Bis(trimethylsilyl)ammonium Salts Obtained by Reaction of Hexamethyldisilazane with $TiCl_4$, $ZrCl_4$, or $SnCl_4$

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Abstract: The reaction of hexamethyldisilazane with $TiCl_4$ in CH_2Cl_2 leads to the formation of $[(Me_3SiNTiCl_2)_8]$ (**3**). According to the crystal structure analysis, **3** is an octameric titanium trimethylsilylimido chloride. The mechanism of the formation of **3** was studied in detail by means of time-dependent ^{14}N NMR spectroscopy. $[(Me_3Si)_2NTiCl_3]$ was identified as an intermediate during the formation of **3**. Two by-products were identified: $[(NH_4)_2TiCl_6]$ and the hitherto unknown bis(trimethylsilyl)ammonium salt $[(Me_3Si)_2NH_2]^+[Ti_2Cl_9]^-$ (**5**). According to the crystal structure analysis, protonation of hexamethyldisilazane to give the cation of **5** causes a significant lengthening of the Si–N bond from 173.5 to 186 pm. Other tetravalent metal chlorides, such as $ZrCl_4$ and $SnCl_4$, also reacted with hexamethyldisilazane to yield bis(trimethylsilyl)ammonium salts. However, the constitution of the corresponding anions differs significantly. In the case of $ZrCl_4$, an anionic chlorotrimethylsilylimidozirconate (**6**) $[(Me_3Si)_2NH_2]_2^+$-$[\{Cl_3ZrCl_3Zr(Cl)(NSiMe_3)\}_2]^{2-}$ was obtained, while $SnCl_4$ reacted to give a novel spiro anion $[N(SnCl_3)_2(SnCl_2)_4$-$(NSiMe_3)_2(NH)_2]^-$ together with the bis(trimethylsilyl)ammonium ion in **7**; this anion is the first species containing a tetrastannylated nitrogen.

Keywords
NMR spectroscopy · silazanes · tin · titanium · zirconium

Introduction

Within the framework of a systematic investigation of nitrido bridges between main group elements and transition metals, we studied the reaction of disilazanes with metal chlorides. Recently, we obtained $[Cl_3Ti\{N(SiMe_2Cl)(SiMe_2NH_2)\}]$ (**1**) by the reaction of $ClMe_2SiNHSiMe_3$ with $TiCl_4$ [Eq. (1)].[1]

$$2\,\mathrm{ClMe_2SiNHSiMe_3} + \mathrm{TiCl_4} \longrightarrow \underset{\mathbf{1}}{[\mathrm{Cl_3Ti\{N(SiMe_2Cl)(SiMe_2NH_2)\}}]} + 2\,\mathrm{Me_3SiCl} \qquad (1)$$

Seyferth et al. have described a precursor with the supposed formula $[Me_3SiNHTiCl_3]$, which should be formed by the reaction of $Me_3SiNHSiMe_3$ with $TiCl_4$, and which might be valuable for the fabrication of thin films of titanium nitride on alumina substrates by a single dip–coat–fire sequence.[2] A detailed investigation concerning the structure and the mechanism of formation of this precursor also seems to be important for the development of novel precursor compounds for ceramics in the Ti–N–Si system. As an unexpected by-product of this reaction we have now synthesized the hitherto unknown bis(trimethylsilyl)ammonium salt $[(Me_3Si)_2NH_2]^+[Ti_2Cl_9]^-$ (**5**).

Results and Discussion

Dropwise addition of hexamethyldisilazane (HMDS, **2**) to a precooled solution of $TiCl_4$ in CH_2Cl_2 leads to the formation of a yellow solution from which a yellow solid precipitates after warming to RT. The solid, which mainly consists of $[(NH_4)_2TiCl_6]$, was removed by filtration. Partial evaporation of the solvent and cooling for several days at $-20\,^{\circ}C$ produced red crystals of $[(Me_3SiNTiCl_2)_8]\cdot 0.3\,CH_2Cl_2$ ($\mathbf{3}\cdot 0.3\,CH_2Cl_2$) [Eq. (2)].

$$8\,\underset{\mathbf{2}}{\mathrm{Me_3SiNHSiMe_3}} + 8\,\mathrm{TiCl_4} \longrightarrow \underset{\mathbf{3}}{[\mathrm{(Me_3SiNTiCl_2)_8}]} + 8\,\mathrm{Me_3SiCl} + 8\,\mathrm{HCl} \qquad (2)$$

