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Unexpected Disproportionation of Tetramethylethylenediamine-Supported Perchlorodisilane $Cl_3SiSiCl_3$

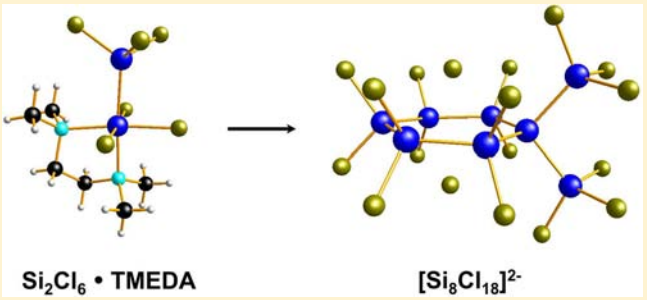
Jan Tillmann,[†] Frank Meyer-Wegner,[†] Andor Nadj,[†] Johanna Becker-Baldus,[‡] Tanja Sinke,[†] Michael Bolte,[†] Max C. Holthausen,[†] Matthias Wagner,[†] and Hans-Wolfram Lerner*[,†]

[†]Institut für Anorganische Chemie, Goethe-Universität Frankfurt am Main, Max-von-Laue-Straße 7, 60438 Frankfurt am Main, Germany

[‡]Institut für Biophysikalische Chemie, Goethe-Universität Frankfurt am Main, Max-von-Laue-Straße 9, 60438 Frankfurt am Main, Germany

Supporting Information

ABSTRACT: The addition compound $Cl_3SiSiCl_3$·TMEDA was formed quantitatively by treatment of $Cl_3SiSiCl_3$ with tetramethylethylenediamine (TMEDA) in pentane at room temperature. The crystal structure of $Cl_3SiSiCl_3$·TMEDA displays one tetrahedrally and one octahedrally bonded Si atom (monoclinic, $P2_1/n$). ^{29}Si CP/MAS NMR spectroscopy confirms this structure. Density functional theory (DFT) calculations have shown that the structure of the *meridional* isomer of $Cl_3SiSiCl_3$·TMEDA is 6.3 kcal lower in energy than that of *facial* coordinate species. Dissolving of $Cl_3SiSiCl_3$·TMEDA in CH_2Cl_2 resulted in an immediate reaction by which oligochlorosilanes Si_nCl_{2n} (n = 4, 6, 8, 10; precipitate) and the Cl^--complexed dianions $[Si_nCl_{2n+2}]^{2-}$ (n = 6, 8, 10, 12; CH_2Cl_2 extract) were formed. The constitutions of these compounds were confirmed by MALDI mass spectrometry. Additionally, single crystals of $[Me_3NCH_2CH_2NMe_2]_2[Si_6Cl_{14}]$ and $[Me_3NCH_2CH_2NMe_2]_2[Si_8Cl_{18}]$ were obtained from the CH_2Cl_2 extract. We found that $Cl_3SiSiCl_3$·TMEDA reacts with MeCl, forming $MeSiCl_3$ and the products that had been formed in the reaction of $Cl_3SiSiCl_3$·TMEDA with CH_2Cl_2. X-ray structure analysis indicates that the structures of $[Me_3NCH_2CH_2NMe_2]_2[Si_6Cl_{14}]$ (monoclinic, $P2_1/n$) and $[Me_3NCH_2CH_2NMe_2]_2[Si_8Cl_{18}]$ (monoclinic, $P2_1/n$) contain dianions adopting an "inverse sandwich" structure with inverse polarity and $[Me_3NCH_2CH_2NMe_2]^+$ as countercations. Single crystals of $SiCl_4$·TMEDA (monoclinic, Cc) could be isolated by thermolysis reaction of $Cl_3SiSiCl_3$·TMEDA (50 °C) in tetrahydrofuran (THF).



INTRODUCTION

Over the past decades the disproportionation reaction of Si_2Cl_6 (**1**) which gives the perchlorinated neopentasilane $Si(SiCl_3)_4$ (**2**) and $SiCl_4$ has been widely investigated.[1−5] However, although this reaction has been known for 60 years, its mechanism has still not yet been fully understood, and no hard evidence regarding the nature of the intermediates exists. Very recently we have repeated the reaction of **1** with NR_3 (R = Me, Et) and found it fully reproducible.[6] Moreover, we were able to monitor the course of the reaction between **1** and NMe_2Et by means of low-temperature two-dimensional heteronuclear correlation spectroscopy (HETCOR) experiments. We found that a resonance at 42.7 ppm in the $^1H/^{29}Si$ 2D spectrum shows a correlation with the methyl protons of NMe_2Et which could be attributed to the Si nuclei of $SiCl_2$·NMe_2Et. Additionally, we calculated the energy barriers of the base-free and the base-catalyzed liberation of $SiCl_2$ from **1**. For the base-free formation of $SiCl_2$, the calculated activation energy of about 50 kcal mol^{-1} is prohibitively high. In the base-catalyzed case, we found a first small barrier associated with the coordination of NMe_3 to the disilane **1**. The subsequent transition state for the disproportionation of the disilane **1** possesses a moderately high energy and lies well below the transition state of the corresponding base-free reaction. We therefore come to the conclusion that the key intermediate of the disproportionation of **1** is the amine-complexed dichlorosilylene and no free silylene[7] will be formed in this reaction.[6]

It should be noted here that the course of the reaction of **1** with pyridine is different compared to the disproportionation of **1** with NMe_3. When using equimolar equivalents of reactants, treatment of **1** with pyridine yielded the disilylated 1,4-dihydropyridine **3**, and in this reaction no perchlorinated neopentasilane **2** was formed (Scheme 1).[8,9] Obviously, a polarization of the central Si−Si bond of **1** had taken place. The positively and negatively-charged fragments of **1**, $Cl_3Si^+\cdots{}^-SiCl_3$, which had been formed, apparently underwent an addition reaction to the pyridine ring to give the disilylated 1,4-dihydropyridine **3**. We had verified the constitution of **3** by HETCOR NMR spectroscopy.[9]

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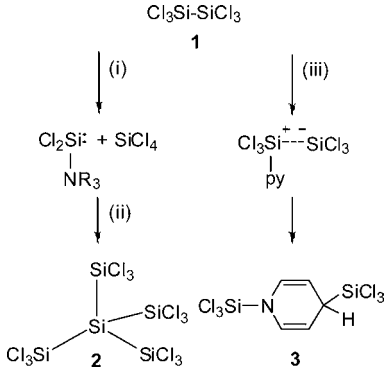
Scheme 1. Reactivity of $Cl_3SiSiCl_3$ (1) Towards NR_3 (R = Me, Et) and Pyridine



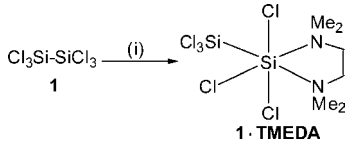
(i) $+NR_3$ (R = Me, Et) in pentane at −10 °C. (ii) × 3, $+Si_2Cl_6$, $-SiCl_4$, $-NR_3$. (iii) +pyridine in benzene at room temperature.

