The Chemistry of 1,3,5-Triazacyclohexane Complexes, 3[◇]

High Yield Synthesis of $[Cr\{N(SiMe_3)_2\}_3]$ and Accurate Structure Determination by Cocrystallization with Me_6Si_2

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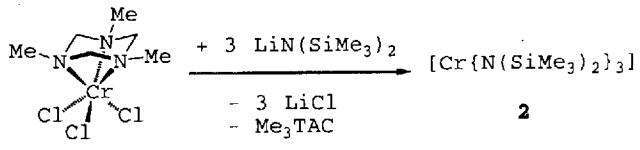
The reaction of *N,N′,N″*-trimethyl-1,3,5-triazacyclohexane chromium trichloride ($(Me_3TAC)CrCl_3$, **1**) with $LiN(SiMe_3)_2$ or $NaN(SiMe_3)_2$ in petroleum ether yields nearly quantitatively $[Cr\{N(SiMe_3)_2\}_3]$ (**2**) with loss of the Me_3TAC ligand. Compound **2** could be crystallized from hexamethyldisilane as $[Cr\{N(SiMe_3)_2\}_3] \cdot (Me_6Si_2)_{0.5}$ which allowed the refinement of the X-ray crystal structure in the trigonal space group *P-31c* (no. 163) ($a = 16.012(3)$ Å, $c = 8.4796(12)$ Å, $V = 1882.8(6)$ Å^3, $Z = 2$) without severe disorder.

The synthesis of $[Cr\{N(SiMe_3)_2\}_3]$ (**2**) from $CrCl_3$ and $NaN(SiMe_3)_2$ was described by Bürger and Wannagat[2] as one of the first transition metal disilylamido compounds. However, the yield was very low. Later, the yields were improved to 75% and the pure product was obtained after recrystallization or sublimation[3]. The syntheses and chemistry of similar tris(amido) compounds of Sc, Ti, V, Fe, and the lanthanides were reviewed in 1977[4]. In this review, the crystal structure of **2** was described as being isostructural to the Fe compound[5] and two bond lengths and one angle were given. However, no other crystal or structural data of **2** have been published so far. Many crystal structures of $M(N(SiMe_3)_2)_3$ with other metals, all in the same space group *P-31c*, have been published and were recently reviewed[6]. All structures suffer from severe disorder or neglect of the solvent molecule (e.g. benzene) built into the large channels of the crystal.

Recently[7], we have synthesized the virtually insoluble, air- and water-stable $(Me_3TAC)CrCl_3$ (**1**) in a quantitative reaction between $CrCl_3(THF)_3$ and Me_3TAC in THF. We now demonstrate, spectroscopically by UV/Vis and chemically by the nearly quantitative synthesis of **2** from **1** and $LiN(SiMe_3)_2$, the weakness of this ring-strained triazacycloalkane ligand.

Results and Discussion

The attempted derivatization of **1** with one equivalent of $NaN(SiMe_3)_2$ in petroleum ether (pet. ether) yielded only **2** and unreacted **1**. The reaction was repeated with 2.8 equivalents of $LiN(SiMe_3)_2$. After a few hours, a deep green solution and a nearly colorless precipitate resulted. After filtration and removal of all volatile components at 40 °C/10^{-3} mbar, 97% of pure green **2** was obtained. In a separate quantitative experiment, the pet. ether-insoluble residue yielded unreacted **1** and 3 equivalents of LiCl within 5% of theory. Inspection of the volatiles, removed after concentration, by ^1H NMR showed only Me_3TAC ($CDCl_3$: $\delta = 3.16$ (br. s, 6H, CH_2), 2.25 (s, 9H, CH_3)), pet. ether ($\delta = 0.8-2$) and a small amount of $HN(SiMe_3)_2$ probably from impurities in $LiN(SiMe_3)_2$.



$[(Me_3TAC)CrCl_3]$
1

2

The low solubility of **1** ensures that the reaction proceeds completely to **2** in the presence of unreacted **1**. The freed ligand Me_3TAC can be removed at 10^{-3} mbar so that pure **2** is the only other pet. ether-soluble product. Thus, this reaction gives **2** in high yield without the need for further purification. This is especially convenient for a small-scale preparation. The ^1H NMR signal of the Me groups can be detected at $\delta = +24.9$ with nearly equal T_1 (0.3841(12) ms) and T_2 ($\approx 1/(\pi\Delta\nu_{1/2}) = 0.3638(21)$ ms) values.

