solved by direct methods and refined anisotropically by the least-squares procedure implemented in the SHELX program system.[36] Hydrogen atoms were included iso-

Table 4. Crystallographic data for the complexes **4** and **6**

	4	**6**
Empirical formula	$C_{15}H_{39}BrCrN_4Si_3$	$C_{16}H_{39}CrN_5Si_3$
Molecular weight	491.68	437.79
Crystal colour	Black	Black
Crystal size [mm]	0.32 × 0.32 × 0.20	0.42 × 0.40 × 0.28
Crystal system	Monoclinic	Monoclinic
space group	*Cc*	*Cc*
a [Å]	17.210(2)	17.168(4)
b [Å]	9.574(2)	9.589(2)
c [Å]	15.835(2)	16.028(4)
β [deg]	110.46(2)	110.85(3)
V [Å^3]	2444.5(6)	2465.9(9)
Z	4	4
$D_{calcd.}$ [g·cm^{-3}]	1.336	1.179
T [K]	180(2)	180(2)
μ [mm^{-1}]	2.256	0.619
$T_{min.}/T_{max.}$	0.532/0.661	0.781/0.845
2θ min./max. [deg]	5.22/50.50	5.20/50.48
$h/k/l$ ranges	−20,20/−11,11/−18,18	−20,20/−11,11/−19,19
Number of reflections collected	7867	7959
Number of unique reflections, n	4411	4403
R_{int} [$I > 2\sigma(I)$]	0.0622	0.0178
Parameters, p	217	226
Refinement method	full-matrix on F^2	full-matrix on F^2
R_1,[a] wR_2[b] [$I > 2\sigma(I)$]	0.0341, 0.0791	0.0226, 0.0568
R_1, wR_2 (all data)	0.0387, 0.0807	0.0236, 0.0572
GoF[c]	0.993	1.038
Largest peak/hole [e·Å^{-3}]	0.856/−0.565	0.255/−0.185

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

tropically using the riding model on the bound carbon atoms. Geometrical calculations were performed with PLATON[37] and illustrations with DIAMOND.[38]

CCDC-183384 and CCDC-183385 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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