In this paper we report the reaction of **1** with tetramethylethylenediamine (TMEDA). The structural features of **1·TMEDA** and its disproportionation behavior have been investigated. In addition we present here the structures of Cl^--complexed dianions $[Si_nCl_{2n+2}]^{2-}$ (n = 6, 8).

RESULTS AND DISCUSSION

Synthesis of 1·TMEDA. When **1** in benzene was treated with the bidentate TMEDA at room temperature, no neopentasilane **2** was formed; however, TMEDA-complexed disilane **1** could be isolated as a white solid (Scheme 2). The

Scheme 2. Synthesis of $Cl_3SiSiCl_3$·TMEDA (1·TMEDA)



(i) +TMEDA, in pentane at room temperature.

addition compound **1·TMEDA** was unambiguously identified by solid-state ^{29}Si NMR spectroscopy (Figure 1) and single crystal X-ray diffraction (Figure 2). We found that **1·TMEDA** is poorly soluble in hydrocarbons such as pentane, hexane, benzene, or toluene, and in diethyl ether and tetrahydrofuran

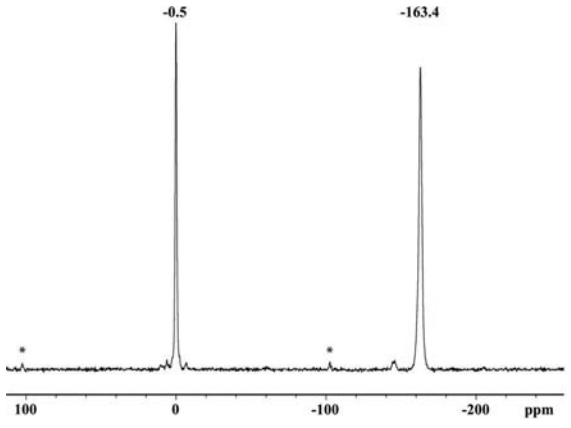


Figure 1. ^{29}Si CP/MAS NMR spectrum $Cl_3SiSiCl_3$·TMEDA (**1·TMEDA**).

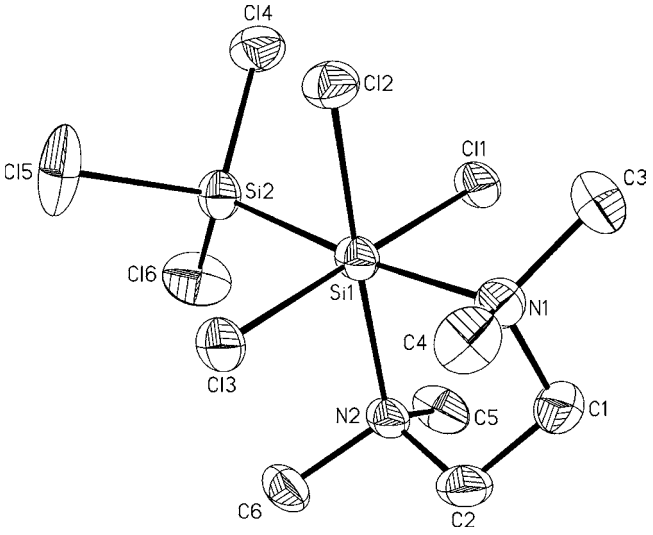


Figure 2. Solid-state structure of $Cl_3SiSiCl_3$·TMEDA. (**1·TMEDA**) (monoclinic, $P2_1/n$). Displacement ellipsoids are drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Si(1)−N(1) = 2.064(5), Si(1)−N(2) = 2.113(5), Si(1)−Cl(3) = 2.176(2), Si(1)−Cl(1) = 2.1929(19), Si(1)−Cl(2) = 2.194(2), Si(1)−Si(2) = 2.405(2), Si(2)−Cl(5) = 2.052(2), Si(2)−Cl(6) = 2.062(3), Si(2)−Cl(4) = 2.073(3); N(1)−Si(1)−N(2) = 84.7(2), N(1)−Si(1)−Cl(3) = 92.66(15), N(2)−Si(1)−Cl(3) = 88.48(14), N(1)−Si(1)−Cl(1) = 88.73(15), N(2)−Si(1)−Cl(1) = 89.68(14), Cl(3)−Si(1)−Cl(1) = 177.58(12), N(1)−Si(1)−Cl(2) = 90.23(17), N(2)−Si(1)−Cl(2) = 174.58(17), Cl(3)−Si(1)−Cl(2) = 89.75(8), Cl(1)−Si(1)−Cl(2) = 92.22(9), N(1)−Si(1)−Si(2) = 174.24(17), N(2)−Si(1)−Si(2) = 98.80(16), Cl(3)−Si(1)−Si(2) = 91.99(8), Cl(1)−Si(1)−Si(2) = 86.74(8), Cl(2)−Si(1)−Si(2) = 86.38(9).

(THF). Single crystals of **1·TMEDA** could be obtained by gas-phase diffusion of hexachlorodisilane and TMEDA. Overall, the analytical data that we found are in good agreement with this structure. The ^{29}Si CP/MAS spectrum of **1·TMEDA** features a resonance at −0.5 ppm which is typical of tetracoordinate silicon atoms and a signal at −163.5 ppm which is in the range found for hexacoordinate silicon atoms. The mass spectrum revealed a peak which could be assigned to **1·TMEDA**. The element ratio has also been confirmed by a combustion analysis.

Reactivity of 1·TMEDA. Surprisingly, the disproportionation of TMEDA-supported **1** in CH_2Cl_2, as shown in Schemes 3, 4, and 5, is quite different from the corresponding reaction of **1** and monodentate organyl-substituted amines NR_3 (R = Me, Et).[6] We observed that dissolving of **1·TMEDA** in CH_2Cl_2 resulted in an immediate reaction and after 1 min the mixture became heterogeneous. Peaks were found in the MALDI$^+$ mass spectrum of the precipitate which could be assigned to the oligochlorosilanes Si_nCl_{2n} (n = 4, 6, 8, 10) whereas the MALDI$^-$ mass spectrum of the solution revealed peaks of oligochlorosilyl dianions $[\mathbf{4a}]^{2-}$, $[\mathbf{4b}]^{2-}$, $[Si_{10}Cl_{22}]^{2-}$, and $[Si_{12}Cl_{26}]^{2-}$ (Scheme 3). In addition we obtained single crystals of $[Me_3NCH_2CH_2NMe_2]_2[\mathbf{4a}]$ and $[Me_3NCH_2CH_2NMe_2]_2[\mathbf{4b}]$ from the CH_2Cl_2 extract. In this context it should be noted that TMEDA reacts with CH_2Cl_2 to give the tetraalkylammonium chlorides **5** and **6**, as shown in Scheme 5.[10] Both compounds are MeCl sources and therefore they are able to transform TMEDA into $[Me_3NCH_2CH_2NMe_2]Cl$. To prove this suggestion, the