Compound **2** could be recrystallized from a concentrated solution in pet. ether at −20 °C and was characterized by X-ray crystallography (space group *P-31c*, $a = 15.989(5)$ Å, $b = 8.569(2)$ Å, $V = 1896.9(9)$ Å^3). This structure differs from the structure mentioned previously in the review[4,5] in that the disordered pet. ether solvent molecules are built into the large channels of the crystal. The amides described in the review were crystallized from benzene. As in the previous crystal structures, the solvent molecules are severely disordered and can be refined only by restricting their geometry. In our case, the structure of the built-in pet. ether

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molecules was unknown. The best approximation were two neopentanes related by a center of inversion along one of the C–Me bonds. The carbon atoms could not be refined without geometry restraints and some electron density was still not accounted for so that the final *R* value was about 8%. However, the proposed arrangement of neopentanes resembled approximately the shape of Me_6Si_2. Therefore, we crystallized **2** from a Me_6Si_2 solution in order to reduce the disorder of the larger solvent molecule. Indeed, **2** · $(Me_6Si_2)_{0.5}$ crystallizes in the same space group *P-31c* with nearly the same cell parameters $a = 16.012(3)$ Å, $b = 8.4796(12)$ Å, $V = 1882.8(6)$ Å^3. Figure 1 shows the structure of **2**, Figure 2 the structure of Me_6Si_2 in **2** · $(Me_6Si_2)_{0.5}$ and Figure 3 the entire structure along the *c* axis.

Figure 1. ZORTEP[8] plot of the molecular structure of **2** in **2** · $(Me_6Si_2)_{0.5}$, ellipsoids are shown with 50% probability; selected bond lengths [pm] and angles [°] (in parentheses the values from the review[4]): Cr–N 188.9(2) (190.3(6)), N–Si 174.75(14) (174.0(4)), Si–$C_{av.}$ 186.5, Si–N–Si 120.6(2) (122.0(2)), Si–N–Cr 119.69(7), N–Si–$C_{av.}$ 111.6

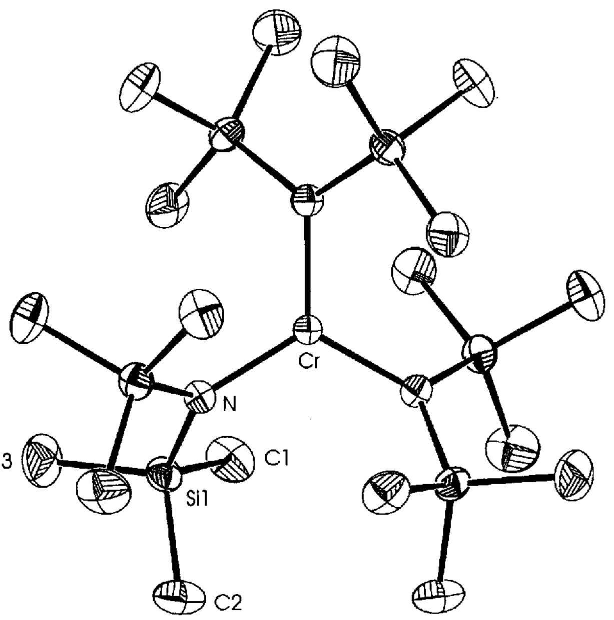


Figure 2. ZORTEP[8] plot of the molecular structure of two half-occupied Me_6Si_2 molecules in **2** · $(Me_6Si_2)_{0.5}$, ellipsoids are shown with 50% probability; selected bond lengths [pm] and angles [°] (in parentheses the values from an ED study[9]): Si–Si 233.7(7) (234.0(9)), Si–C 185.4(9) (187.7(3)), Si–Si–C 110.3(4) (108.4(4)), C–Si–C 108.6(4) (110.5(4))

