

Interactions of chloromethyldisilanes with tetrakis(dimethylamino)ethylene (TDAE), formation of $[\text{TDAE}]^{\cdot+}$ $[\text{Si}_3\text{Me}_2\text{Cl}_7]^-$

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Abstract

The chlorodisilanes $\text{SiClMe}_2\text{-SiClMe}_2$ (**1**), $\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$ (**2**), $\text{SiCl}_3\text{-SiCl}_3$ (**3**) and a 9:1 mixture of **2** and $\text{SiCl}_3\text{-SiCl}_2\text{Me}$ (**4**) were reacted with the electron-rich alkene tetrakis-(dimethylamino)-ethylene (TDAE) in *n*-hexane as well as in polar solvents. While **1** gave no reaction at all, **3** underwent a disproportionation reaction into SiCl_4 and $\text{Si}(\text{SiCl}_3)_4$. Also **2** and mixtures of **2** and **4** were disproportionated into MeSiCl_3 (**2a**) and methylchlorooligosilanes. Additionally a crystalline mixture of $\text{Si}_3\text{Me}_3\text{Cl}_6\cdot\text{TDAE}$ (**5a**) plus $\text{Si}_3\text{Me}_2\text{Cl}_7\cdot\text{TDAE}$ (**5b**) was obtained by reaction of a 9:1 mixture of **2** and **4** with TDAE in *n*-hexane as well as in 1,2-dimethoxyethane. The reaction of **2** with TDAE in acetonitrile (MeCN) led to a crystalline precipitation of $[\text{TDAE}]_2\cdot\text{MeCN}$ (**6**·MeCN) in addition to MeSiCl_3 and methylchlorooligosilanes. The structures of **5b** and **6**·MeCN were determined by X-ray crystallography beside their NMR and IR spectroscopic characterization. Compound **5b** crystallizes in the monoclinic space group *P2₁/c* (*Z* = 4), **6**·MeCN in the orthorhombic space group *Pna2₁* (*Z* = 4). The structure of **5b** reveals a $[\text{TDAE}]^{\cdot+}$ radical cation and a $1,2\text{-Me}_2\text{Si}_3\text{Cl}_7^-$ anion with a pentacoordinated central silicon atom.

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1. Introduction

Chloromethyldisilanes are by-products of the MÜLLER-ROCHOW process [1,2]. Via a catalytic disproportionation reaction they can be converted into oligo- or polysilanes, which represent promising precursor compounds of silicon carbide ceramics. Key steps of the disproportionation of $\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$ (**2**) [3–5] are outlined in Scheme 1.

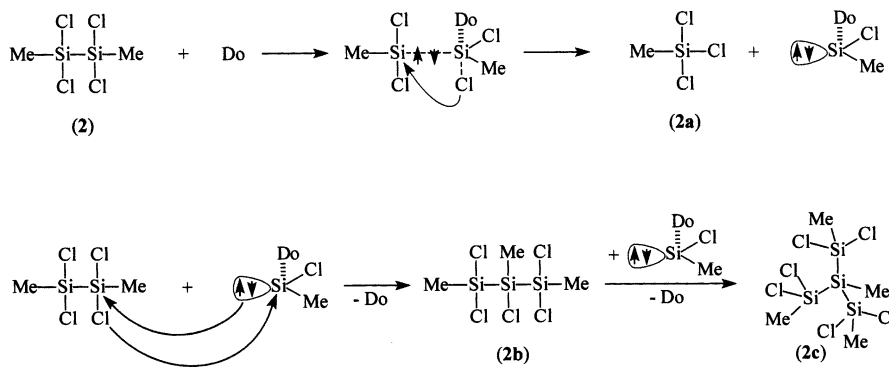
Most probably the catalytic disproportionation proceeds via a 1,2-shift of one of the chlorine substituents at the donor coordinated Si-atom followed by the subsequent cleavage of the Si–Si bond. Insertion reaction of the as-formed donor stabilized silylene into a Si–Cl bond of a further molecule of **2** leads to oligo- and

finally polysilanes. Oligosilanes containing up to seven silicon atoms were isolated and identified by Herzog et al. [5]. Hildebrandt and Engels [6] studied theoretically the mechanism of the Lewis-base catalyzed disproportionation of chlorodisilanes. From their calculations they concluded that the activation energy of the disproportionation as well as the location and the geometry of the transition state on the reaction coordinate are significantly influenced by the used Lewis-base. But besides this, their computation results do not support the common assumption that the disproportionation is initiated by the preformation of a disilane-donor complex. However, they have found a strong stabilization effect of the intermediate silylene by coordination of Lewis-bases.

Previously applied disproportionation catalysts are electron-pair donors such as amines, phosphanes, AgCN, hexamethylphosphoric acid triamide or N-heterocycles like *N*-methylimidazol [7–9]. In contrast

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Scheme 1. Supposed mechanism of the Lewis-base catalyzed disproportionation of **2**.

to these types of catalytically active compounds, which represent electron pair donors, tetrakis(dimethylamino)ethylene (TDAE) should be able to transfer either one or two electrons to the disilane molecule. Thus it may form radical cation or dication salts. Based on this behavior of the TDAE Bürger and Moritz [10] converted polyhalomethanes into halomethanide anions. This prompted us to find out, whether an e^- -transfer to the disilane is able to initiate the disproportionation process of disilanes. A specific N-coordination of the TDAE to a disilane molecule or silylene species is sterically hindered by the bulky dimethylamino groups [11,12]. Some steps of the redox process should be affected significantly by the used solvent.

2. Results and discussion

2.1. Disproportionation of disilanes with TDAE in *n*-hexane

In order to reveal mechanistic details of the disproportionation process we have investigated the reactivity of $\text{SiClMe}_2\text{-SiClMe}_2$ (**1**), $\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$ (**2**), $\text{SiCl}_3\text{-}$

SiCl_3 (**3**) and a 9:1 mixture of **2** and $\text{SiCl}_2\text{Me-SiCl}_3$ (**4**) towards TDAE.