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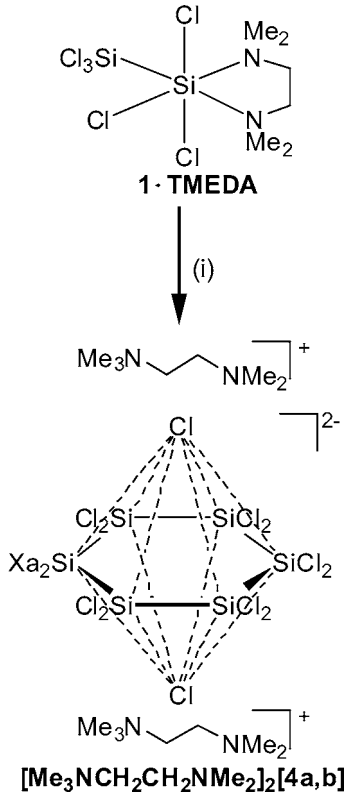
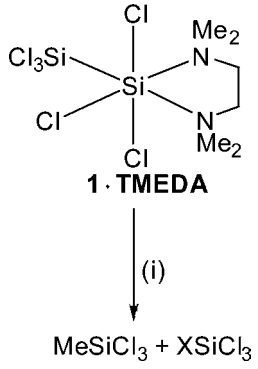
Scheme 3. Main Reaction of Si_2Cl_6·TMEDA (1·TMEDA) with MeCl (80%) or with $[Me_3NCH_2CH_2NMe_2]Cl$



(i) +MeCl/+$[Me_3NCH_2CH_2NMe_2]Cl$, $-SiCl_4$, −TMEDA, at −78 °C; $[4a]^{2-}$ ($[Si_6Cl_{14}]^{2-}$, Xa = Cl); $[4b]^{2-}$ ($[Si_8Cl_{18}]^{2-}$, Xa = $SiCl_3$).

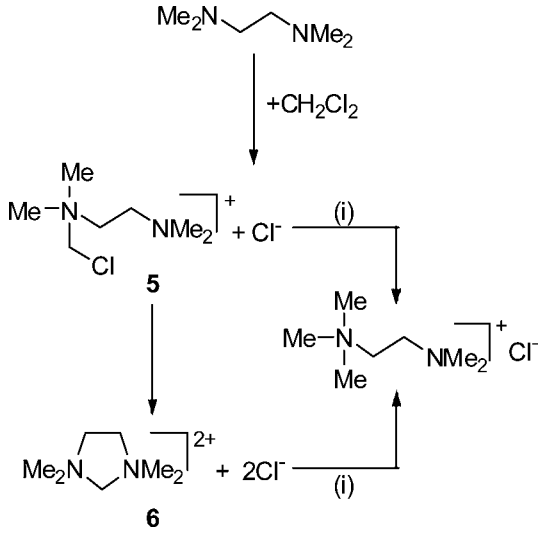
Scheme 4. Side Reaction of Si_2Cl_6·TMEDA (1·TMEDA) with MeX (X = Cl, I) (20%)



(i) +MeX (X = Cl, I), at −78 °C.

reaction of **1·TMEDA** with MeCl was also investigated. We found that the TMEDA-supported disilane **1·TMEDA** reacts with MeCl, forming $MeSiCl_3$ and the same products that had been formed in the reaction of **1·TMEDA** with CH_2Cl_2 (Scheme 3 and 4). The products were identified by MALDI mass spectrometry, ^{29}Si NMR spectroscopy, and X-ray diffraction. The signal of $MeSiCl_3$ in the ^{29}Si NMR spectrum of the reaction solution of **1·TMEDA** with MeCl could be recognized unambiguously. Now the question arises whether $MeSiCl_3$ is formed from MeCl and $SiCl_3^-$ by nucleophilic substitution or from MeCl and $SiCl_2$ by silylene insertion. To get more insight we decided to examine additionally the

Scheme 5. Generation of $[Me_3NCH_2CH_2NMe_2]Cl$ and the MeCl Sources, the Tetraalkylammonium Chlorides 5 and 6, by the Reaction of TMEDA with CH_2Cl_2



(i) +TMEDA, $-C_6H_{15}ClN_2$.

behavior of **1·TMEDA** toward MeI. In neat MeI the decomposition of **1·TMEDA** yielded $MeSiCl_3$ along with other oligochlorosilanes.[11] The formation of $MeSiCl_3$ indicates an "ionic" mechanism in the disproportionation of **1·TMEDA** which was found in the pyridine-induced decomposition of **1**.

Reaction of **1·TMEDA** with Me_3SiN_3 and subsequent treatment with LiMe yielded the silanimine dimer $(Me_2SiNSiMe_3)_2$ (**9**)[12] and the silatetrazoline $Me_2Si{=}N\text{-}SiMe_3$ × Me_3SiN_3 (**11**)[12−14] together with a number of unknown compounds. Both literature-known compounds, the silanimine dimer **9** and the silatetrazoline **11**, were identified by NMR spectroscopy and gas chromatography mass spectrometry (GC-MS). In this reaction obviously a heterolytic cleavage of the Si−Si bond of **1·TMEDA** with liberation of $SiCl_3^-$ had taken place. As depicted in Scheme 6, the transient silyl anion $SiCl_3^-$, which had been formed, apparently underwent a Staudinger-like reaction to give the silanimine **7** which dimerizes[15] to **8** or reacts with abundant Me_3SiN_3 by [2 + 3] cycloaddition[14] to the silatetrazoline **10**. A similar sequence was found by the reactions of the silanides $NaSiRtBu_2$ (R = *t*Bu, Ph)[16,17] with the silylazides tBu_2XSiN_3 (X = halogen).[17,18] The reaction of LiMe with dimeric silanimine **8** and the silatetrazoline **10** yielded the methyl derivatives **9** and **11**, respectively (Scheme 6).

It is worth to mention that by heating the hexachlorodisilane **1** in the presence of 10 mol % **1·TMEDA**, the neopentasilane **2** can be synthesized as well. It is remarkable that the disilane **1** was transformed to the neopentasilane **2** by a catalytical amount of the adduct **1·TMEDA** (Scheme 7).

The addition compound **1·TMEDA** can be stored without significant decomposition under an inert gas atmosphere for several weeks at room temperature. However, by heating a mixture of **1·TMEDA** and THF to 50 °C we isolated the 1:1 adduct of $SiCl_4$ with TMEDA. This result was also confirmed by X-ray crystallography. Obviously, over the period of heating the addition compound **1·TMEDA** underwent a disproportionation reaction to give $SiCl_4$ and dichlorosilylene. However, the dichlorosilylene seems to be instable in the presence of THF and decomposes into several Cl−Si bonds containing