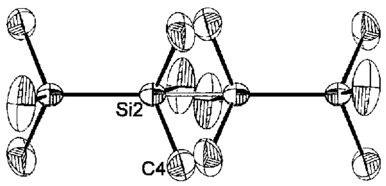
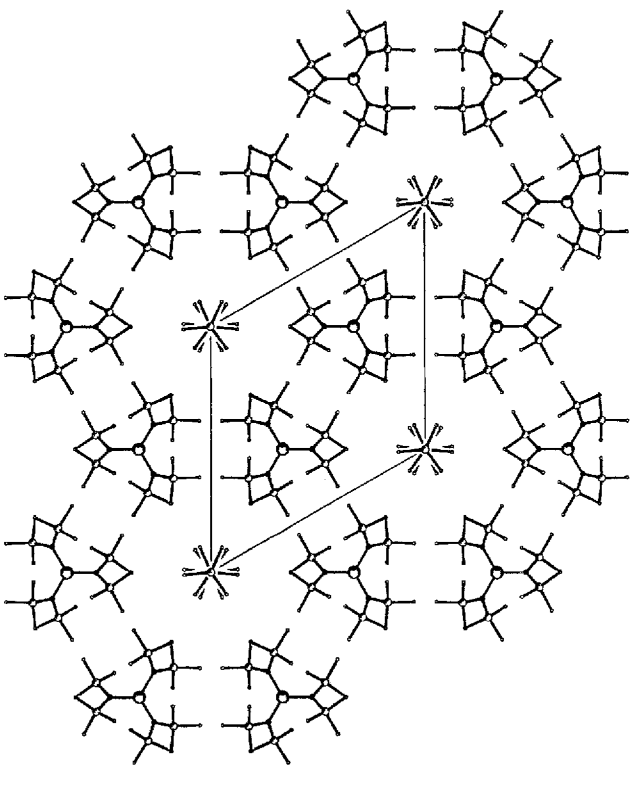


Figure 3. View of the the crystal structure along the *c* axis



The Cr–N and N–Si bond lengths and the Si–N–Si bond angle are similar but more accurate than the ones reported earlier[4]. As in all other tris(amides) with M–N < 200 pm, the Cr lies in the plane of the three nitrogen atoms. The nitrogen atoms are planar and all N–Si–Me angles are equal within 2.2° and larger than 109.5°, thus showing no sign of an agostic interaction with the chromium atom.

For the Me_6Si_2, all non-hydrogen atoms could be refined anisotropically. The Me_6Si_2 are still disordered along the *c* axis where each molecule is half occupied. This is the first X-ray crystal structure of the simplest hexaalkyldisilane Me_6Si_2 and shows bond lengths and angles similar to those obtained from an electron diffraction study[9]. Since the Me_6Si_2 length does not match the repeat distance at the widest parts in the channel along the *c* axis ($c/2 = 424$ pm), the bond angles are different from the gas phase structure by 2°, so the molecule becomes longer and narrower for a better fit into the channel. The successful cocrystallization of Me_6Si_2 with **2** shows that the open channels of the crystal structure of **2** may serve as hosts for other molecules of similar size that are difficult to examine directly by X-ray crystallography.

This reaction indicates that the macrocyclic Me_3TAC can easily be replaced by a strong and bulky ligand, which is an indication of the weak metal ligand interaction due to the acute N–Cr–N angle in these complexes[7]. The weak ligand field strength of Me_3TAC can also be demonstrated by the UV/Vis spectrum of **1**, from which the ligand field parameters $10\ Dq = 14660$ cm^{-1} and $B' = 570$ cm^{-1} can be deduced. This ligand field splitting is much smaller than the average of 10 *Dq* of $[CrCl_6]^{3-}$ (13200 cm^{-1}) and of a hexaamine complex, e.g. $[Cr(en)_3]^{3+}$ (21850 cm^{-1}), which should be an estimate for the expected 10 *Dq* of $(amine)_3CrCl_3$.

This study indicates chemically that R_3TAC is a very weak tris(amine) ligand in the replacement reaction with

$LiN(SiMe_3)_2$. Since $(Me_3TAC)CrCl_3$ is an air-stable and easily accessible compound it may also serve as an excellent starting material for other chromium complexes.

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Experimental

All procedures were carried out either on a vacuum line or in a Braun Labmaster 130 glove box under dry oxygen-free argon. Petroleum ether (b.p. ≈ 40 °C) was condensed into the reaction flask directly from Na/benzophenone. Compound **1** was prepared as previously described[7]. – UV/Vis reflectance spectrum of **1** (KBr): λ_{max} = 14660, 20420 cm^{-1} (relative intensity 1:1.6). – NMR spectra: Bruker WP-80SY (80 MHz) at 304 K.

