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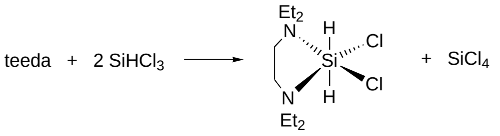
An unexpected redistribution of trichlorosilane. Synthesis, structure and bonding of (*N*,*N*,*N′*,*N′*-tetraethylethylenediamine)dichlorosilane

Philip Boudjouk,*,† Steven D. Kloos, Beon-Kyu Kim, Michael Page and David Thweatt

Center for Main Group Chemistry, Department of Chemistry, North Dakota State University, Fargo, ND 58105, USA

N,*N*,*N′*,*N′*-Tetraethylethylenediamine (teeda) redistributes trichlorosilane to form the novel six-co-ordinate complex, (teeda)SiH_2Cl_2 and tetrachlorosilane.

Amid the abundance of amine-co-ordinated silanes[1] is a conspicuous absence of well characterized complexes composed of aliphatic diamines and simple halosilanes. Over thirty years ago, Campbell-Ferguson and Ebsworth reported that the reactions of *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (tmeda) with SiH_3Cl, SiH_2Cl_2 and $SiHCl_3$ gave 1 : 1 adducts, but that their low solubilities indicated polymeric or ionic structures.[2] During the course of our studies of the diamine–copper oxide catalyzed hydrosilylation of functionalized olefins[3] we discovered that not only do aliphatic diamines form molecular complexes with simple halosilanes but that *N*,*N*,*N′*,*N′*-tetraethylethylenediamine (teeda) will redistribute trichlorosilane to form the novel six-co-ordinate complex, (teeda)SiH_2Cl_2 **1**,‡ and tetrachlorosilane, equation (1).[4]

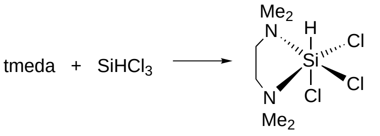


(1)

1

The addition of $SiHCl_3$ (22.9 g, 169 mmol) to a solution of teeda (7.2 g, 4.2 mmol) in dry CH_2Cl_2 (20 ml) proceeds exothermically to give a homogeneous solution, which, upon addition of pentane (20 ml) at room temperature, produces white crystals of **1** (10.40 g, 90.2% yield based on silane) within a few minutes. The $SiCl_4$ can be removed from the reaction mixture by distillation. No other products are observed. Mixtures of products are frequently observed when halosilanes are treated with amines. For example, Fleischer recently reported that bis(dichlorosilyl)amine reacts in chloroform solution with 2-picoline (2-methylpyridine, 2-pic) to give SiH_3Cl, SiH_2Cl_2 and $SiHCl_3$ and that 3-picoline (3-pic) forms two six-co-ordinate silicon compounds, SiH_2Cl_2(3-pic)$_2$ and [SiH_2(3-pic)$_4$]Cl_2.[5]

In contrast to the redistribution promoted by teeda, tmeda reacts with $SiHCl_3$ to give (tmeda)$SiHCl_3$ **2**§ exclusively, equation (2). Precipitation of this complex from CH_2Cl_2 is immediate and nearly quantitative. Complex **2** is sparingly soluble in CH_2Cl_2 and virtually insoluble in THF.



(2)

2

It was in our attempt to prepare a soluble diamine–trichlorosilane complex that we treated $SiHCl_3$ with teeda and found that the reaction takes a different course, *i.e.*, equation (1) and, in fact, **1** is soluble in CH_2Cl_2.

The structures of complexes **1** and **2** (Figs. 1 and 2) were determined by single crystal X-ray analyses¶ and possess several noteworthy features. In addition to demonstrating that the complexes are indeed 1 : 1, neutral and six-co-ordinate, the data show that the Cl atoms are positioned *cis* in **1** and *fac* in **2**. This is unexpected because the dominant trend for five- and six-co-ordinate silanes is for the more electronegative atoms to be *trans*.[7] Selected structural data are given in Tables 1 and 2.