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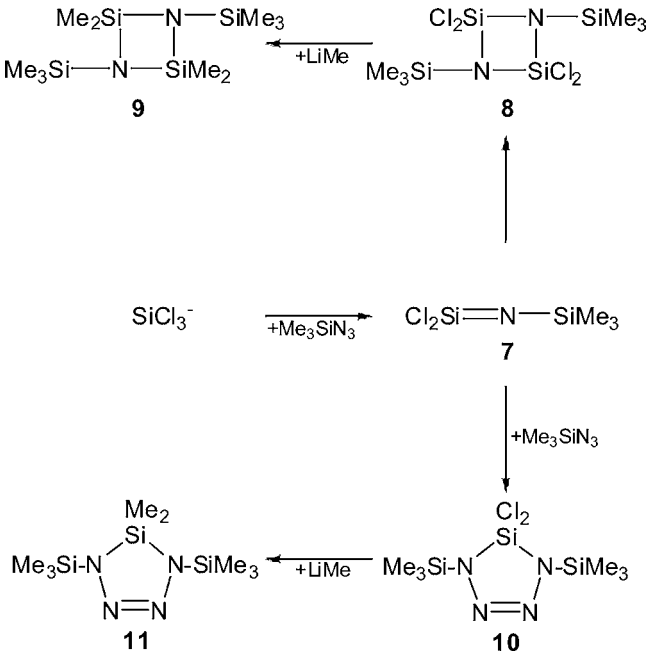
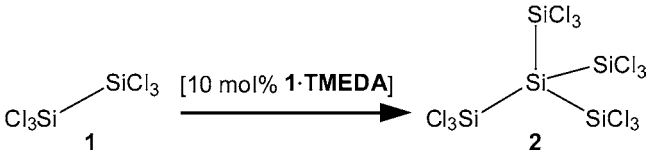
Scheme 6. Reactivity of $SiCl_3^-$ Generated from 1·TMEDA Towards Me_3SiN_3



Scheme 7. Synthesis of the Perchlorinated Neopentasilane 2



compounds. Therefore the poorly soluble complex $SiCl_4$·TMEDA could be crystallized as the only isolable compound of this reaction.

X-ray quality crystals of **1·TMEDA** were obtained by gas-phase diffusion of disilane **1** and TMEDA. Figure 2 represents the molecular structure of **1·TMEDA** (monoclinic, $P2_1/n$); the selected bond lengths and angles are listed in the figure caption. The solid-state structure of **1·TMEDA** reveals one tetrahedrally and one octahedrally bonded Si atom in which the six-coordinate Si atom is chelated by TMEDA. The calculated values of the *meridional* isomer are in good agreement with those found in the solid-state structure (Table 1). The DFT calculations indicate that the *facial* structure of **1·TMEDA** is energetically disfavored (Figure 3). In this context it should be noted that structures of disilanes are rare which reveals one tetrahedrally and one octahedrally bonded Si atom. The only structurally characterized example which can be found in the

Table 1. Selected Averaged Bond Lengths [Å] for Disilanes with One Tetrahedrally and One Octahedrally Bonded Si Atom, Si_2Cl_6·TMEDA (1·TMEDA) and $Si_2Me_2Cl_4$·2,2′-bipy[19]

	Si–Si	Si[c]–Cl	Si[d]–Cl
mer-**1·TMEDA**[a]	2.405 Å	2.188 Å	2.062 Å
mer-**1·TMEDA**[b]	2.410 Å	2.196 Å	2.090 Å
fac-**1·TMEDA**[b]	2.560 Å	2.172 Å	2.110 Å
fac-$Si_2Me_2Cl_4$·2,2′-bipy[a],[19]	2.367 Å	2.333 Å	2.081 Å

[a]X-ray structure analysis. [b]Calculated. [c]Octahedral. [d]Tetrahedral.

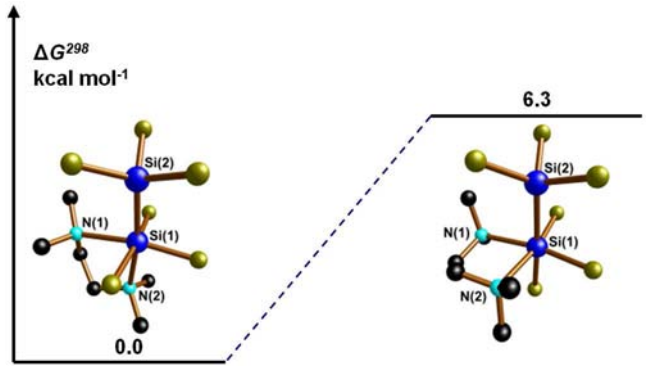


Figure 3. Calculated structures of *meridional* and *facial* isomers of $Cl_3SiSiCl_3$·TMEDA (**1·TMEDA**).

CCDC displays an octahedrally bonded Si atom as found in the *facial* isomer of **1·TMEDA**.[19] In contrast to the solid-state structure of *meridional* **1·TMEDA** the N atoms of the chelate ligand are *cis*-coordinated to the silyl substituent.

Crystals of $[Me_3NCH_2CH_2NMe_2]_2[4a]$ and $[Me_3NCH_2CH_2NMe_2]_2[4b]$ were grown from methylene chloride at room temperature. X-ray structure analysis indicates that both compounds contain dianions adopting an "inverse sandwich" structure,[20] however, with inverse polarity and $Me_3NCH_2CH_2NMe_2^+$ as countercations (Figures 4 and 5). The central structure motif of $[Me_3NCH_2CH_2NMe_2]_2[4a]$ and $[Me_3NCH_2CH_2NMe_2]_2[4b]$ consists of planar Lewis acidic Si_6 rings coordinated by Cl^- as Lewis base. This motif is similar to those of a series of Si_6-ring compounds which have been structurally characterized by Boudjouk and co-workers.[21,22] In contrast to $[Me_3NCH_2CH_2NMe_2]_2[4b]$ the complex $[Me_3NCH_2CH_2NMe_2]_2[4a]$ has an inversion center in the middle of the Si_6 ring. It is interesting to note that for both complexes, $[Me_3NCH_2CH_2NMe_2]_2[4a]$ and $[Me_3NCH_2CH_2NMe_2]_2[4b]$, the Si–Si distances in the Si_6 ring were 2.32–2.34 Å and feature very small deviations. The Si–Si–Si angles in both compounds are nearly 120°, giving a planar hexagonal Si_6 ring. One of the most interesting features of these dianions is the strong interaction between the Si_6 ring and the apical halides. The contacts between the Si atoms and the apical Cl^- anions in both complexes are very similar (averaged Si–Cl contacts: 3.020 Å in $[Me_3NCH_2CH_2NMe_2]_2[4a]$, 3.014 Å in $[Me_3NCH_2CH_2NMe_2]_2[4b]$). These distances are significantly shorter than a typical Si–Cl van der Waals bond (3.9 Å) but longer than the sum of the covalent radii (2.16 Å).[23] Apparently the Si–Cl interactions play a key role in the ring formation. The formation of the unsymmetrically substituted ring in the dianion $[4b]^{2-}$ can be explained by a $SiCl_2$ insertion reaction in the Si–Cl bond of Si_6Cl_{12}. It was found that Cl–$SiSi_3$ bonds are more favored than Cl–$SiClSi_2$ for $SiCl_2$ insertion.[6] The silyl anion $SiCl_3^-$ can be considered as a dichlorosilylene donor adduct and therefore as a $SiCl_2$ source.