An analysis of the crystal structure (Table 1) revealed an octameric trimethylsilylimido titanium dichloride (**3**). The monomeric units are linked by Cl bridges (Figure 1). Additional solvent molecules (CH_2Cl_2) were found in the crystal structure. An

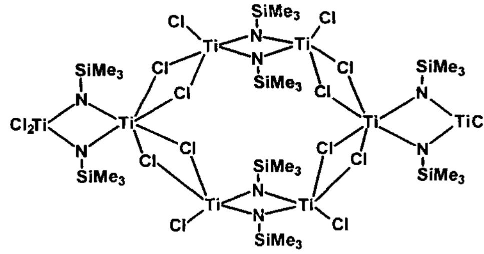

Figure 1. Octameric $[(Me_3SiNTiCl_2)_8]$ (**3**).

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Table 1. Details of the crystal structure analysis for **3**, **5**, **6**, and **7**. All data were obtained with a Siemens P4 four-circle diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm, graphite monochromator).

	3	**5**	**6**	**7**
formula	$C_{24}H_{72}Cl_{16}N_8Si_8Ti_8 \cdot 0.3\,CH_2Cl_2$	$C_6H_{20}Cl_9NSi_2Ti_2$	$C_{18}H_{54}Cl_{14}N_4Si_6Zr_4 \cdot 0.5\,CH_2Cl_2$	$C_{12}H_{40}Cl_{14}N_6Si_4Sn_6 \cdot 0.5\,CH_2Cl_2$
M_r	1648	577.26	1356.37	1589.30
crystal system	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/m$ (no. 11)	$P\bar{1}$ (no. 2)
a (pm)	1827.1(2)	1051.24(5)	1858.4(4)	1166.73(9)
b (pm)	2095.2(2)	1558.34(7)	1515.6(3)	1433.49(9)
c (pm)	2151.5(2)	1493.26(7)	2208.9(4)	1677.95(10)
α (°)				71.884(5)
β (°)	95.43(2)	110.215(4)	105.21(3)	71.139(5)
γ (°)				71.358(6)
V (10^6 pm^3)	8199.38	2295.6(2)	6003.6(21)	2448.0(3)
Z	4	4	4	2
ρ_{calcd} (g cm^{-3})	1.335	1.670	1.501	2.156
$F(000)$	3328	1152	2688	1496
absorption coefficient (mm^{-1})	1.53	1.837	1.436	3.89
T (K)	293	173	293	173
crystal size [mm^3]	$0.60 \times 0.40 \times 0.14$	$0.20 \times 0.25 \times 0.35$	$0.35 \times 0.25 \times 0.18$	$0.45 \times 0.25 \times 0.20$
range (°)	$2 \leq 2\theta \leq 55°$	$4 \leq 2\theta \leq 50°$	$3 \leq 2\theta \leq 50°$	$3 \leq 2\theta \leq 50°$
h,k,l	$-1 \leq h \leq 23$ $-1 \leq k \leq 27$ $-27 \leq l \leq 27$	$-1 \leq h \leq 12$ $-1 \leq k \leq 16$ $-17 \leq l \leq 17$	$-1 \leq h \leq 22$ $-1 \leq k \leq 18$ $-26 \leq l \leq 25$	$-1 \leq h \leq 13$ $-16 \leq k \leq 16$ $-19 \leq l \leq 19$
scan type	ω	ω	ω	ω
total no. reflns	21970	5017	12885	9910
independent reflns	18590 ($R_{int} = 0.056$)	3963 ($R_{int} = 0.020$)	10874 ($R_{int} = 0.038$)	8528 ($R_{int} = 0.031$)
observed reflns	6254 ($F_o \geq 3\sigma(F_o)$)	3961 ($F_o^2 \geq 0\sigma(F_o^2)$) (011, 002 suppressed)	10874 ($F_o^2 \geq 0\sigma(F_o^2)$)	8528 ($F_o^2 \geq 0\sigma(F_o^2)$)
refined parameters	567	148	404	384
corrections	Lorentz, polarization	Lorentz, polarization	Lorentz, polarization	Lorentz, polarization, extinction
absorption correction	empirical (ψ-scans)	empirical (ψ-scans)	empirical (ψ-scans)	empirical (ψ-scans)
min./max. transmission ratio	0.560/0.965	0.424/0.488	0.506/0.618	0.167/0.253
min./max. residual electron density [e Å^{-3}]	−0.86/1.77	−0.455/0.57	−0.951/1.648	−0.878/3.01
extinction coefficient	0.00008(2)			0.0040(2)
GOF	1.21	1.032	1.016	1.167
R indices (all data)	$R = 0.1143$ (against F_o) $wR = 0.0752$ ($w^{-1} = \sigma^2(F_o) + 0.000005\,F_o^2$)	$R1 = 0.0428$ $wR2 = 0.0703$	$R1 = 0.087$ ($F_o \geq 4\sigma(F_o)$) $wR2 = 0.2257$ ($F_o^2 \geq 2\sigma(F_o^2)$)	$R1 = 0.0388$ $wR2 = 0.0953$