Compound **1** gave no reaction when a mixture with TDAE *n*-hexane was heated to reflux for 2 h.

On the other hand, the higher chlorofunctionalized disilanes **2** and **3** reacted with TDAE under disproportionation, see Table 1.

Additionally in case of the reaction of TDAE with **2** a dark red precipitation was observed. MAS NMR spectra of this highly air sensitive product revealed the formation of **5a** but in mixture with smaller amounts of a second compound which was later found to be **5b**. The formation of **5b** is understandable by the fact that the used **2** contained small amounts (1–2%) of methylpentachlorodisilane (**4**) as was detected by ^{29}Si NMR

Table 1

^{29}Si -NMR spectroscopic identification of the products of the reaction of TDAE with chlorosubstituted disilanes in *n*-hexane

Educt disilanes	Identified products	Relative amount (%)
1	$\text{SiClMe}_2\text{-SiClMe}_2$ (1) (no reaction)	100
2	$\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$ (2)	97
	MeSiCl_3 (2a)	1
	$\text{SiClMe}(\text{SiCl}_2\text{Me})_2$ (2b)	2
3	$\text{SiCl}_3\text{-SiCl}_3$ (3)	46
	SiCl_4 (3a)	48
	$\text{Si}(\text{SiCl}_3)_4$ (3b)	6
2/4 (9:1)	$\text{SiCl}_2\text{Me-SiCl}_2\text{Me}$ (2)	69
	MeSiCl_3 (2a)	21
	$\text{SiClMe}(\text{SiCl}_2\text{Me})_2$ (2b)	5
	$\text{SiMe}(\text{SiCl}_2\text{Me})_3$ (2c)	5

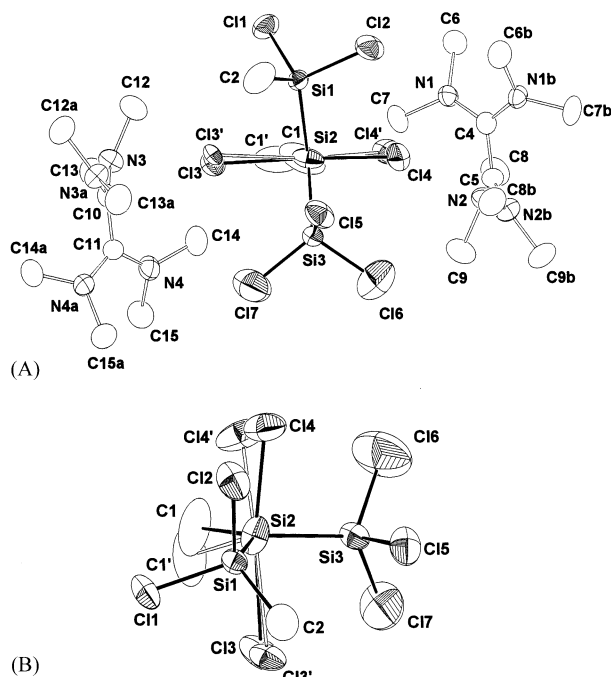


Fig. 1. (A) ORTEP plot of the molecular structure of **5b**. (B) ORTEP plot of the trisilanide ion $\text{Si}_3\text{Me}_2\text{Cl}_7^-$ in **5b**. Positions of C1, C13 and C14 marked by an apostrophe have an occupation factor of 36.5%, the positions without an apostrophe have an occupation factor of 63.5%.

Table 2
Selected bond lengths (Å), bond angles (°) and dihedral angles (°) of **5b**

<i>Bond lengths</i>			
Si(1)–Si(2)	2.326(2)	Si(1)–C(2)	1.892(6)
Si(1)–Cl(1)	2.079(2)	Si(1)–Cl(2)	2.081(3)
Si(2)–C(1)	1.80(4)	Si(2)–C(1)′	2.04(6)
Si(2)–Cl(3)	2.498(13)	Si(2)–Cl(3)′	2.583(15)
Si(2)–Cl(4)	2.328(9)	Si(2)–Cl(4)′	2.140(20)
Si(2)–Si(3)	2.325(2)	Si(3)–Cl(5)	2.079(3)
Si(3)–Cl(6)	2.008(3)	Si(3)–Cl(7)	2.021(3)
C(4)–C(5)	1.416(10)	N(1)–C(4)	1.353(6)
N(2)–C(5)	1.365(6)	C(10)–C(11)	1.408(11)
N(3)–C(10)	1.367(6)	N(4)–C(11)	1.363(6)
<i>Bond angles</i>			
Cl(1)–Si(1)–Cl(2)	103.66(10)	C(2)–Si(1)–Cl(1)	108.1(2)
C(2)–Si(1)–Cl(2)	105.6(2)	C(2)–Si(1)–Si(2)	120.9(3)
Cl(1)–Si(1)–Si(2)	106.01(9)	Cl(2)–Si(1)–Si(2)	111.27(10)
Si(1)–Si(2)–Si(3)	118.15(9)	C(1)–Si(2)–Cl(3)	93.8(10)
C(1)′–Si(2)–Cl(3)′	84.8(20)	C(1)–Si(2)–Cl(4)	95.7(11)
C(1)′–Si(2)–Cl(4)′	98.8(18)	Cl(3)–Si(2)–Cl(4)	170.2(4)
Cl(3)′–Si(2)–Cl(4)	172.6(4)	C(1)–Si(2)–Si(1)	120.1(13)
C(1)′–Si(2)–Si(1)	116.1(16)	Cl(3)–Si(2)–Si(1)	82.4(6)
Cl(3)′–Si(2)–Si(1)	73.6(5)	Cl(4)–Si(2)–Si(1)	94.7(3)
Cl(4)′–Si(2)–Si(1)	99.0(5)	C(1)–Si(2)–Si(3)	121.0(12)
C(1)′–Si(2)–Si(3)	118.9(20)	Cl(3)–Si(2)–Si(3)	85.4(3)
Cl(3)′–Si(2)–Si(3)	85.3(4)	Cl(4)–Si(2)–Si(3)	87.8(3)
Cl(4)′–Si(2)–Si(3)	98.4(12)	Cl(5)–Si(3)–Si(2)	105.47(9)
Cl(6)–Si(3)–Si(2)	114.38(16)	Cl(7)–Si(3)–Si(2)	117.97(12)
Cl(5)–Si(3)–Cl(6)	105.19(15)	Cl(5)–Si(3)–Cl(7)	106.75(13)
Cl(6)–Si(3)–Cl(7)	106.12(16)		
N(1)–C(4)–C(5)	120.5(3)	N(2)–C(5)–C(4)	120.2(3)
N(1)–C(4)–N(1b)	119.0(7)	N(2)–C(5)–N(2b)	119.6(7)
N(3)–C(10)–C(11)	121.0(3)	N(4)–C(11)–C(10)	120.8(4)
N(3)–C(10)–N(3a)	117.9(7)	N(4)–C(11)–N(4a)	118.5(7)
<i>Dihedral angles</i>			
N(1)–C(4)–C(5)–N(2)	36.2(3)	N(3)–C(10)–C(11)–N(4)	37.1(3)