The addition compound $SiCl_4$·TMEDA shown in Figure 6 (selected bond lengths see in the figure caption), crystallizes in the monoclinic space group *Cc*. The octahedrally coordinated Si atom in $SiCl_4$·TMEDA is complexed to one TMEDA molecule in a bidentate fashion as found in the solid-state structures of **1·TMEDA** and $HSiCl_3$·TMEDA.[23,24] The Si–Cl distances vary only little and are in the expected range and comparable with those in **1·TMEDA** and $HSiCl_3$·TMEDA. In

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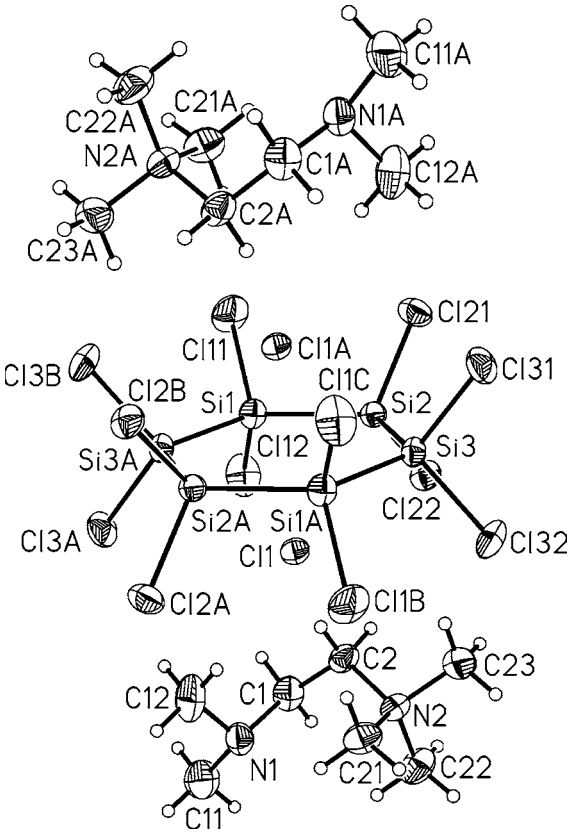

Figure 4. Solid-state structure of $[Me_3NCH_2CH_2NMe_2]_2$[**4a**] (monoclinic, $P2_1/n$). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg.): Si(1)−Cl(11) = 2.074(2), Si(1)−Cl(12) = 2.0772(19), Si(1)−Si(2) = 2.3174(17), Si(1)−Si(3A) = 2.3239(18), Si(2)−Cl(21) = 2.0754(18), Si(2)−Cl(22) = 2.0783(17), Si(2)−Si(3) = 2.3260(18), Si(3)−Cl(31) = 2.0676(17), Si(3)−Cl(32) = 2.0783(18), Si(3)−Si(1A) = 2.3239(18); Cl(11)−Si(1)−Cl(12) = 102.27(9), Cl(11)−Si(1)−Si(2) = 107.83(7), Cl(12)−Si(1)−Si(2) = 108.65(8), Cl(11)−Si(1)−Si(3A) = 109.12(8), Cl(12)−Si(1)−Si(3A) = 108.49(7), Si(2)−Si(1)−Si(3A) = 119.17(7), Cl(21)−Si(2)−Cl(22) = 102.08(7), Cl(21)−Si(2)−Si(1) = 108.21(7), Cl(22)−Si(2)−Si(1) = 107.17(7), Cl(21)−Si(2)−Si(3) = 107.64(7), Cl(22)−Si(2)−Si(3) = 108.63(7), Si(1)−Si(2)−Si(3) = 121.44(7), Cl(31)−Si(3)−Cl(32) = 102.31(7), Cl(31)−Si(3)−Si(1A) = 107.90(7), Cl(32)−Si(3)−Si(1A) = 108.92(8), Cl(31)−Si(3)−Si(2) = 108.73(8), Cl(32)−Si(3)−Si(2) = 108.27(7), Si(1A)−Si(3)−Si(2) = 119.37(6). Symmetry transformations used to generate equivalent atoms: #1 $-x + 1, -y + 2, -z + 1$.

the end the related metric parameters of all three compounds are very similar.

EXPERIMENTAL SECTION

General Considerations. All experiments were carried out under dry argon or nitrogen using standard Schlenk and glovebox techniques. Alkane solvents were dried over sodium and freshly distilled prior to use. Benzene, toluene, and THF were distilled from sodium/benzophenone. Benzene-d_6, toluene-d_8, and THF-d_8 were distilled from sodium/benzophenone and stored under a nitrogen atmosphere. TMEDA was dried with Li*n*Bu. All other starting materials were purchased from commercial sources and used without further purification. Solution-state NMR spectra were recorded on a Bruker DPX 250, a Bruker Avance 300, and a Bruker Avance 400. Solid-state MAS NMR spectra were recorded on a Bruker Avance II WB 400 spectrometer equipped with a 4 mm MAS DVT triple resonance probe in double resonance mode at Larmor frequencies of 293.8 and 78.03