analogous solvent-free compound has already been reported by Strähle et al. from the reaction of $(Me_3Si)_3N$ and $TiCl_4$ [Eq. (3)].[3] In both compounds the molecule **3** shows nearly the same conformation and coordination for all atoms; however, the packing of the molecules in the solid differs significantly.

$$8(Me_3Si)_3N + 8\,TiCl_4 \longrightarrow \underset{\mathbf{3}}{[(Me_3SiNTiCl_2)_8]} + 16\,Me_3SiCl \qquad (3)$$

Abstract in German: *Die Reaktion von Hexamethyldisilazan (HMDS) mit $TiCl_4$ in Dichlormethan führt zur Bildung von $[(Me_3SiNTiCl_2)_8]$ (**3**). Nach der Röntgenstrukturanalyse läßt sich **3** als oktameres Titan(trimethylsilylimid)chlorid beschreiben. Durch ^{14}N-NMR-Spektroskopie wurde der Reaktionsmechanismus untersucht und $[(Me_3Si)_2NTiCl_3]$ als Zwischenprodukt identifiziert. $[(NH_4)_2TiCl_6]$ und das bis jetzt unbekannte Bis(trimethylsilyl)ammonium-Salz $[(Me_3Si)_2NH_2]^+[Ti_2Cl_9]^-$ (**5**) sind Nebenprodukte dieser Reaktion. Die Protonierung von HMDS führt laut Röntgenstrukturanalyse im Kation von **5** zu einer signifikanten Verlängerung der Si–N Bindung von 173.5 auf 186 pm. Auch andere Chloride vierwertiger Metalle reagieren mit HMDS unter Bildung von Bis(trimethylsilyl)ammonium-Salzen. Im Falle von $ZrCl_4$ bildet sich das Chlortrimethylsilylimidozirconat $[\{(Me_3Si)_2NH_2\}]_2^+[\{Cl_3ZrCl_3Zr(Cl)(NSiMe_3)\}_2]^{2-}$ (**6**), und bei der Umsetzung von $SnCl_4$ mit HMDS entsteht **7**, das neben dem Bis(trimethylsilyl)ammonium-Ion das Spiro-Anion $[N(SnCl_3)_2(SnCl_2)_4(NSiMe_3)_2(NH)_2]^-$ enthält. Das Salz **7** ist das erste Beispiel für eine am Stickstoffatom tetrastannylierte Verbindung.*

Time-dependent ^{14}N NMR investigations (Figure 2) of the reaction between HMDS and $TiCl_4$ reveal the intermediate for-

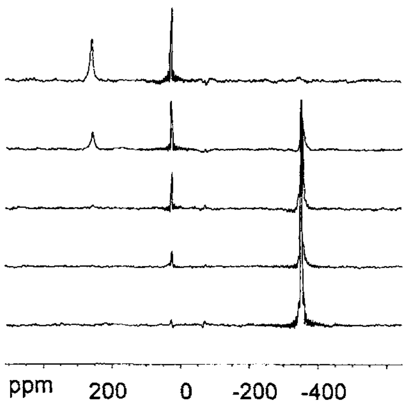

Figure 2. Time-dependent ^{14}N NMR spectra monitoring the reaction of HMDS and $TiCl_4$ (1:1) in CH_2Cl_2. $\delta = -353$ (HMDS), $+26$ $[\{(Me_3Si)_2NTiCl_3\}]$, $+264$ $[(Me_3SiNTiCl_2)_2]$. Measurements after 0, 4, 8, 12, and 16 minutes (from bottom to top).