Positions of C1, Cl3 and Cl4 marked by an apostrophe have an occupation factor of 36.5%, the positions without an apostrophe have an occupation factor of 63.5%.

spectroscopy. We were not able to obtain single crystals of **5a** suitable for X-ray analysis. However, if the reaction was repeated with a 9:1 molar mixture of **2** and **4** a crystalline mixture of **5a** and **5b** containing larger amounts of **5b** was obtained. In this case single crystals of **5b** could be isolated and characterized by crystal structure analysis (Fig. 1A and B). Selected bond lengths and angles are listed in Table 2.

Compound **5b** crystallizes in the monoclinic space group $P2_1/c$ with four formula units in the unit cell. The asymmetric unit contains two halves of a $[\text{TDAE}]^+$ radical cation resulting in two crystallographically independent cations each having crystallographic C_2 symmetry. The anion clearly consists of the trisilane $[\text{Cl}_2\text{MeSi}-\text{SiMeCl}_2-\text{SiCl}_3]^-$, i.e. the central silicon atom Si2 of the trisilane has picked up an additional chloride ion.

Refinement of the structure was hampered by a disorder of the methyl and chlorine substituents at Si2 which was modeled with these atoms in two alternative

positions with an occupancy ratio of 63.5:36.5%. Although the geometry of the hypervalent central silicon atom can be described as a distorted trigonal bipyramid, individual bond lengths and angles should be regarded

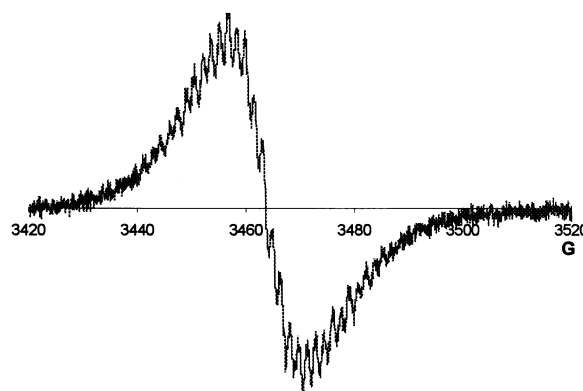


Fig. 2. EPR spectrum of the red precipitation of **5a** and **5b** resulting from the disproportionation of a 9:1 molar mixture of **2** and **4** with TDAE.