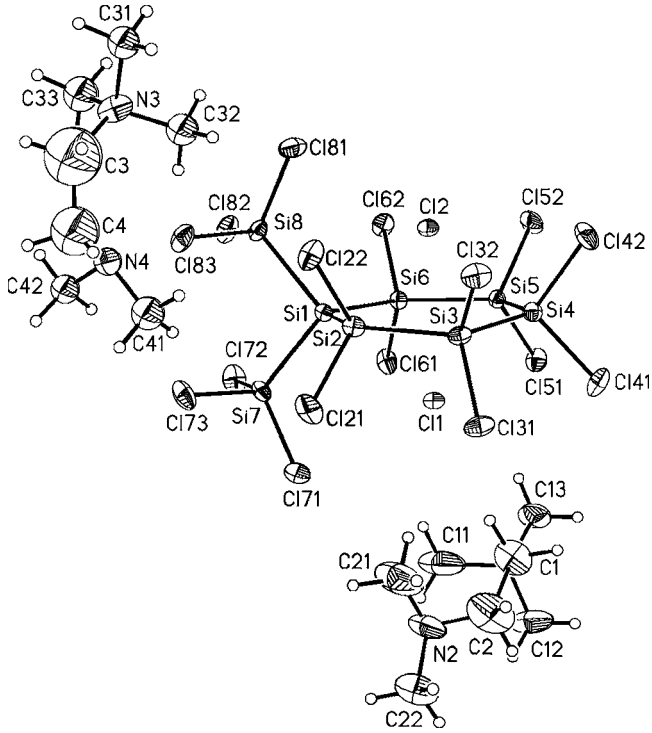

Figure 5. Solid-state structure of $[Me_3NCH_2CH_2NMe_2]_2$[**4b**] (monoclinic, $P2_1/n$). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg.): Si(1)−Si(6) = 2.322(5), Si(1)−Si(2) = 2.340(5), Si(1)−Si(8) = 2.359(5), Si(1)−Si(7) = 2.363(4), Si(2)−Cl(22) = 2.077(5), Si(2)−Cl(21) = 2.080(5), Si(2)−Si(3) = 2.320(5), Si(3)−Cl(32) = 2.075(5), Si(3)−Cl(31) = 2.087(5), Si(3)−Si(4) = 2.327(6), Si(4)−Cl(42) = 2.074(4), Si(4)−Cl(41) = 2.083(5), Si(4)−Si(5) = 2.309(5), Si(5)−Cl(52) = 2.079(5), Si(5)−Cl(51) = 2.081(5), Si(5)−Si(6) = 2.315(5), Si(6)−Cl(61) = 2.075(4), Si(6)−Cl(62) = 2.081(5), Si(7)−Cl(71) = 2.033(6), Si(7)−Cl(73) = 2.037(5), Si(7)−Cl(72) = 2.041(5), Si(8)−Cl(81) = 2.023(5), Si(8)−Cl(82) = 2.038(5), Si(8)−Cl(83) = 2.045(5); Si(6)−Si(1)−Si(2) = 116.55(18), Si(6)−Si(1)−Si(8) = 108.28(18), Si(2)−Si(1)−Si(8) = 110.11(18), Si(6)−Si(1)−Si(7) = 110.25(17), Si(2)−Si(1)−Si(7) = 109.65(17), Si(8)−Si(1)−Si(7) = 100.85(17), Cl(22)−Si(2)−Cl(21) = 103.3(2), Cl(22)−Si(2)−Si(3) = 108.87(18), Cl(21)−Si(2)−Si(3) = 106.4(2), Cl(22)−Si(2)−Si(1) = 107.7(2), Cl(21)−Si(2)−Si(1) = 106.46(18), Si(3)−Si(2)−Si(1) = 122.5(2), Cl(32)−Si(3)−Cl(31) = 100.7(2), Cl(32)−Si(3)−Si(2) = 106.7(2), Cl(31)−Si(3)−Si(2) = 110.5(2), Cl(32)−Si(3)−Si(4) = 108.43(19), Cl(31)−Si(3)−Si(4) = 109.6(2), Si(2)−Si(3)−Si(4) = 119.30(19), Cl(42)−Si(4)−Cl(41) = 101.6(2), Cl(42)−Si(4)−Si(5) = 110.7(2), Cl(41)−Si(4)−Si(5) = 108.1(2), Cl(42)−Si(4)−Si(3) = 109.4(2), Cl(41)−Si(4)−Si(3) = 107.9(2), Si(5)−Si(4)−Si(3) = 117.92(18), Cl(52)−Si(5)−Cl(51) = 101.4(2), Cl(52)−Si(5)−Si(4) = 108.43(19), Cl(51)−Si(5)−Si(4) = 108.6(2), Cl(52)−Si(5)−Si(6) = 107.4(2), Cl(51)−Si(5)−Si(6) = 107.11(19), Si(4)−Si(5)−Si(6) = 121.95(19), Cl(61)−Si(6)−Cl(62) = 102.6(2), Cl(61)−Si(6)−Si(5) = 108.5(2), Cl(62)−Si(6)−Si(5) = 106.93(18), Cl(61)−Si(6)−Si(1) = 107.84(17), Cl(62)−Si(6)−Si(1) = 108.6(2), Si(5)−Si(6)−Si(1) = 120.92(18), Cl(71)−Si(7)−Cl(73) = 106.0(2), Cl(71)−Si(7)−Cl(72) = 106.2(2), Cl(73)−Si(7)−Cl(72) = 104.8(2), Cl(71)−Si(7)−Si(1) = 115.5(2), Cl(73)−Si(7)−Si(1) = 110.6(2), Cl(72)−Si(7)−Si(1) = 112.9(2), Cl(81)−Si(8)−Cl(82) = 107.0(2), Cl(81)−Si(8)−Cl(83) = 105.5(2), Cl(82)−Si(8)−Cl(83) = 105.7(2), Cl(81)−Si(8)−Si(1) = 116.5(2), Cl(82)−Si(8)−Si(1) = 110.1(2), Cl(83)−Si(8)−Si(1) = 111.4(2).

MHz for ^{1}H and ^{29}Si, respectively. The ^{29}Si CP/MAS spectra were recorded at sample spinning rates of 8 kHz with a cross-polarization step of 5 ms, 100 kHz Spinal6[25] and ^{1}H decoupling during an

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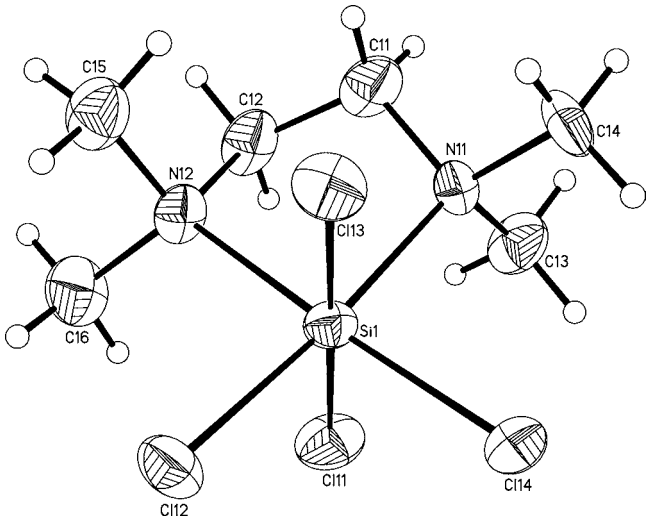

Figure 6. Solid-state structure of one from two crystallographically independent molecules of $SiCl_4$·TMEDA in the asymmetric unit (monoclinic *Cc*). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å): Si(1)−N(12) = 2.083(9), Si(1)−N(11) = 2.104(9), Si(1)−Cl(13) = 2.176(4), Si(1)−Cl(12) = 2.178(4), Si(1)−Cl(14) = 2.182(4), Si(1)−Cl(11) = 2.186(4).

acquisition time of 20 ms and a recycle delay of 3 s. The ^{29}Si CP/MAS spectrum of $Cl_3SiSiCl_3$·TMEDA was acquired using 24576 transients and was indirectly referenced to trimethylsilane using the trimethylsilyl signal of tetrakis(trimethyl)silane at −9.86 ppm.[26] Elemental analyses were performed at the microanalytical laboratories of the Universität Frankfurt and by the Microanalytical Laboratory Pascher. Mass spectrometry was performed with a Fisons VG Platform II. GC-MS measurements were performed with a Thermo Scientific Trace GC Ultra/ITQ 900 MS (column: Machery-Nagel Optima-210MS, ID = 0.32 mm, film thickness = 0.5 μm, length = 25 m).

Synthesis of 1·TMEDA. A flask was charged with **1** (1.56 g, 5.8 mmol) in 10 mL of pentane to which TMEDA (0.51 g, 4.35 mmol) was added at once. Immediately a colorless solid was deposited. The colorless solid was filtered off and washed with pentane (2 × 10 mL). Drying of the solid in vacuo yielded pure **1·TMEDA**. Yield 1.49 g (89%).

1·TMEDA. ^{29}Si CP/MAS NMR: −0.5 ($SiCl_3$), −163.4 ($SiCl_3N_2$). *m/z* (MALDI$^+$) (%): 381 (100) $[M]^+$ (correct isotope pattern). Elem. Anal. Calcd for $C_6H_{16}Cl_6Si_2$ C, 18.71%; H, 4.19%; N, 7.27%; Cl, 55.24%. Found: C, 18.62%; H, 4.13%; N, 7.95%; Cl, 54.20%.

Remark: Single crystals of **1·TMEDA** as colorless needles were obtained by gas-phase diffusion of hexachlorodisilane (6.25 g, 22.0 mmol) and TMEDA (2.71 g, 23.0 mmol) at room temperature.