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mation of $[(Me_3Si)_2NTiCl_3]$ (**4**) [Eq. (4)]. The unambiguous

$$Me_3SiNHSiMe_3 + TiCl_4 \longrightarrow \underset{\mathbf{4}}{[(Me_3Si)_2NTiCl_3]} + HCl \qquad (4)$$

identification of **4** by ^{14}N NMR was possible after a straightforward, independent synthesis of $[(Me_3Si)_2NTiCl_3]$ according to Equation (5).[4]

$$[(Me_3Si)_2N]_2Pb + 2TiCl_4 \longrightarrow PbCl_2 + 2\underset{\mathbf{4}}{[(Me_3Si)_2NTiCl_3]} \qquad (5)$$

In a subsequent reaction, **4** eliminates Me_3SiCl with formation of $[Me_3SiNTiCl_2]$, which is detectable by ^{14}N NMR after 10 min. However, spectroscopy did not reveal any evidence as to whether $[Me_3SiNTiCl_2]$ forms dimers or higher oligomers in solution. Solid-state ^{29}Si MAS NMR (Figure 3) of the octameric $[(Me_3SiNTiCl_2)_8]$ shows four broad signals which correspond to the eight distinguishable crystallographic Si sites in the solid, owing to the approximate mirror symmetry of the molecule **3**.

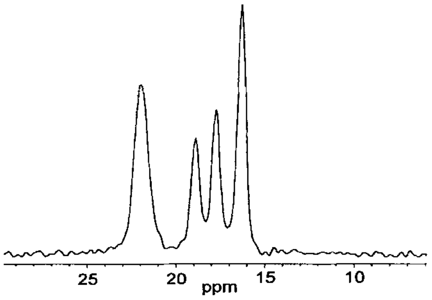


Figure 3. ^{29}Si CP MAS NMR spectrum (39.76 MHz) of $[(Me_3SiNTiCl_2)_8]$ ($3 \cdot CH_2Cl_2$) (ν_{rot} = 2.6 KHz, repetition time 4 s, contact time 4 ms, pulse length $^{29}Si/^1H$ 6 μs).

An essential by-product of the reaction between HMDS and $TiCl_4$ [Eq. (2)] is HCl; this leads to the formation of $[(NH_4)_2TiCl_6]$ in a side reaction [Eq. (6)]. A further by-product of the reaction between HMDS and $TiCl_4$ is the hitherto unknown bis(trimethylsilyl)ammonium salt **5**, which forms according to Equation (7). Yellow crystals of **5** were obtained approximately 15 min after combining an equimolar mixture of HMDS and $TiCl_4$ at −78 °C and warming to RT. The single crystals of **5** have to be isolated quickly after their formation as they are rather sensitive to moisture. Rapid transfer of the crystals to the four-circle diffractometer operating at −100 °C is necessary in order to avoid decomposition.

$$2Me_3SiNHSiMe_3 + 6HCl + TiCl_4 \longrightarrow [(NH_4)_2TiCl_6] + 4Me_3SiCl \qquad (6)$$

$$Me_3SiNHSiMe_3 + HCl + 2TiCl_4 \longrightarrow \underset{\mathbf{5}}{[(Me_3Si)_2NH_2]^+[Ti_2Cl_9]^-} \qquad (7)$$

According to the crystal structure analysis (Table 1), **5** contains the novel bis(trimethylsilyl)ammonium cations and $[Ti_2Cl_9]^-$ anions (Figure 4). The Si–N bonds in the cation (average 186 pm) are significantly lengthened compared to non-protonated $Me_3SiNHSiMe_3$ (173.5 pm).[5] Protonation of HMDS results in a positive polarization at N that leads to a significant destabilization of the Si–N single bonds (calculated length 180 pm).[6] As expected, the Si-N-Si angle in the cation (128.3(2)°) is slightly larger than that in HMDS (125.5(2)°).[5] The hydrogens on the nitrogen were located unambiguously by X-ray structure analysis. The solid-state ^{29}Si MAS NMR spectrum of **5** has one signal at $\delta = +32$ (Figure 5), the ^{29}Si nucleus is typically deshielded (e.g. δ of HMDS: +2.4) in the neighborhood of a quaternary nitrogen atom.

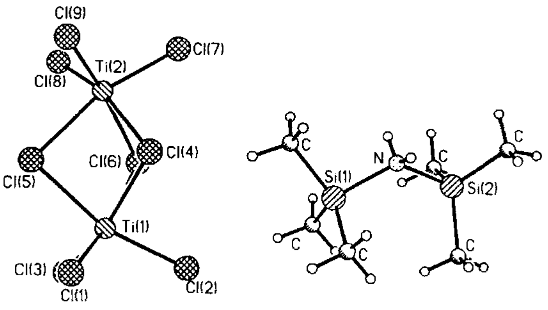


Figure 4. $[(Me_3Si)_2NH_2]^+$ and $[Ti_2Cl_9]^-$ ions of **5** in the solid state. Selected bond lengths (pm) and angles (°): Si–N 185.9(2) and 186.0(2), Si-N-Si 128.3(2); Ti–Cl_{term} 219.7(1)–222.5(1), Ti–Cl_{bridge} 248.0(1)–255.6(1). The hydrogen positions at N were located unambiguously during the X-ray structure analysis.

