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Synthesis of the First Compound with a Rhombohedral $Ti_6(\mu_3\text{-}NH)_6(\mu_3\text{-}N)_2$ Core Structure by Ammonolysis of a Titanium Chelate in a Two-Phase System

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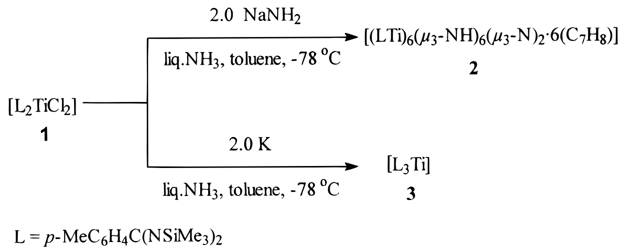
Summary: Reaction of $[\{p\text{-}MeC_6H_4C(NSiMe_3)_2\}_2TiCl_2]$ (***1***) *with* $NaNH_2$ *gave the novel titanium aggregate* $[\{p\text{-}MeC_6H_4C(NSiMe_3)_2Ti\}_6(\mu_3\text{-}NH)_6(\mu_3\text{-}N)_2\text{·}6C_7H_8]$ (***2***). *Treatment of **1** with potassium in liquid ammonia and toluene produced the titanium(III) complex* $[\{p\text{-}MeC_6H_4C(NSiMe_3)_2\}_3Ti]$ (***3***). *Compound **2** contains the largest Ti−N core so far reported.*

In recent years the interest in titanium-nitrogen precursors for the preparation of titanium nitride has increased.[1] In general gold-colored TiN is prepared using ammonia and a variety of titanium-containing compounds. In this context, we are interested in studying the intermediates with amido (NH_2), imido (NH), and nitrido (N) groups formed during the ammonolysis of substituted titanium compounds.

We reported already on the reaction of Cp^*TiMe_3 ($Cp^* = C_5Me_5$) with excess ammonia[2] to yield $[(Cp^*Ti)_3(\mu\text{-}NH)_3(\mu_3\text{-}N)]$. More recently Mena et al.[3] prepared $(Cp^*Ti)_4(\mu_3\text{-}N)_4$ from $Cp^*Ti(NMe_2)_3$ and ammonia. Attempts to detect or isolate larger aggregates using the Cp* ligand on titanium have so far failed.

Scheme 1



Consequently, we changed the ligand on titanium and the method of preparation. From the reaction of $LTiCl_3$ ($L = p\text{-}MeC_6H_4C(NSiMe_3)_2$) with $NaNH_2$ in liquid ammonia and toluene we were not able to isolate a definite compound due to the insolubility of the resulting product in organic solvents. In contrast, treatment of L_2TiCl_2 (**1**) with 2 equiv of $NaNH_2$ in liquid ammonia and toluene at −78 °C affords $[(LTi)_6(\mu_3\text{-}NH)_6(\mu_3\text{-}N)_2\text{·}6C_7H_8]$ (**2**) and an insoluble solid, while the reduction of the same starting material by means of a solution of K (or Na) in liquid ammonia and toluene leads to the formation of L_3Ti (**3**; Scheme 1).[4] The labile character of L for the preparation of **2** is similar to that of Cp for the preparation of $[(CpTi)_6(\mu_3\text{-}O)_8]$,[5] $[(CpTi)_5(\mu_3\text{-}S)_6]$,[6] and

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$[(CpTi)_6(\mu_3\text{-}Te)_6(\mu_3\text{-}O)_2]$,[7] respectively. The reaction of **1** with K (or Na) gives nonextractable titanium-containing solids. The yield of the single crystals of **2** is small. The filtrate was concentrated and kept at −20 °C; over 2 weeks a yellow solid was formed. From the elemental analysis, the solid was impure **2**, which was difficult to purify.

Compounds **2** (yellow) and **3** (green) are crystalline solids,[8] which are thermally very stable. **2** starts to decompose at 300 °C, while **3** is stable above the melting point (301 °C). Under an inert atmosphere or in solution (toluene) no decomposition was observed for **2** and **3**. However, **3** is sensitive to air and moisture. The IR spectrum of **2** shows a broad absorption at 3381 cm^{-1}, assignable to the N−H stretching frequency. We were not able to dissolve compound **2** without decomposition to obtain reliable NMR spectra. The largest fragment in the EI mass spectrum of **2** was observed at *m*/*e* 2537 ($M^+ - NSiMe_3$) with very low intensity due to the poor volatility of **2.** Compound **3** exhibits the peak of the molecular ion at *m*/*e* 879 with 62% relative intensity (190, 100%).