Decomposition of 1·TMEDA in CH_2Cl_2. A flask was charged with **1·TMEDA** (1.0 g, 2.6 mmol) to which was added 10 mL of CH_2Cl_2. Immediately a colorless precipitate was formed. In the MALDI$^+$ mass spectrum of the precipitate peaks were found which could be assigned to the oligochlorosilanes Si_nCl_{2n} (*n* = 4, 6, 8, 10) (*m/z* (MALDI$^+$) (%): 395.8 (100, correct isotope pattern) $[Si_4Cl_8]^+$, 593.6 (100, correct isotope pattern) $[Si_6Cl_{12}]^+$, 791.4 (100, correct isotope pattern) $[Si_8Cl_{16}]^+$, 989.2 (100, correct isotope pattern) $[Si_{10}Cl_{20}]^+$. The MALDI$^-$ mass spectrum of the CH_2Cl_2 solution revealed peaks of oligochlorosilyl dianions $[\mathbf{4a}]^{2-}$, $[\mathbf{4b}]^{2-}$, $[Si_{10}Cl_{22}]^{2-}$, and $[Si_{12}Cl_{26}]^{2-}$ (*m/z* (MALDI$^-$) (%): 336.5 (16) 335.5 (76) 334.5 (25) 333.6 (85) 332.5 (44) 331.6 (100) 330.7 (12) 329.6 (65) $[Si_6Cl_{14}]^{2-}$ ($[\mathbf{4a}]^{2-}$), calcd for $[Si_6Cl_{14}]^{2-}$ 337.7, 337.2, 336.7 (5) 336.2, 335.7 (12) 335.2,

Table 2. Crystal Data and Structure Refinement Parameters for 1·TMEDA, $[Me_3NCH_2CH_2NMe_2]_2[\mathbf{4a}]$, $[Me_3NCH_2CH_2NMe_2]_2[\mathbf{4b}]$, and $SiCl_4$·TMEDA

	1·TMEDA	$[Me_3NCH_2CH_2NMe_2]_2[\mathbf{4a}]$	$[Me_3NCH_2CH_2NMe_2]_2[\mathbf{4b}]$	$SiCl_4$·TMEDA
empirical formula	$C_6H_{16}C_{16}N_2Si_2$	$C_{14}H_{38}Cl_{14}N_4Si_6$	$C_{14}H_{38}Cl_{18}N_4Si_8$	$C_6H_{16}C1_4N_2Si$
color	colorless	colorless	colorless	colorless
shape	plate	block	block	block
fw	385.09	927.32	1125.30	286.10
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	*Cc*
a, Å	8.5178(9)	10.1630(8)	12.382(2)	23.2626(13)
b, Å	16.642(2)	10.4876(10)	18.150(2)	14.4338(7)
c, Å	10.5528(11)	18.4868(16)	20.566(3)	14.3613(8)
β, deg	90.255(8)	98.913(7)	91.806(14)	92.825(5)
volume, (Å^3)	1495.9(3)	1946.6(3)	4619.6	4816.2(4)
Z	4	2	4	16
density (calcd.), Mg/m^3	1.710	1.582	1.618	1.578
abs coeff μ(MoK$_\alpha$), mm^{-1}	1.285	1.193	1.294	1.043
F(000)	784	944	2272	2368
crystal size, mm^3	0.1 × 0.06 × 0.05	0.27 × 0.27 × 0.25	0.1 × 0.1 × 0.02	0.28 × 0.26 × 0.22
θ-range, deg	2.69 to 27.69	3.64 to 25.71	3.45 to 25.78	3.25 to 25.85
index ranges	$-10 \le h \le 11$	$-12 \le h \le 12$	$-14 \le h \le 15$	$-28 \le h \le 28$
	$-21 \le k \le 21$	$-12 \le k \le 12$	$-22 \le k \le 22$	$-17 \le k \le 17$
	$-13 \le l \le 13$	$-21 \le l \le 22$	$-25 \le l \le 25$	$-17 \le l \le 17$
no. of reflections collected	19798	23116	48470	8157
no. of independent reflections	3455	3652	8681	7637
R(int)	0.0918	0.0876	0.1282	0.0984
T_{min}, T_{max}	0.9385 and 0.8822	0.7546 and 0.7388	0.9746 and 0.8815	0.8030 and 0.7588
no. of data/restraints/parameter	3455/0/146	3652/0/172	8681/57/391	8158/2/471
goodness of fit on F^2	0.999	1.148	1.027	1.988
final *R* indices [$I > 2\sigma(I)$], R1, wR2	0.0692, 0.1149	0.0729, 0,1158	0.1128, 0.1906	0.0918, 0.2194
R indices (all data), R1, wR2	0.1144, 0.1292	0.0991, 0.1235	0.2174, 0.2277	0.0964, 0.2210
peak/hole e Å^{-3}	0.515 and −0.368	0.565 and −0.400	1.111 and −0.484	0.881 and −0.783

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334.7 (30) 334.2, 333.7 (56.5) 333.2, 332.7 (81) 332.2, 331.7, 331.2 (100) 330.7, 330.2 (55) 329.7, 329.2, 328.7 (65); 436.5 (21) 435.5 (43) 434.5 (30) 433.5 (30) 432.5 (80) 431.5 (100) 430.5 (42) 429.4 (92) 427.5 (42) $[Si_8Cl_{18}]^{2-}$([**4b**]$^{2-}$), calcd for $[Si_8Cl_{18}]^{2-}$ 437.1, 436.6, 436.1 (5) 435.6, 435.1 (13) 434.6, 434.1 (28) 433.6, 433.1 (54) 432.6, 432.1 (82) 431.6, 431.2 (100) 430.6, 430.1 (96) 429.6, 429.1, 428.6 (100) 428.1, 427.6 (17), 536.3 (48) 534.3 (13) 533.4 (85) 532.4 (40) 531.4 (44) 530.4 (52) 529.4 (100) 527.3 (64) 525.4 (19) $[Si_{10}Cl_{22}]^{2-}$, calcd for $[Si_{10}Cl_{22}]^{2-}$ 536.5, 536.0, 535.5 (5) 535.0, 534.5 534.0 (15), 532.5 532.0 (40) 531.5, 531.0 (57) 530.5, 530.0 (67) 529.5, 529.0, 528.5 (100) 528.0, 527.5, 527.0, 526.5 (47) 526.0, 525.5 (4); 633.2 − 623.9 $[Si_{12}Cl_{26}]^{2-}$, calcd for $[Si_{12}Cl_{26}]^{2-}$ 632.4 − 623.5). At first single crystals of [**$Me_3NCH_2CH_2NMe_2$**]$_2$[**4a**] were grown from the CH_2Cl_2 extract (yield 15%). After 6 days at room temperature a second crop of crystals of [**$Me_3NCH_2CH_2NMe_2$**]$_2$[**4b**] were obtained (yield 5%). However, the oligochlorsilanes Si_nCl_{2n} (n = 4, 6, 8, 10) could not be separated.