The crystal structure of **1** shows short Si–H and Si–N bonds with average bond distances of 1.29 and 2.13 Å, respectively (Table 1). Compared to the interatomic distances calculated by Wittbrodt and Shlegel[8] for SiH_2Cl_2, the average Si–H bond in **1** is shortened by approximately 0.17 Å and the average Si–Cl bond length is increased by approximately 0.18 Å. Co-ordination of a nitrogen lone pair *trans* to a Si–Cl bond is known to lengthen the Si–Cl bond to form a more balanced three-center bond. Compared to the Si–Cl bonds of uncomplexed SiH_2Cl_2 (average = 2.044 Å), the average Si–Cl bond length in **1** (2.228 Å) is longer by 0.18 Å. However, the Si–Cl bonds of **1** are still short compared to Si–Cl bonds in six-co-ordinate silicon compounds (2.1–2.4 Å) and the Si–N bonds are short compared to other dative N→Si bonds (1.95–2.7 Å).[12] The H–Si–H linkage, with an angle of 163.4°, is bent toward the diamine fragment. The H–Si–H contraction is probably due to

Table 1 Selected bond lengths (Å)

Silane	Si–H	Si–Cl(1)	Si–Cl(2)	Si–Cl(3)	Si–N
SiH_2Cl_2	1.469[a]	2.048[a] (2.02 ± 0.03[c])			
$SiHCl_3$	1.454[b]	2.038[b] (1.98 ± 0.02[d])			
1	1.266(57), 1.314(61)	2.223(4)	2.233(4)		2.134(8), 2.126(8)
2	1.363(30)	2.205(5)	2.152(2)	2.202(2)	2.075(4), 2.087(5)

[a] Calculated data, ref. 8. [b] Calculated data, ref. 9. [c] Electron diffraction data, ref. 10. [d] Electron diffraction data, ref. 11.

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† E-Mail: boudjouk@plains.nodak.edu

‡ Selected data for complex **1**: IR (cm^{-1}): ν(Si–H) 2178; NMR ($CDCl_3$): ^1H δ 1.13 (t, 12 H), 2.78 (s, 4 H), 2.91 (q, 8 H), 4.99 (s, 2 H); ^{13}C δ 10.0, 47.57, 48.50; ^{29}Si δ −120.2 (t, $^1J_{SiH} = 404$ Hz); m.p.: 101–102 °C (Found: C, 44.05; H, 9.66; N, 10.34. Calc. for $C_{10}H_{26}Cl_2N_2Si$: C, 43.94; H, 9.59; N, 10.25%).

§ Selected data for complex **2**: IR (cm^{-1}): 2128; NMR ($CDCl_3$): ^1H δ 2.68 (br, 12 H), 2.95 (br, 4 H), 4.92 (s, 1 H); ^{29}Si δ −145.6 (d, $^1J_{SiH} = 392$ Hz) (Found: C, 26.68; H, 6.57; N, 11.0. Calc. for $C_6H_{17}Cl_3N_2Si$: C, 28.64; H, 6.81; N: 11.13%).

¶ Crystal data for complex **1**: $C_{10}H_{26}Cl_2N_2Si$, $M = 273.3$, orthorhombic, space group $P2_12_12_1$, $a = 7.8230(5)$, $b = 9.8720(10)$, $c = 19.248(2)$ Å, $T = 298$ K, $Z = 4$, $\mu = 4.497$ mm^{-1}, 1584 reflections measured, $R = 0.0751$, $R' = 0.708$. Crystal data for complex **2**: $C_6H_{17}Cl_3N_2Si$, $M = 251.7$, monoclinic, space group $P2_1/n$, $a = 8.068(2)$, $b = 12.670(3)$, $c = 12.035(2)$ Å, $\beta = 108.93(3)°$, $T = 298$ K, $Z = 4$, $\mu = 0.846$ mm^{-1}, 2060 reflections measured, $R = 0.0536$, $R' = 0.0670$. CCDC reference number 186/885.