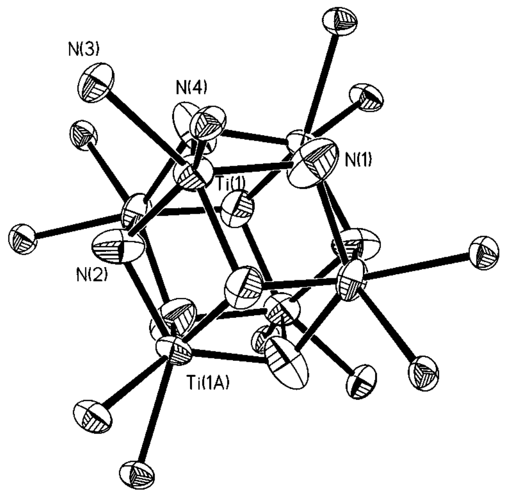

Figure 1. Structure of the inorganic core of **2** in the crystal. Selected bond lengths (Å) and angles (deg): Ti(1)−N(2) = 1.958(5), Ti(1)−N(1) = 1.998(6), Ti(1)−N(1)#1 = 2.003(6), Ti(1)−N(1)#2 = 2.014(5), Ti(1)−N(4) = 2.193(4), Ti(1)−N(3) = 2.196(4); N(2)−Ti(1)−N(1) = 123.5(3), N(2)−Ti(1)−N(1)#1 = 78.6(2), N(1)−Ti(1)−N(1)#1 = 75.2(2), N(2)−Ti(1)−N(1)#2 = 78.3(2), N(1)−Ti(1)−N(1)#2 = 75.0(2), N(1)#1−Ti(1)−N(1)#2 = 122.1(4), Ti(1)#3−Ti(1)−Ti(1)#4 = 60.0, Ti(1)#3−Ti(1)−Ti(1)#2 = 90.0, Ti(1)#4−Ti(1)−Ti(1)#2 = 60.94(2), Ti(1)#3−Ti(1)−Ti(1)#1 = 60.94(2), Ti(1)#4−Ti(1)−Ti(1)#1 = 90.0, Ti(1)#2−Ti(1)−Ti(1)#1 = 58.12(4).

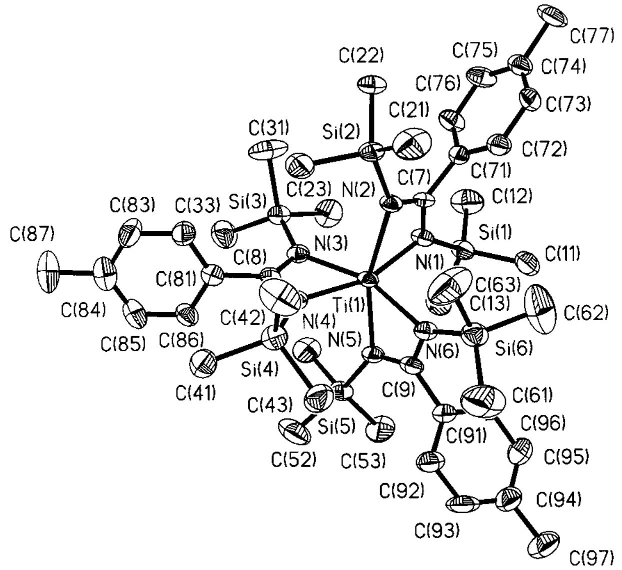

Figure 2. Molecular structure of **3** in the crystal. Selected bond lengths (Å) and angles (deg): Ti(1)−N(3) = 2.133(5), Ti(1)−N(6) = 2.154(5), Ti(1)−N(2) = 2.160(4), Ti(1)−N(1) = 2.164(5), Ti(1)−N(5) = 2.177(4), Ti(1)−N(4) = 2.188(5); N(3)−Ti(1)−N(6) = 160.1(2), N(3)−Ti(1)−N(2) = 95.3(2), N(6)−Ti(1)−N(2) = 102.5(2), N(3)−Ti(1)−N(1) = 102.2(2), N(6)−Ti(1)−N(1) = 93.7(2), N(2)−Ti(1)−N(1) = 63.6(2), N(3)−Ti(1)−N(5) = 101.1(2), N(6)−Ti(1)−N(5) = 63.4(2), N(2)−Ti(1)−N(5) = 160.6(2), N(1)−Ti(1)−N(5) = 102.4(2), N(3)−Ti(1)−N(4) = 63.7(2), N(6)−Ti(1)−N(4) = 102.5(2), N(2)−Ti(1)−N(4) = 105.2(2), N(1)−Ti(1)−N(4) = 162.3(2), N(5)−Ti(1)−N(4) = 91.4(2).