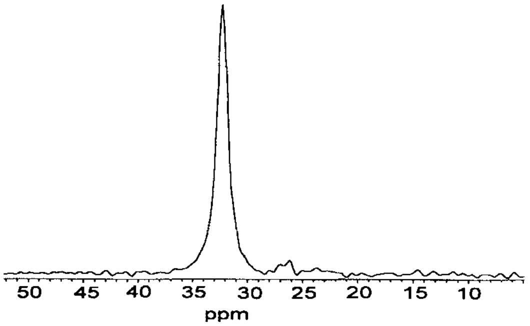


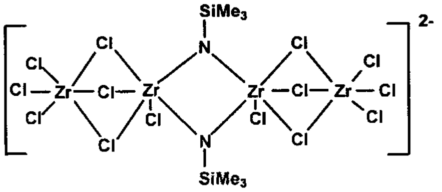
Figure 5. ^{29}Si CP MAS NMR spectrum (39.7 MHz) of $[(Me_3Si)_2NH_2]^+[Ti_2Cl_9]^-$ (**5**) (ν_{rot} = 2.6 KHz, repetition time 4 s, contact time 4 ms, pulse length $^{29}Si/^1H$ 6 μs).

There have been no reports in the literature of any evidence for the existence of bis(trimethylsilyl)ammonium salts. Thus, the question arose: is the formation of the salt **5** a unique peculiarity or is this reaction applicable to other metal chlorides? To our surprise, the reactions of HMDS with $ZrCl_4$ or even $SnCl_4$ also lead to the formation of novel bis(trimethylsilyl)-ammonium salts. However, the constitution of the corresponding anions differed significantly in each case.

Dropwise addition of HMDS to a suspension of $ZrCl_4$ and CH_2Cl_2 at room temperature lead to the formation of the bis(trimethylsilyl)ammonium salt **6** [Eq. (8)], which is obtained as colorless crystals.

$$\begin{aligned}4Me_3SiNHSiMe_3 + 4ZrCl_4 \longrightarrow {} & 2Me_3SiCl + \\ & \underset{\mathbf{6}}{[(Me_3Si)_2NH_2]_2^+[\{Cl_3ZrCl_3Zr(Cl)(NSiMe_3)\}_2]^{2-}}\end{aligned} \qquad (8)$$

According to the crystal structure analysis (Table 1), an anionic chlorotrimethylsilylimidozirconate anion is formed along with the $[(Me_3Si)_2NH_2]^+$ ions (Scheme 1, Figure 6). The four-membered ring $Zr_2(NSiMe_3)_2$, the central structural feature of the anion, and its μ-chloro bridges between Zr atoms show



Scheme 1. Structure of the anion in **6**.

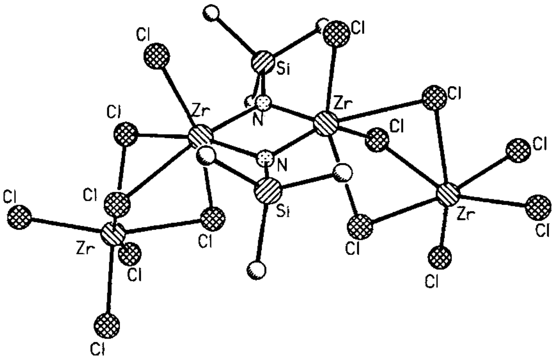


Figure 6. $[\{Cl_3ZrCl_3Zr(Cl)(NSiMe_3)\}_2]^{2-}$ ion in the crystal structure of **6**·$0.5CH_2Cl_2$.

similarities to **3**, obtained from the analogous reaction of HMDS with $TiCl_4$. Accordingly, the synthesis of **6** includes elements of the formation of both the octameric trimethylsilylimido titanium dichloride (**3**) and the bis(trimethylsilyl)ammonium salt (**5**).

Solid-state ^{29}Si MAS NMR spectroscopy of **6** (Figure 7) shows signals at $\delta = +32$ and -1.8 which, in accordance with **5**, must be attributed to the $[(Me_3Si)_2NH_2]^+$ ions ($\delta = 32$) and the $N(SiMe_3)$ groups in the anion ($\delta = -1.8$), respectively. In contrast to the uncharged octameric molecule **3**, the ^{29}Si nuclei in the anion of **6** are significantly shielded.