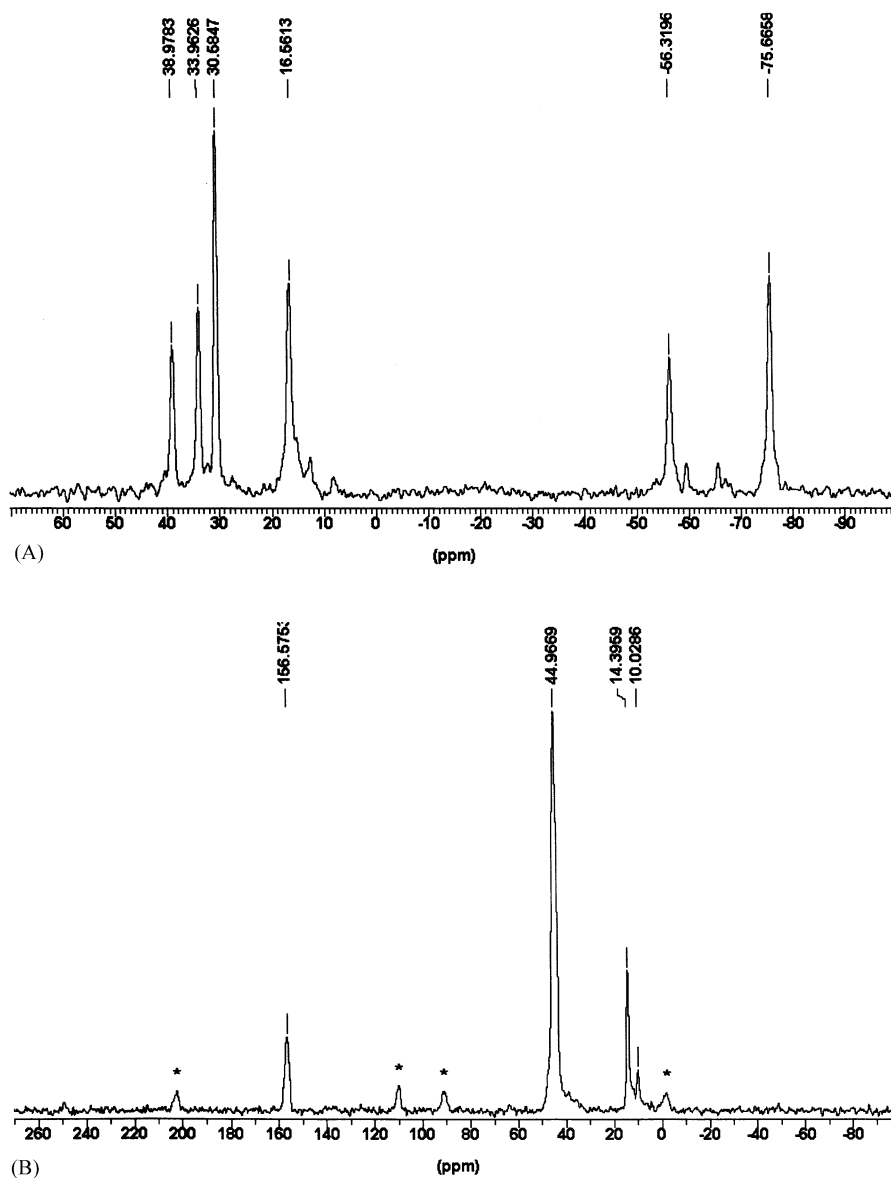


Fig. 3. (A) ^{29}Si CP MAS NMR spectrum of **5a**+**5b**. (B) ^{13}C CP MAS NMR spectrum of **5a**+**5b** (rotational sidebands are marked by asterisks). Due to the unpaired electron in the $[\text{TDAE}]^{\cdot+}$ radical cation the signals at 157 and 45 ppm are broadened in comparison with the signals of the SiMe units at 10 and 14 ppm.

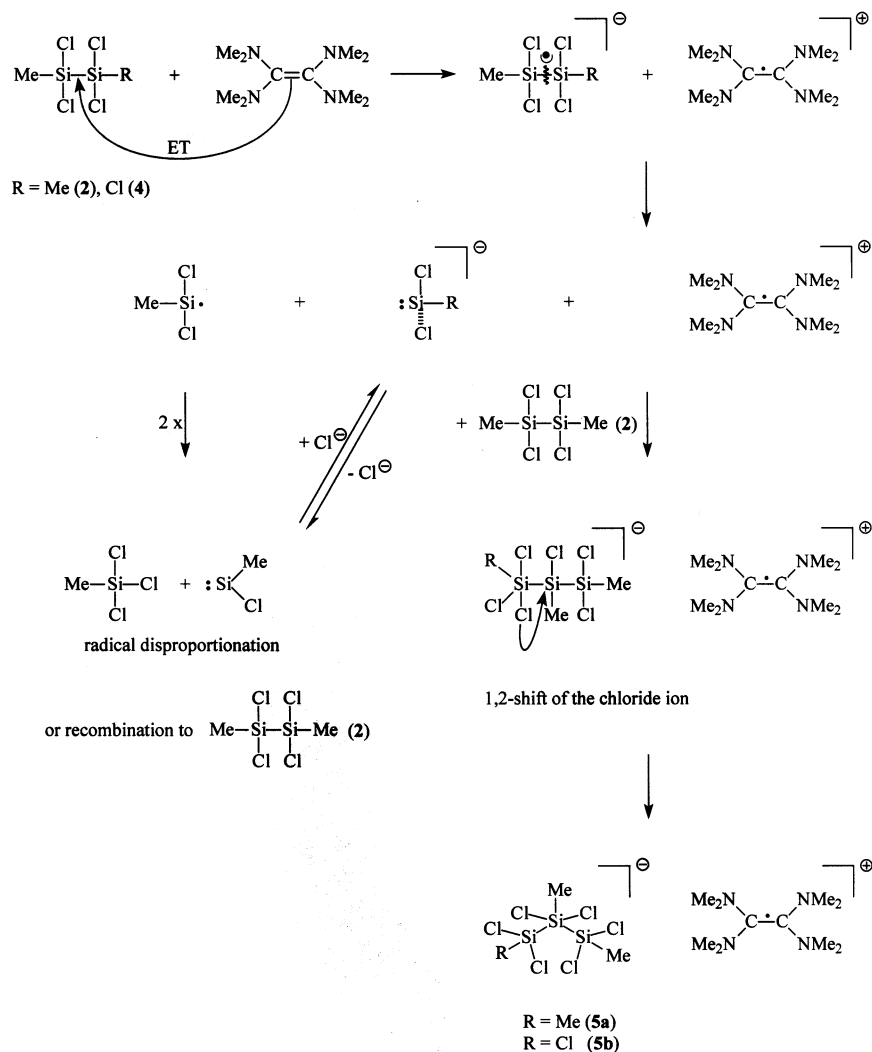
with caution due to the disorder. However, the data strongly suggest that the coordination geometry consists of two silyl groups and one methyl substituent in equatorial and two chlorine atoms in axial positions.

There is one further example of an chlorinated oligosilane coordinated by additional chloride anions, namely the $\text{Si}_6\text{Cl}_{14}^{2-}$ anion reported by Boudjouk and coworkers [13]. But in that case the two additional chloride ions are above and below the centre of a planar Si_6 ring with equal distances to all silicon atoms.

The C–C distance of the $\text{TDAE}^{\cdot+}$ cation in **5b** corresponds to the values calculated by Hino et al. [14] for the mono cation (1.337 Å in TDAE^0 , 1.417 Å in $\text{TDAE}^{\cdot+}$ and 1.539 Å in TDAE^{2+}). Another indicator

is the dihedral angle N–C–C–N. Mutual repulsion of the methyl groups gives rise to nonzero dihedral angles in TDAE^0 of 28° [15]. The increased dihedral angles of $36\text{--}37^\circ$ in **5b** reflects the decreased energy gain of the π -bond which is occupied by only one electron in the radical cation $\text{TDAE}^{\cdot+}$.