X-ray Crystal Structures of 2 and 3. The central inorganic core of **2** and the molecular structure of **3**[9] are shown in Figures 1 and 2, respectively. Details of

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(4) (a) Synthesis of **2**: Ammonia (40 mL) was condensed onto a solution of **1** (1.35 g, 2.01 mmol) in toluene (60 mL) with stirring at −78 °C. $NaNH_2$ (0.16 g, 4.10 mmol) was added to the resulting mixture. The mixture was stirred for 1 h at −78 °C. Then the excess of ammonia was allowed to evaporate from the reaction mixture under stirring over 4 h. During this period the mixture was warmed slowly to room temperature. After filtration and partial removal of the solvent in vacuo, the resulting reddish brown solution was kept at room temperature for 3 weeks. Yellow single crystals of **2** were obtained in a yield of 0.05 g. After concentration of the filtrate (to ca. 10 mL) and addition of hexane (15 mL), the solution was kept at −20 °C for 2 weeks. A yellow solid of impure **2** (0.21 g) was formed. (b) Synthesis of **3**: Ammonia (50 mL) was condensed onto a suspension of **1** (2.02 g, 3.0 mmol) and K (0.24 g, 6.0 mmol) in toluene (80 mL) at −78 °C with stirring. The stirring of the mixture was continued for 1 h at this temperature. Then the excess ammonia was allowed to evaporate from the reaction mixture over 4 h. During this period the mixture was slowly warmed to room temperature. After filtration and concentration to about 15 mL in vacuo, the dark green solution was kept at −20 °C for 2 weeks. Green crystals of **3** were obtained: yield 0.87 g.

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(8) (a) Characterization data for **2**. Dec pt: 300−330 °C. IR (Nujol): $\tilde{\nu}$ 3381, 1612, 1441, 1248, 994, 845, 728, 473 cm^{-1}. EI-MS: *m*/*e* 2537 ($M^+ - NSiMe_3$). Anal. Calcd for $C_{126}H_{204}N_{20}Si_{12}Ti_6$ (2623.6): N, 10.7; Ti, 11.0. Found: N, 10.7; Ti, 11.7. (b) Characterization data for **3**. Mp: 301 °C. IR (Nujol): $\tilde{\nu}$ 1613, 1457, 1385, 1244, 981, 844, 758, 466 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ 8.58−8.62 (m, 6H, C_6H_4), 8.31−8.34 (m, 6H, C_6H_4), 2.16 (s, 9H, ArMe), 0.21 (br, 54H, $SiMe_3$, $\Delta\nu_{1/2} = 5.9$ Hz). EI-MS: *m*/*e* (%) 879 (62) (M^+), 190 (100) ($L^+ - NSiMe_3$). Anal. Calcd for $C_{42}H_{75}N_6Si_6Ti$ (880.52): C, 57.3; H, 8.6; N, 9.5; Ti, 5.4. Found: C, 58.0; H, 8.8; N, 9.9; Ti, 5.2.

(9) (a) X-ray structure determination of **2**: Single crystals of **2** suitable for X-ray structural analysis were obtained from toluene by keeping the reaction mixture at room temperature for 3 weeks. Data for the structure were collected on a Stoe-Siemens-Huber diffractometer with a Siemens CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ **Å**). Intensity measurements were performed at 133(2) K on a rapidly cooled crystal in an oil drop.[13] The structure was solved by direct methods (SHELXS-90)[14] and refined with all data by full-matrix least squares on F^2.[15] The hydrogen atoms of N−H bonds (occupancy 0.75) and those of C−H bonds were added in idealized positions. Other details of the data collection, structure solution, and refinement are listed in Table 1. (b) X-ray structure determination of **3**: Single crystals of **3** suitable for X-ray structural analysis were obtained from toluene by keeping the reaction mixture at −20 °C for 2 weeks. Data for the structure were collected on a Stoe-Siemens-AED2 four-circle diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Intensity measurements were performed at 200(2) K on a crystal in an oil drop. The structure was solved by direct methods (SHELXS-90)[14] and refined with all data by full-matrix least squares on F^2.[15] Hydrogen atoms were added in idealized positions. Other details of the data collection, structure solution, and refinement are listed in Table 1.