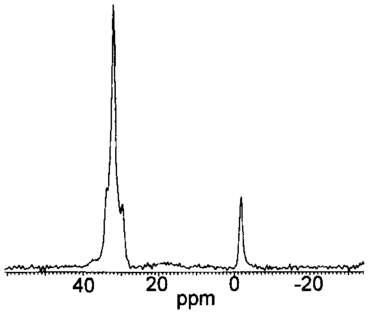
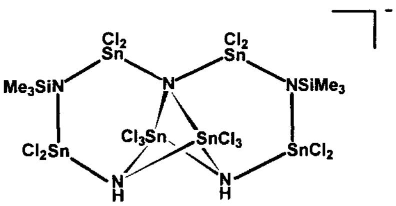


Figure 7. ^{29}Si CP MAS NMR spectrum (39.7 MHz) of $[(Me_3Si)_2NH_2]_2^+[\{Cl_3ZrCl_3Zr(Cl)(NSiMe_3)\}_2]^{2-}$ (**6**·$0.5\,CH_2Cl_2$); $\delta = +32$ ($[Me_3Si)_2NH_2]^+$), -1.8 ($NSiMe_3$) ($\nu_{rot} =$ 2.6 KHz, repetition time 4 s, contact time 4 ms, pulse length $^{29}Si/^1H$ 6 μs).

Not only did chlorides of tetravalent transition metals, such as $TiCl_4$ and $ZrCl_4$, yield bis(trimethylsilyl)ammonium salts during reaction with HMDS, but the main-group metal chloride $SnCl_4$ did as well. Dropwise addition of HMDS to a precooled solution of $SnCl_4$ in CH_2Cl_2 led to the precipitation of a white solid after warming to room temperature. After removal of the solid by-product by filtration, the solution was left to stand for several weeks to produce colorless crystals of **7** [Eq. (9)].

$$6\,Me_3SiNHSiMe_3 + 6\,SnCl_4 \longrightarrow 8\,Me_3SiCl + 2\,HCl + \underset{\mathbf{7}}{[(Me_3Si)_2NH_2]^+[N(SnCl_3)_2(SnCl_2)_4(NSiMe_3)_2(NH)_2]^-} \quad (9)$$

The crystal structure analysis (Table 1) revealed a novel spiro anion (Scheme 2, Figure 8), together with $[(Me_3Si)_2NH_2]^+$ ions. The rings of the anion are formed by alternating Sn and N atoms. The resulting distances Sn–N (200.0(6) to 229.4(6) pm) are comparable to Sn–N single bonds (214 pm).[7] Both $NSiMe_3$ groups represent fragments of the starting material HMDS.



Scheme 2. Structure of the spiro anion in **7**.

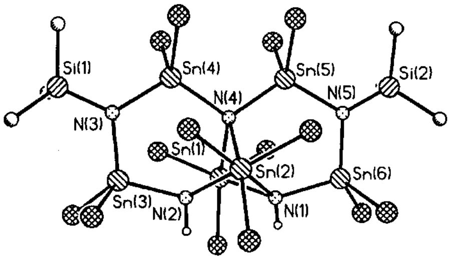


Figure 8. Complex spiro anion in **7**. Selected bond lengths (pm): N 4–$SnCl_2$ 208.7(6) and 209.0(6), N 4–$SnCl_3$ 226.9(6) and 229.4(6), N 3–$SnCl_2$ 200.0(6) and 200.8(7), N 5–$SnCl_2$ 200.2(7) and 200.8(7), N 1–$SnCl_2$ 206.6(6), N 1–$SnCl_3$ 217.3(6) and 219.2(6), N 2–$SnCl_2$ 205.4(6), N 2–$SnCl_3$ 217.9(6) and 219.3(6), N 3–$SiMe_3$ 176.9(6), N 5 $SiMe_3$ 176.9(7), Sn–Cl 230.0(2) to 239.6(2), $Cl_3Sn\cdots SnCl_3$ 309.1(1).

The quaternary nitrogen atoms N 1, N 2, and N 4 possess a formal positive charge (ammonium) and are not directly bound to Si. Nevertheless, all of them must have been formed by substitution of $SnCl_2$ and $SnCl_3$ groups to $Me_3SiNHSiMe_3$ under complete elimination of Me_3SiCl during the complex formation of the spiro anion. Accordingly, HMDS acts as a synthon for nitrogen in the framework of alternating Sn and N atoms of the anion. To the best of our knowledge compound **7** represents the first example of a tetrastannylated nitrogen.