To the best of our knowledge the crystal structure analysis of **5b** is the first structural characterization of a $\text{TDAE}^{\cdot+}$ radical cation. A compound $[\text{TDAE}]\text{C}_{60}$ which shows superconductivity and ferromagnetism [16], has been known for some time and a structural characterization has been reported in [17], but the internal coordinates of the TDAE unit could not be refined due to the quality of the X-ray data. So far it is

Scheme 2. Proposal of a mechanism regarding the reaction of chloromethyldisilanes with TDAE in *n*-hexane.

still to decide whether this compound contains TDAE^{•+} or a mixture of TDAE⁰ and TDAE²⁺ besides C₆₀⁻ [18,19].

In the TDAE²⁺ dication there is no electron left in the π -orbital resulting in an even larger dihedral angle N–C–C–N, see also compound **6**, Section 2.2).

Table 3
²⁹Si and ¹³C MAS NMR data of the obtained TDAE salts of trisilanes (**5a**, **5b**)

Compound	δ (ppm)	
	²⁹ Si	¹³ C
$[\text{Cl}_2\text{MeSi}^{\text{A}}\text{-Si}^{\text{B}}\text{Cl}_2\text{Me-Si}^{\text{A}}\text{Cl}_2\text{Me}]^-$	A: 38.9/33.9	SiMe: 10.1; 14.5
$[(\text{Me}_2\text{N})_2\text{C-C}(\text{NMe}_2)_2]^+ \text{ (5a)}$	B: -56.3	C–C: 156.5
$[\text{Cl}_2\text{MeSi}^{\text{A}}\text{-Si}^{\text{B}}\text{Cl}_2\text{Me-Si}^{\text{C}}\text{Cl}_3]^-$	A: 30.5	NMe ₂ : 45.0
$[(\text{Me}_2\text{N})_2\text{C-C}(\text{NMe}_2)_2]^+ \text{ (5b)}$	B: -75.6	
	C: 16.5	

The unpaired electron of the TDAE^{•+} radical cation in **5a** and **5b** gives rise to an EPR signal with a *g*-factor of 2.006 (Fig. 2). Due to the hyperfine structure coupling with the ¹H and ¹⁴N nuclei a splitting into 1521 lines should be expected. But like in [20] and [21] we could only observe a partial resolution.

The ²⁹Si CP MAS NMR spectrum of the mixture of **5a** and **5b** shows six lines (Fig. 3A). There are three resonances in the region of SiCl₂Me units, one is caused by the SiCl₂Me unit of **5b**, the other two must be correlated with compound **5a**, which contains two such units. The assignment of the signals of the ²⁹Si CP MAS NMR spectrum (Fig. 3A) as well as a ¹³C CP MAS NMR spectrum (Fig. 3B) is given in Table 3. The signal of the carbon atoms of the C=C unit (TDAE⁰ $\delta_{\text{C}} = 131.2$ ppm) is shifted to $\delta_{\text{C}} = 156.5$ ppm in the spectrum of **5a**+**5b**. This drastic effect is a result of the formation of the radical cation [TDAE]^{•+}. Despite of the radical properties of the [TDAE]^{•+} cation its ¹³C CP MAS NMR signals could be observed, however they are

broadened to a line width of several ppm. As already stated in [20], the unpaired electron is largely delocalized across the whole radical cation resulting in a low probability density at each carbon atom. In the ^{29}Si CP MAS NMR spectrum the signals of the central Si atoms of the trisilane units exhibit the expected highfield shifts of 50–70 ppm due to pentacoordination in comparison with the parent trisilanes $\text{Si}^{\text{A}}\text{Cl}-\text{Me}(\text{Si}^{\text{B}}\text{Cl}_2\text{Me})_2$ (δ_{Si} : -4.9 (A), 23.8 ppm (B) [5]) and $\text{Cl}_3\text{Si}^{\text{A}}-\text{Si}^{\text{B}}\text{ClMe}-\text{Si}^{\text{C}}\text{Cl}_2\text{Me}$ (δ_{Si} : 5.9 (A), -4.7 ppm (B), 21.9 ppm (C) [4]). However, while δ_{Si} of the central silicon atoms in both trisilanes are almost equal, the ^{29}Si NMR signal of the central silicon atom in **5b** is almost 20 ppm upfield from that of **5a** revealing a stronger coordination of the additional chloride substituent in **5b** in accordance with a higher chlorofunctionalization and hence a higher acceptor strength of the trisilane fragment in **5b**.

On the other hand the signals of the terminal silicon atoms in **5a** and **5b** are shifted downfield by 10–15 ppm compared to the trisilanes $\text{SiClMe}(\text{SiCl}_2\text{Me})_2$ and $\text{Cl}_3\text{Si}-\text{SiClMe}-\text{SiCl}_2\text{Me}$.

Obviously **5a** and **5b** are reactive intermediates of the base catalyzed disproportionation of **2** and **4**.

Starting from these results a proposal concerning the mechanistic pathway of the reaction of chloromethyldisilanes with TDAE in *n*-hexane can be developed, see Scheme 2.

The process should be initiated by an electron transfer step from the TDAE to the disilane. The as-formed $[\text{TDAE}]^{\cdot+}$ radical cation is stabilized by the electron donating dimethylamino groups. The disilane radical intermediate may decay into a silyl radical plus a chloride stabilized silylene that may also be understood as a dichlorosilanide anion. The latter can insert into a Si–Cl bond of a further disilane molecule leading to a trisilane species. A subsequent 1,2-shift of a chloride to the middle silicon atom could create the anions found in **5a** (R = Me) or **5b** (R = Cl). The silyl radical should be able either to disproportionate into trichloromethylsilane (**2a**) and the corresponding silylene or to undergo a recombination step.