Table 1. Crystallographic Data for 2 and 3

	2	**3**
empirical formula	$C_{84}H_{156}N_{20}Si_{12}Ti_6 \cdot 6C_7H_8$	$C_{42}H_{75}N_6Si_6Ti$
fw	$2070.73 + 6 \times 92.14$	880.52
cryst size (mm)	$0.4 \times 0.4 \times 0.4$	$1.0 \times 0.6 \times 0.6$
cryst syst	rhombohedral	triclinic
space group	$R\bar{3}$	$P\bar{1}$
a (Å)	24.519(4)	14.635(7)
b (Å)	24.519(4)	18.261(10)
c (Å)	18.127(4)	19.417(8)
α (deg)	90	90.41(4)
β (deg)	90	97.43(3)
γ (deg)	120	90.78(5)
cell vol V (Å^3)	9438(3)	5145(4)
Z	3	4
ρ_c (g mm^{-3})	1.385	1.137
μ (mm^{-1})	0.536	0.340
F(000)	4200	1900
2θ range (deg)	4.44−55.04	7.04−45.10
no. of data: measd, unique	147 127, 4811 ($R_{int} = 0.091$)	14 439, 10162 ($R_{int} = 0.0395$)
R1,[a] wR2[b] ($I > 2\sigma(I)$)	0.0892, 0.2312	0.0676, 0.1757
R1, wR2 (all data)	0.1302, 0.2734	0.0782, 0.1886
goodness of fit, S[c]	1.090	1.128
no. of refined params	235	1033
no. of restraints	174	0
largest diff peak, hole (e Å^{-3})	+1.421/−0.658	+0.657/−0.342

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)]^{1/2}$. [c] $S = [\sum w(F_o^2 - F_c^2)^2]/\sum(n - p)]^{1/2}$.

the data collection, structure solution, and refinement are given in Table 1.

Compounds **2** and **3** crystallize in the rhombohedral and triclinic space groups $R\bar{3}$ and $P\bar{1}$, respectively. The molecular structure of **2** in the crystal consists of an octahedron, with the titanium atoms positioned on the vertexes. The angles between adjacent titanium atoms are either about 60 or 90°. The titanium triangles are topped each by a nitrogen atom, and these nitrogen atoms consist of two nitrides and six imides. The six imide hydrogen atoms statistically distribute over eight facial positions, the occupancy being 0.75. The coordination sphere of each titanium is completed by the chelating ligand L. The Ti−N bond lengths (in the range 1.958(5)−2.014(5) Å, average 1.993 Å) are only slightly larger than those found in $[(Cp^*Ti)_3(\mu\text{-}NH)_3(\mu_3\text{-}N)]$ (average 1.924 Å)[2] and in $(Cp^*Ti)_4(\mu_3\text{-}N)_4$ (average 1.939 Å)[3] and are very similar to the theoretically calculated Ti−N single-bond distance (1.981 Å).[10] The Ti−N distances are also close to the Ti−O distances observed in $[(CpTi)_6(\mu_3\text{-}O)_8]$ (average 1.973 Å)[5]. Since compound **2** is not completely symmetric, the Ti_6N_8 core is distorted. The molecular structure of **3** in the crystal shows that three L ligands complete the coordination sphere of Ti, and the core of **3** resembles a wheel with three vanes. A comparable arrangement is found in $[\{(\eta^5\text{-}Cp)_2TiF_2\}_3\text{-}Ti]$,[11] in which the Ti(III) is surrounded by three $(\eta^5\text{-}Cp)_2TiF_2$ ligands, and also found in $[\{PhC(NSiMe_3)_2\}_2\text{-}TiCl]$,[12] in which the Ti(III) is surrounded by two $PhC(NSiMe_3)_2$ ligands and one Cl atom. The average Ti−N bond length (2.163 Å) of **3** is comparable to that found in $[\{PhC(NSiMe_3)_2\}_2TiCl]$ (average 2.101 Å).

In conclusion, changing the ligand on titanium and the method of preparation leads to larger nitrogen−titanium aggregates when a chelating titanium compound is used as a starting material. The core structure of **2** can be regarded as a dimer of the previously reported $[Ti_3(\mu\text{-}NH)_3(\mu_3\text{-}N)]$ cluster.[2] Moreover, the reactions yielding **2** and **3** have in common that L−Ti bonds are cleaved using either $NaNH_2$ or potassium (sodium) in liquid ammonia. The latter reaction gives a reduced titanium product with migration of L. The two-phase system (NH_3/toluene) is important for these reactions.

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structures **2** and **3** reported in this paper. This material is available free of charge via the Internet at http://pubs.acs.org. These data have also been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 138530 and 138531. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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