Conclusion

For the first time, firm evidence for the existence of bis(trimethylsilyl)ammonium salts has been obtained. The formation of this cation, which had remained unnoticed in the reaction between hexamethyldisilazane and $TiCl_4$,[8] has been investigated thoroughly. An essential prerequisite for the synthesis of the $[(Me_3Si)_2NH_2]^+$ ions seems to be the elimination of HCl during the initial reaction of $TiCl_4$ with $(Me_3Si)_2NH$. Apparently, the insolubility of the solid bis(trimethylsilyl)ammonium salt is a further prerequisite for its formation, while $[(Me_3Si)_2NH_2]^+$ would presumably deprotonate in solution. According to our results, the bis(trimethylsilyl)ammonium salts only form during the reaction between HMDS and an appropriate metal chloride (e.g. $TiCl_4$, $ZrCl_4$, $SnCl_4$), while a simple reaction of HMDS with an acid did not yield them. Essentially, the metal chloride must be able to form stable chloro complexes. However, the formation of strong bonds between the metal and nitrogen competes with the metal–Cl bonds. In the case of $SnCl_4$, Sn–N bond formation gave quaternary N (ammonium). This represents the first tetrastannylated nitrogen.

No evidence for the existence of simple silylammonium ions with the formula $[(R_3Si)_nNH_{(4-n)}]^+$ with $n = 1-4$ has been obtained in the past.[9] Obviously, Me_3SiNH_2 is too unstable to undergo protonation and easily forms HMDS,[10] while in the case of $(Me_3Si)_3N$ the gain in energy on formation of the ammonium ion is small with respect to the energetically unfavorable increase in steric repulsion.

Recently, the first bis(trimethylstannyl)ammonium salt $[(Me_3Sn)_2NH_2]^+[SnMe_3Cl_2]^-$ has been characterized.[11]

Experimental Section

General techniques: All reactions were performed under Ar with standard Schlenk techniques. CH_2Cl_2 was refluxed with P_4O_{10} and distilled prior to use. ^{14}N NMR spectra were recorded at 18.1 MHz on a Bruker ARX250 spectrometer and are referenced to neat CH_3NO_2 as an external reference. ^{29}Si and ^{13}C NMR spectra were recorded at 49.7 MHz and 62.9 MHz, respectively, on the same spectrometer and are referenced to TMS as an external standard. ^{29}Si CPMAS NMR spectra were recorded at 39.76 MHz on a Bruker MSL 200 and are referenced to TMS as an external standard. Infrared spectra were obtained on a FT–IR Bruker IFS 66v spectrometer (KBr pellets).

$[(Me_3SiNTiCl_2)_8]$ (3): Hexamethyldisilazane (8.6 g, 54 mmol) was added dropwise at −78 °C to a solution of $TiCl_4$ (10.4 g, 54 mmol) in CH_2Cl_2 (50 mL). The mixture was allowed to warm to RT and the yellow precipitate was removed by filtration. The filtrate was concentrated to 30 mL and red crystals were obtained from the solution at −20 °C. After recrystallization from CH_2Cl_2 **3** (5.2 g, 3.1 mmol) was isolated in 47% yield. ^1H NMR (CD_2Cl_2): $\delta = 0.42$ (s); ^{13}C NMR (CD_2Cl_2): $\delta = 1.67$ (s); ^{14}N NMR (CD_2Cl_2): $\delta = 264$ (s); ^{29}Si NMR (CD_2Cl_2, 37 °C): $\delta = 16$ (s); IR (KBr, 4000–400 cm^{-1}): $\tilde{\nu} = 2958/2898$ (w, ν CH_3), 1409 (w, δ_{as} H_3C–Si), 1252 (s, δ_s H_3C–Si), 843 (vs, ρ C–Si), 820 (vs, ν Si–N–Ti), 764 (s, ρ Me–Si), 664 s (ν_{as} SiC_3), 438/478 cm^{-1} (w, ν Ti–Cl).

Time-dependent ^{14}N NMR investigation: Hexamethyldisilazane (64 mg, 0.4 mmol) was added at −78 °C to a solution of $TiCl_4$ (86 mg, 0.45 mmol) in CH_2Cl_2 (1 mL). The mixture was allowed to warm to RT for a few minutes and then measurements were started and repeated every 4 minutes.