[**$Me_3NCH_2CH_2NMe_2$**]$_2$[**4a**]. ^{1}H NMR (CD_3CN, internal TMS): δ 2.23 (s, 6H, Me_2NCH_2), δ 2.67 (m, 2H, Me_2NCH_2), δ 3.20 (s, 9H, Me_3NCH_2), δ 3.52 (t, J = 6 Hz, 2H, Me_3NCH_2). ^{29}Si{^{1}H}NMR (CD_2Cl_2, external TMS): δ −20.1. Elem. Anal. Calcd for $C_{14}H_{38}Cl_{14}N_4Si_6$ C, 18.13%; H, 4.13%; N, 6.04%. Found: C, 17.49%; H, 4.15%; N, 5.74%.

[**$Me_3NCH_2CH_2NMe_2$**]$_2$[**4b**]. ^{1}H NMR (CD_3CN, internal TMS): δ 2.23 (s, 6H, Me_2NCH_2), δ 2.68 (m, 2H, Me_2NCH_2), δ 3.20 (s, 9H, Me_3NCH_2), δ 3.55 (t, J = 6 Hz, 2H, Me_3NCH_2). ^{29}Si{^{1}H}NMR (CD_2Cl_2, external TMS): δ 11.1 ($SiCl_3$), δ −20.6 (2 × $SiCl_2$), δ −20.8 ($SiCl_2$), n.o. ($Si(SiCl_3)_2Si_2$). Elem. Anal. Calcd for $C_{14}H_{38}Cl_{18}N_4Si_8$ C, 14.94%; H, 3.40%; N, 4.98%. Found: C, 15.01%; H, 3.44%; N, 4.91%.

Decomposition of 1·TMEDA in MeCl. Methyl chloride (10 g, 198.2 mmol) and TMEDA (3.2 g, 27.0 mmol) were condensed on **1** (7.8 g, 27.0 mmol) which was cooled by liquid nitrogen (−196 °C). The mixture was stirred for 24 h at −78 °C. The reaction solution was warmed up to room temperature over a 12 h period. After removing all volatiles in vacuo, the residue was extracted in CH_2Cl_2. The MALDI mass spectrum of the CH_2Cl_2 solution revealed peaks of oligochlorosilyl dianions [**4a**]$^{2-}$, [**4b**]$^{2-}$, $[Si_{10}Cl_{24}]^{2-}$, and $[Si_{12}Cl_{26}]^{2-}$ whereas in the MALDI mass spectrum of the remaining insoluble material peaks were found which could be assigned to Si_nCl_{2n} (n = 4, 6, 8, 10). The ^{29}Si NMR spectrum of the methylene chloride solution revealed signals of $MeSiCl_3$ and the oligochlorosilylanions [**4a**]$^{2-}$ and [**4b**]$^{2-}$. X-ray quality crystals of [**$Me_3NCH_2CH_2NMe_2$**]$_2$[**4b**] were grown from the methylene chloride solution at room temperature (yield 20%).

Decomposition of 1·TMEDA in MeI. Methyl iodide (0.5 mL) was condensed on a mixture of **1·TMEDA** (0.20 g, 0.52 mmol) and 1 mL of CD_2Cl_2 which was cooled by liquid nitrogen (−196 °C). The reaction mixture was warmed up to −78 °C. In the ^{1}H NMR and ^{29}Si NMR spectrum of the reaction solution the signals of $MeSiCl_3$ were observable. The MALDI mass spectrum of the reaction mixture revealed peaks of the oligochlorosilanes Si_nCl_{2n} (n = 4, 6, 8, 10).[11]

Thermolysis of 1·TMEDA in the Presence of Me_3SiN_3. **1·TMEDA** (0.15 g, 0.38 mmol) and Me_3SiN_3 (0.41 g, 3.80 mmol) in 5 mL of benzene was heated to 55 °C for 15 h. After cooling to room temperature a solution of LiMe (5 mmol) in ether was added to the benzene solution. After filtration, **9** and **11** were identified by ^{1}H NMR spectroscopy and by GC-MS (**9**, τ = 1.49 min; m/z (EI$^+$): 275 [M-Me]$^+$; **11**, τ = 2.02 min; m/z (EI$^+$): 260 [M]$^+$).

Synthesis of $SiCl_4$·TMEDA. Generally $SiCl_4$·TMEDA was synthesized in preparative scale following this synthetic route: A solution of $SiCl_4$ (1.48 g, 8.71 mmol) in pentane (10 mL) was treated at room temperature with a solution of TMEDA (1.01 g, 8.71 mmol) in pentane (10 mL). After stirring for 1 h the solvent was removed under reduced pressure, and $SiCl_4$·TMEDA could be obtained as colorless microcrystalline solid. The product was identified by powder diffraction. Yield: 2.29 g (92%). ^{29}Si CP/MAS NMR: −161.0 ($SiCl_4$·TMEDA). Elem. Anal. Calcd for $C_6H_{16}Cl_4Si$ C, 25.19%; H, 5.64%; N, 9.79%. Found C, 25.25%; H, 6.05%; N, 9.90%.

Thermolysis of **1·TMEDA** in THF: A NMR-tube was charged with **1** (0.20 g, 0.74 mmol) in THF-d_8 (0.5 mL), and TMEDA (0.08 g, 0.1 mL, 0.67 mmol) was added at room temperature. Immediately a colorless solid was deposited. The tube was sealed in vacuo and heated to 50 °C for 1 min. Crystals of $SiCl_4$·TMEDA were obtained within 2 d at −30 °C. Yield 0.03 g (13%).

Thermolysis of 1·TMEDA in Si_2Cl_6. **1·TMEDA** (0.06 g, 0.15 mmol) in neat Si_2Cl_6 (0.81 g, 3.0 mmol) was heated to 55 °C for 15 h. In the ^{29}Si NMR spectrum of the reaction solution **2** can be assigned as the major product of this reaction. After filtration and removal of all volatile components in vacuo, **2** could be isolated as a colorless solid. Yield: 0.34 g (80%).

X-ray Structure Determination. Data collections were performed on a Stoe-IPDS-II diffractometer, empirical absorption correction using MULABS.[27] The structures were solved with direct methods[28] and refined against F^2 by full-matrix least-squares calculation with SHELXL-97.[29] Hydrogen atoms were placed on ideal positions and refined with fixed isotropic displacement parameters using a riding model. CCDC reference number: 884758 (**1·TMEDA**), 884757 ([**$Me_3NCH_2CH_2NMe_2$**]$_2$[**4b**]), 884756 ([**$Me_3NCH_2CH_2NMe_2$**]$_2$[**4a**]), and 793314 ($SiCl_4$·TMEDA).

Computational Details. Geometry optimizations and harmonic frequency calculations have been carried out with the Gaussian09[30] program employing the hybrid functional B3LYP(V),[31] incorporating the VWN5 parametrization[32] as local correlation functional. The DFT calculations were done in combination with the SVP[33] basis set and the dispersion correction of Grimme (D2).[34] Thermal and entropy corrections were obtained from computed Hessians using the standard procedures in Gaussian09.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The table of X-ray parameters, atomic coordinates and thermal parameters, and bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Fax: +49-69798-29260. E-mail: lerner@chemie.uni-frankfurt.de.

Notes

The authors declare no competing financial interest.

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