2.2. Disproportionation of chloromethyldisilanes with TDAE in polar solvents

The reaction of TDAE with a 9:1 mixture of **2** and **4** in 1,2-dimethoxyethane (DME) yielded an orange–red precipitation consisting of **5a** and **5b** besides the monosilane **2a** plus the oligomers **2b** as well as **2c**.

It should be noted that the ^{29}Si -NMR signal of the central SiClMe moiety of the trisilane **2b** was shifted to -12.2 ppm (in CDCl_3 or *n*-hexane a signal at -4.9 ppm is observed). This may be explained by a partial coordination of additional chloride ions at the central silicon atom in solution.

The analogous reaction in acetonitrile led to the formation of two liquid phases plus a precipitation of $[\text{TDAE}]\text{Cl}_2$ (**6**·MeCN). The result of the X-ray structure analysis is presented in Fig. 4. Selected bond lengths and angles are listed in Table 4.

The crystal structure of **6**·MeCN consists of the TDAE^{2+} cation plus two isolated chloride ions. The C(1)–C(2) distance (1.502 Å) as well as the dihedral angles N–C–C–N of 71.2 and 72.0° in **6** are in good agreement with the calculated C–C distance of 1.539 Å in TDAE^{2+} [14] as well as the experimental values for other TDAE^{2+} compounds: $[\text{TDAE}]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (C–C: 1.52 Å, N–C–C–N: 76°), $[\text{TDAE}]\text{Br}_2 \cdot 2\text{H}_2\text{O}$ (C–C: 1.51 Å, N–C–C–N: 67°) [22], $[\text{TDAE}](\text{PF}_6)_2$ (C–C: 1.511 Å, N–C–C–N: 72°) [23], $[\text{TDAE}][\text{TCNE}]_2$ (C–C: 1.513 Å, N–C–C–N: 61.5°) [24], $[\text{TDAE}][\text{TCNE}]$ (C–C: 1.516 Å, N–C–C–N: 71.3°), $[\text{TDAE}][\text{TCNQ}]_2$ (C–C: 1.515 Å, N–C–C–N: 63.9°) [25] and $[\text{TDAE}](\text{SCF}_3)_2$ [26].

Obviously two electrons from the TDAE were transferred to the disilane molecule and chloride ions were split off.

As demonstrated, the pathway of the disproportionation and the kind of the products depend strongly on the properties like polarity or donor strength of the used solvent. In nonpolar solvents, such as *n*-hexane, the reaction of TDAE with chloromethyldisilanes **2** and **4** gives reactive isolable intermediates (**5a** and **5b**). In the more polar solvent DME the intermediates (**5a** + **5b**) as well as the known disproportionation products **2a**, **2b**

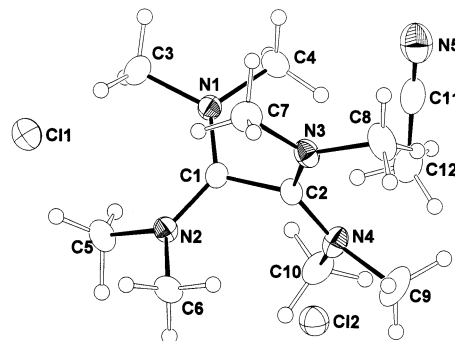


Fig. 4. ORTEP plot of the molecular structure of **6**·MeCN.

Table 4
Selected bond lengths (Å), bond angles (°) and dihedral angles (°) of **6**·MeCN

Bond lengths			
C(1)–C(2)	1.502(2)	N(1)–C(1)	1.323(2)
N(2)–C(1)	1.317(2)	N(3)–C(2)	1.317(2)
N(4)–C(2)	1.326(2)		
Bond angles			
N(1)–C(1)–C(2)	116.12(14)	N(2)–C(1)–C(2)	116.85(14)
N(3)–C(2)–C(1)	116.83(13)	N(4)–C(2)–C(1)	116.50(13)
Dihedral angles			
N(1)–C(1)–C(2)–N(3)	71.2(2)	N(2)–C(1)–C(2)–N(4)	72.0(2)

Table 5
Crystallographic parameters and experimental details for the compounds **5b** and **6·MeCN**

	5b	6·MeCN
Empirical formula	C ₁₂ H ₃₀ Cl ₇ N ₄ Si ₃	C ₁₂ H ₂₇ Cl ₂ N ₅
Molecular mass (g mol ⁻¹)	562.82	312.29
<i>T</i> (K)	173(2)	173(2)
Radiation (λ , Å)	Mo–K α (0.71073)	Mo–K α (0.71073)
Crystal system	Monoclinic	Orthorhombic
Space group	<i>P</i> 2 ₁ <i>c</i>	<i>Pna</i> 2 ₁
Unit cell dimensions		
<i>a</i> (Å)	19.921(4)	13.1709(3)
<i>b</i> (Å)	9.550(17)	12.1745(3)
<i>c</i> (Å)	14.136(3)	10.5631(3)
β (°)	92.784 (4)	
<i>V</i> (Å ³)	2686.3(8)	1693.78(7)
<i>D</i> _{calc} (g cm ⁻³)	1.392	1.225
<i>Z</i>	4	4
Crystal size (mm ³)	0.38 × 0.18 × 0.16	1.0 × 0.60 × 0.35
μ (mm ⁻¹)	0.880	0.380
Scan mode	ω -Scan	ω -Scan
θ Range for collection (°)	1.02–30.86	2.28–30.36
Index range	–28 ≤ <i>h</i> ≤ 27, –13 ≤ <i>k</i> ≤ 11, –20 ≤ <i>l</i> ≤ 20	–18 ≤ <i>h</i> ≤ 10, –16 ≤ <i>k</i> ≤ 15, –7 ≤ <i>l</i> ≤ 15
Measured reflections	20 882	7651
Independent reflections	7745	3053
Observed reflections	3445	2785
Completeness to θ_{\max} (%)	91.5	87.3
Final <i>R</i> ₁ / <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0855/0.2598	0.0272/0.0655
<i>R</i> ₁ / <i>wR</i> ₂ (all data)	0.1931/0.3234	0.0320/0.0682
Goodness-of-fit on <i>F</i> ²	1.097	1.030
Max/min e-density (e Å ⁻³)	0.908/–1.438	0.157/–0.231