$[(Me_3Si)_2NH_2]^+[Ti_2Cl_9]^-$ (5): Hexamethyldisilazane (0.45 g, 2.7 mmol) was added dropwise at −78 °C to a solution of $TiCl_4$ (0.5 g, 2.7 mmol) in CH_2Cl_2 (1.5 mL). The mixture was allowed to warm to RT without stirring. The solution was then cooled to −78 °C for a few minutes. After repeating this procedure twice, yellow crystals were obtained. The solution was decanted quickly and the crystals were dried. Yield: 0.5 g, 0.8 mmol, 57% of **5**. IR (KBr, 4000–400 cm^{-1}): $\tilde{\nu} = 3187/3155$ (s, ν NH_2), 2960 (w, ν CH_3), 1526 (w, δ NH_2), 1403 (w, δ_{as} H_3C–Si), 1264 (s, δ_s H_3C–Si), 850 (vs, ρ C–Si), 761 (s, ρ Me–Si), 421/441 cm^{-1} (w, ν Ti–Cl); anal. calcd for $[(Me_3Si)_2NH_2]^+[Ti_2Cl_9]^-$ (577.26): C 12.41, N 2.43, Cl 55.19, Ti 16.58, Si 9.7; found C 13.1, N 2.71, Cl 55.4, Ti 15.9, Si 9.06.

$[(Me_3Si)_2NH_2]_2^+[\{Cl_3ZrCl_3Zr(Cl)(NSiMe_3)\}_2]^{2-}$ (6): Hexamethyldisilazane (1.4 g, 8.5 mmol) was added dropwise to a suspension of $ZrCl_4$ (2 g, 8.5 mmol) in CH_2Cl_2 (14 mL). The mixture was stirred at RT for 24 h and the white precipitate was removed by filtration. Crystals were obtained from the solution after several weeks at RT. After isolation of the crystals, the filtrate was concentrated to 7 mL and **6** was finally obtained (0.5 g, 0.4 mmol) in 20% yield. IR (KBr, 4000–400 cm^{-1}): $\tilde{\nu} = 3153$ (m, ν NH_2), 2958 (w, ν CH_3), 1526 (w, δ NH_2), 1404 (w, δ_{as} H_3C–Si), 1266 (s, δ_s H_3C–Si), 845 (vs, ρ C–Si), 870 (s, ν Si-N-Zr), 746 (s, ρ Me–Si), 651 (s, ν SiC_3), 420 cm^{-1} (w, ν Zr–Cl).

$[(Me_3Si)_2NH_2]^+[N(SnCl_3)_2(SnCl_2)_4(NSiMe_3)_2(NH)_2]^-$ (7): Hexamethyldisilazane (2.3 g, 14 mmol) was added dropwise at −78 °C to a solution of $SnCl_4$ (3.6 g, 14 mmol) in CH_2Cl_2 (14 mL). The mixture was allowed to warm to RT and the white precipitate was removed by filtration. Crystals were obtained from the solution after several weeks at RT. After isolation of the crystals, the filtrate was concentrated to 5 mL and **7** was obtained (0.2 g, 0.1 mmol) in 10% yield. IR (KBr, 4000–400 cm^{-1}): $\tilde{\nu} = 3226/3200$ (s, ν NH_2), 2953 (w, ν CH_3), 1523 (w, δ NH_2), 1415 (w, δ_{as} H_3C–Si), 1254 (s, δ_s H_3C–Si), 845 (vs, ρ C–Si), 657 (s, ν SiC_3), 605 (w, ν_{as} N–Sn), 458 cm^{-1} (s, ν_s N–Sn).

Crystal structure determination (see also Table 1): Crystals of **3**, **5**, **6**, and **7** were sealed in a glass capillary under inert gas (Ar). The final unit cell parameters were refined on the basis of at least 40 high angle reflections, equally distributed in the reciprocal space. All structures were solved by applying direct methods using the programs SHELXTL V. 5.03 (**5**, **6**, **7**) and SHELXTL-PLUS V. 4.2 (**3**). The crystal structures were refined by full-matrix least-squares against F^2 using SHELXTL V. 5.03 (**5**, **6**, and **7**) and against F for compound **3** (SHELXTL-PLUS V. 4.2). The hydrogen atoms on the nitrogens of the anion in **7** and the cation in **5** were located by difference Fourier syntheses. The remaining hydrogens were calculated in ideal positions. All hydrogens were refined with fixed U values by means of the riding model. The non-hydrogen atoms, except those which are in split positions, and the C atoms C 7, C 14, C 19, C 21–C 24 in compound **3** were refined with anisotropic temperature factors. Because of disorder in the anion, the cation, and in the solvent molecules of compound **6**, the quality of the reflection data was poor. Therefore, despite the unequivocally correct molecular topology and conformation, we will not discuss the bond lengths and bond angles.

Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany) on quoting the depository numbers CSD-406592 (**3**), CSD-405897 (**5**), CSD-406590 (**6**), and CSD-406591 (**7**), respectively.

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