$(Me_3TAC)CrCl_3$ (**1**) (73 mg, 254 μmol) and $LiN(SiMe_3)_2$ (119 mg, 711 μmol) were stirred in pet. ether for 3 days. The green solution was filtered off, the residue washed with pet. ether until the washings were colorless, and all volatile components of the combined pet. ether solutions were removed at 40 °C/10^{-3} mbar yielding 123 mg of **2** (97%), m.p. 186 °C (slow dec.). – ^1H NMR (C_6D_6): δ = +24.9 [$\Delta\nu_{1/2}$ = 875(5) Hz, T_1 = 0.3841(12) ms]. – $C_{18}H_{54}N_3CrSi_6$ (533.16): calcd. C 40.55, H 10.21, N 7.88; found C 39.65, H 10.26, N 7.92.

X-ray Crystallographic Determinations

Green hexagonally shaped single crystals of **2** · $(Me_6Si_2)_{0.5}$ were obtained by slow evaporation of a solution of **2** in Me_6Si_2 in a glove box. $C_{21}H_{63}CrN_3Si_7$ (606.35 g/mol), crystal size 1.5 × 0.32 × 0.32 mm, trigonal crystal system, space group *P-31c* (no. 163) a = 16.012(3), c = 8.4796(12), V = 1882.8(6), Z = 2, $d_{calc.}$ = 1.070 g/cm^3, μ = 0.531 mm^{-1}. Data collection was carried out on an Enraf-Nonius CAD4 four circle diffractometer equipped with a low temperature device. Data were collected at −110 °C with $\omega-2\Theta$ scans ($5° \leq 2\Theta \leq 55°$) using Mo-K_α radiation. Every 200 reflections intensity data were monitored through the measurement of three standard reflections. All 1561 data (1438 unique) were corrected for Lorentz and polarization effects[10]. Structure solution was obtained using direct methods (SHELX-86)[11] and refinement using difference-fourier methods (SHELX-93)[12]. The refinement was done with full-matrix least-squares techniques on F^2. The input files for the SHELX programs were prepared with the program UTILITY[13]. Hydrogen atoms were refined isotropically and all non hydrogen atoms anisotropically. The final refinement with 1404 observed reflections ($I > 2\sigma(I)$) resulted in R = 0.040 and R_w = 0.105, GOF = 1.099, largest diff. peak and hole 0.331 and −0.736 (e $Å^{-3}$). Every asymmetric unit contains a half molecule of hexamethyldisilane. No attempts were undertaken to calculate missing hydrogen atoms on these anisotropically refined atoms. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-404271, the names of the authors and the journal citation.

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[1] R. D. Köhn, G. Kociok-Köhn, M. Haufe, *J. Organomet. Chem.* **1995**, *501*, 303–307.
[2] H. Bürger, U. Wannagat, *Monatsh. Chem.* **1964**, *95*, 1099–1102.
[3] D. C. Bradley, R. G. Copperthwaite, *Inorg. Synth.* **1978**, *18*, 112–120.
[4] P. G. Eller, D. C. Bradley, M. B. Hursthouse, D. W. Meek, *Coord. Chem. Rev.* **1977**, *24*, 1–95.
[5] D. C. Bradley, M. B. Hursthouse, P. F. Rodesiler, *Chem. Commun.* **1969**, 14–15.
[6] M. Westerhausen, M. Hartmann, A. Pfitzner, W. Schwarz, *Z. Anorg. Allg. Chem.* **1995**, *621*, 837–850.
[7] R. D. Köhn, G. Kociok-Köhn, *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1877–1878.
[8] L. Zsolnai, H. Pritzkow, *ZORTEP, ORTEP Program for PC*, Universität Heidelberg, **1994**.
[9] B. Beagley, J. J. Monaghan, T. G. Hewitt, *J. Mol. Structure* **1971**, *8*, 401–411.
[10] R. Fröhlich, *XCAD4*, *Program for Data Reduction*, Universität Münster, FRG, **1994**.
[11] G. M. Sheldrick, *SHELX-86*, *Program for Crystal Structure Solution*, Universität Göttingen, FRG, **1986**.
[12] G. M. Sheldrick, *SHELX-93*, *Program for Crystal Structure Determination*, University of Camebridge, England, **1993**.
[13] J. Pickardt, *UTILITY*, *Program for Preparing SHELX Input Files*, TU-Berlin, FRG, **1994**.

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