and **2c** result. In this medium the disproportionation reactivity is higher than in *n*-hexane. Obviously the more polar solvent acetonitrile promotes the transfer of two electrons from TDAE delivering the ionic [TDAE]Cl₂·MeCN (**6·MeCN**). With increasing dielectric constant (DC; *n*-hexane: 1.88, DME: 7.2 [27]) the formation of the monocation TDAE^{•+} (**5a**+**5b**) is changed to the production of the dication TDAE²⁺ (acetonitrile: DC: 37.5 [27]). Thus by means of the properties of the solvents used it seems possible to control and adjust a defined state of the electron transfer process.

3. Experimental

3.1. General

All reactions were carried out under an inert gas atmosphere (argon) applying standard Schlenk techniques. Solvents were dried prior to use.

The measurements of the liquid samples were performed on a BRUKER DPX 400 spectrometer at 79.495, 100.613 and 400.130 MHz for ²⁹Si, ¹³C and ¹H, respectively. All spectra were recorded using external CDCl₃ and Me₄Si as internal reference. The measurements of the solids were performed on a BRUKER MSL

300 spectrometer at 59.672 (²⁹Si) and 75.467 MHz (¹³C) using MAS CP techniques.

EPR spectra were recorded on a BRUKER ESP 300 E spectrometer. Microwave frequency: 9722.051 MHz (X-band), microwave power: 2000 W, temperature: 25 °C, modulation frequency: 100 kHz, modulation amplitude: 1.995 G.

IR spectra (4000–400 cm⁻¹) were measured with a NICOLET-FT-IR spectrometer using pressed KBr pellets.

3.2. X-ray crystal analyses

X-ray structure analysis measurements were performed on a BRUKER AXS SMART 1K CCD. Crystal data of **5b** and **6·MeCN** as well as data collection and refinement details are given in Table 5.

The unit cells were determined with the program SMART [28]. For data integration and refinement of the unit cells the program SAINT [28] was used. The space groups were determined using the program XPREP [28]. All data were corrected for absorption using SADABS [29]. The structures were solved using direct methods (SHELX-97 [30]) and refined using least-squares-methods (SHELX-97). Molecular structure representations were done with ZORTEP [31]. The ellipsoids at the nonhydrogen atoms are at the 50% probability level. The positions

of the hydrogen atoms of **6** were taken from the electron density difference map and refined freely. The hydrogen atoms of **5b** were positioned as riding model to their neighboring atom.

3.3. Synthesis of methylchlorodisilanes

3.3.1. 1,2-Dichlorotetramethyldisilane (**1**)

Compound **1** was prepared by chlorination of hexamethyldisilane (28.1 g, 191.9 mmol) with aluminum chloride (50.7 g, 380.0 mmol) and acetyl chloride (33.8 g, 430.5 mmol) at 0 °C [32]. After stirring for 20 h **1** was condensed into a trap at –78 °C. Redistillation gave 28 g (78%) of **1** [²⁹Si NMR [32]: 17.4 ppm; ¹³C NMR: 1.2 ppm; ¹H NMR: 0.55 ppm; ¹J_{SiC}: 48.7 Hz]. Bp. 148 °C.

3.3.2. 1,1,2,2-Tetrachlorodimethyldisilane (**2**) and methylpentachlorodisilane (**4**)

The preparation of **2** by chlorination of technical disilane fraction with acetyl chloride and aluminum chloride at 125 °C was carried out as described in [32]. The resulting product was in fact a mixture of 90 mol% 1,1,2,2-tetrachlorodimethyldisilane (**2**) (²⁹Si NMR: 17.6 ppm; ¹³C NMR: 5.8 ppm; ¹H NMR: 0.99 ppm [32]) and 10 mol% pentachloromethyldisilane (**4**) [²⁹Si NMR [33]: δ^A 13.7 ppm, δ^B –0.8 ppm (CH₃Cl₂Si^A–Si^BCl₃); ¹³C NMR: 5.01 ppm; ¹H NMR: 1.06 ppm; ¹J_{SiC}: 60.7 Hz].

In a second experiment the reaction mixture (same as above) was heated up to 115 °C only. Separation and distillation of the crude product gave almost pure **2**, containing 1–2% **4**, Bp. 153 °C.

3.3.3. Hexachlorodisilane (**3**)

Compound **3** was obtained by the chlorination of hexaphenyldisilane (15 g, 28.95 mmol), diluted in *n*-hexane, with aluminum chloride (27.1 g, 202.7 mmol) and acetyl chloride (15.9 g, 202.7 mmol). After stirring overnight 10 ml *n*-hexane was added, the upper phase separated and the *n*-hexane removed in vacuo. Redistillation gave 4.3 g (55%) of pure **3** (²⁹Si NMR [34]: –6.8 ppm). Bp. 144 °C.

3.4. Homogeneous disproportionation of chlorodisilanes

3.4.1. Disproportionation of **1**

Compound **1** (2 g, 10.74 mmol) was diluted with 3 ml *n*-hexane. TDAE (2.15 g, 10.74 mmol) was added dropwise with stirring to this solution at room temperature. After stirring for 5 h ²⁹Si- and ¹³C NMR spectra of the solution were recorded which revealed the starting materials only. There was no further reaction when the mixture was heated to reflux for 2 h.

3.4.2. Disproportionation of **3**

Compound **3** (3.12 g, 11.6 mmol) was dissolved in 10 ml *n*-hexane, and 2.32 g (11.6 mmol) TDAE was added

at 0 °C. The reaction mixture discolored, and a red solid was obtained immediately. The solution was stirred for 1 h. After that the solution was investigated by ²⁹Si NMR spectroscopy (see Table 1).

3.4.3. Disproportionation of **2**

Compound **2** (2.54 g, 11.14 mmol, containing 1–2% **4**, Section 3.3.2) was dissolved in 3 ml *n*-hexane. TDAE (2.23 g, 11.14 mmol) was added dropwise at room temperature with stirring. The color of the solution changed to orange, and a red solid of **5a** (containing small amounts of **5b**; characterized by ²⁹Si MAS NMR) was obtained immediately. ²⁹Si- and ¹³C NMR spectra of the filtrated solution showed only the signals of the educts [²⁹Si NMR: δ 17.3 ppm (**2**); ¹³C NMR: δ 4.9 (**2**), 41.0 (N(CH₃)₂), 131.5 ppm (C=C)]. The experiment was repeated, but additionally the solution was refluxed for 2 h. ²⁹Si- and ¹³C NMR spectra of the separated liquid product mixture were recorded (²⁹Si NMR assignment: see Table 1; ¹³C NMR: δ 4.9 (**2**), 9.6 (**2a**), 41.0 (N(CH₃)₂), 131.5 ppm (C=C)].

3.4.4. Disproportionation of a 9:1 mixture of **2** and **4** in *n*-hexane

Ten grams of the mixture of **2** and **4** was diluted with 30 ml *n*-hexane and 8.77 g (43.8 mmol) TDAE was added dropwise under stirring at 0 °C. A red precipitation of **5a** and **5b** was observed immediately. After stirring for 2 h a part of the solution was separated and ²⁹Si and ¹³C NMR spectra were recorded [²⁹Si NMR assignment: see Table 1; ¹³C NMR: δ 5.1 ppm (**2**), δ 6.9 ppm (Si^ACH₃ of [(Cl₂CH₃Si^A)₂Si^BCH₃Cl]), broad signals at δ 41.0 ppm (N(CH₃)₂) and δ 131.9 ppm (C=C)]. Besides ¹³C and ²⁹Si MAS NMR, EPR and an X-ray structure analysis the red precipitate of **5a** and **5b** was characterized by IR and elemental analysis. IR (KBr, cm^{–1}): ν_{C=C}: 1671 (s), ν_{SiCl}: 514, 498 and 416 cm^{–1}; ²⁹Si and ¹³C MAS NMR: see Table 3; Anal. Calc. for C₁₃H₃₃Cl₆N₄Si₃ (**5a**) (542.36 g mol^{–1}); C, 28.8; H, 6.1; Cl, 39.2; N, 10.3; Si, 15.5 and C₁₂H₃₀Cl₇N₄Si₃ (**5b**) (562.82 g mol^{–1}); C, 25.6; H, 5.3; Cl, 44.1; N, 9.9; Si, 14.9. Found: C, 29.1; H, 5.6; Cl, 40.0; N, 10.7; Si, 14.3%.

3.4.5. Disproportionation of **2** in 1,2-dimethoxyethane

Compound **2** (5.06 g, 22.2 mmol) (containing 1–2% **4**) was diluted in 20 ml DME. TDAE (4.44 g, 22.2 mmol) was added dropwise with stirring at room temperature. Discoloring of the solution and precipitation of a yellow solid took place. The solution was separated and ²⁹Si- and ¹³C NMR spectra were recorded [²⁹Si NMR: δ 13.6 (**2a**), δ 18.8 (**2**), δ^A 24.4, δ^B –12.2 ppm ((Cl₂CH₃Si^A)₂Si^BCH₃Cl, **2b**), δ^A 31.7, δ^B –62.9 ppm ((Cl₂CH₃Si^A)₃Si^BCH₃, **2c**); ¹³C NMR: δ 9.2 (**2a**), δ 4.8 (**2**), δ^A 7.3 ppm (Cl₂CH₃Si^A)₂Si^BCH₃Cl, **2b**), δ^A 9.1, δ^B –12.5 ppm (Cl₂CH₃Si^A)₃Si^BCH₃, **2c**), broad signals at δ 41.2 (N(CH₃)₂) and 131.7 ppm (C=C)].

3.4.6. Disproportionation of a 9:1 mixture of **2** and **4** in acetonitrile

The 9:1 molar mixture of **2** and **4** (4.44 g, 22.2 mmol) were diluted in 20 ml acetonitrile. TDAE (4.44 g, 22.2 mmol) was added dropwise with stirring at room temperature. The formation of two phases and a discoloring of the solution occurred. Both phases were investigated by ^{29}Si - and ^{13}C NMR [^{29}Si NMR: upper phase δ 14.7 (**2a**), 20.0 (**2**), δ^{A} 22.3 and δ^{B} -53.0 ppm (no assignment), lower phase: δ 12.5 (**2a**), 17.9 ppm (**2**); ^{13}C NMR: upper phase: δ 5.9 (**2**), 10.0 ppm (**2a**); lower phase: δ 5.2 (**2**), 9.8 (**2a**), 41.2 (N(CH₃)₂), 131.4 ppm (C=C)]. Additionally we obtained colorless crystals (**6**·MeCN). M.p. 243–245 °C; (KBr, cm⁻¹): $\nu_{\text{C}=\text{C}}$: 1670 (s); ^{13}C NMR (D₂O): δ 41.5, 42.4 (N(CH₃)₂), δ 154.9 ppm (C–C); ^1H NMR (D₂O): δ 3.30, 3.59 ppm (N(CH₃)₂) [22], 2.06 ppm (CH₃CN); Anal. Calc. for C₁₂H₂₇Cl₂N₅ (312.29): C, 46.1; H, 8.7; Cl, 22.7; N, 22.4, Found: C, 44.8; H, 8.6; Cl, 22.5; N, 18.7%.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 179841 and 179842 for compounds **5b** and **6**·MeCN. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>)

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