Table 2 Selected bond angles (°)

Silane	H(1)–Si–H(2)	H(1)–Si–Cl(1)	H(1)–Si–Cl(2)	H(1)–Si–Cl(3)	N(1)–Si–N(2)
SiH_2Cl_2	112.75[a]		108.54[a]		
$SiHCl_3$			109.40[b]		
1	163.4(40)	97.0(27)	94.9(26)		84.8(3)
2		90.2(14)	175.5(15)	92.9(17)	85.0(2)

[a] Calculated data, ref. 8. [b] Calculated data, ref. 9.

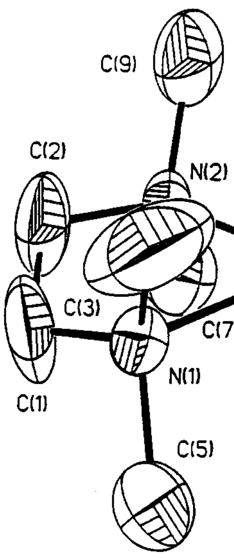

Fig. 1 An ORTEP[6] plot of compound **1** (four terminal methyl groups are omitted for clarity). Selected bond distances (Å) and angles (°): Si–H(1) 1.266(57), Si–H(2) 1.341(61), Si–Cl(1) 2.223(4), Si–Cl(2) 2.233(4), Si–N(1) 2.134(8), Si–N(2) 2.126(8); H(1)–Si–H(2) 163.4(40), N(1)–Si–N(2) 84.8(3)

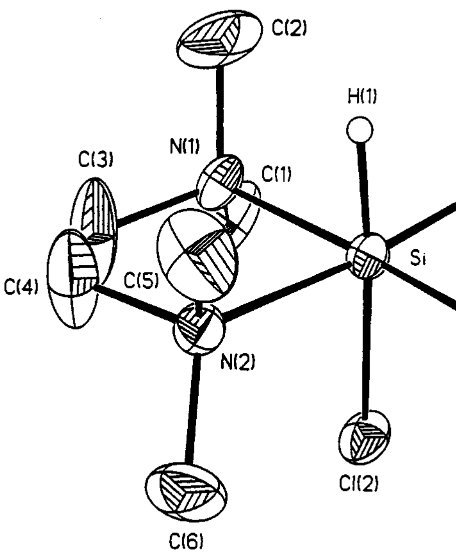

Fig. 2 An ORTEP plot of compound **2**. Selected bond distances (Å) and angles (°): Si–H(1) 1.363(30), Si–Cl(1) 2.205(2), Si–Cl(2) 2.152(2), Si–Cl(3) 2.202(2), Si–N(1) 2.087(5), Si–N(2) 2.075(4); H(1)–Si–Cl(2) 175.5(15), N(1)–Si–N(2) 85.0(2)

Table 3 IR and NMR * data of silanes

Silane	ν(Si–H)/cm^{-1}	δ(^{1}H)/ppm	δ(^{29}Si)/ppm	^1J(^{29}Si–^{1}H)/Hz
SiH_2Cl_2[13]	2200	5.40	−11.5	288
$SiHCl_3$[14]	2274	6.13	−9.5	368
1	2178	4.99	−120.2	404
2	2128	4.92	−145.6	392

* Solvent $CDCl_3$, internal standard $Si(CH_3)_4$.

Table 4 Si–H bond characters from SCF/CEP-31G* calculations

Silane	% s Character	% p Character	% d Character
SiH_4	24.1	65.2	10.7
SiH_3Cl	26.6	61.2	12.1
SiH_2Cl_2	30.6	57.8	11.6
(en)SiH_2Cl_2[a]	40.9	47.4	11.7
(en)SiH_2Cl_2[b]	31.0	57.5	11.4
$SiHCl_3$	35.3	52.8	11.9
(en)$SiHCl_3$	35.8	52.6	11.6

[a] *cis*-Cl isomer. [b] *trans*-Cl isomer.

repulsion from the large electron clouds of the chlorine atoms.

The crystal structure of **2** shows a slightly longer Si–H bond than that in **1**. However, the average Si–Cl and Si–N bonds in **2** are slightly shorter than **1**. Compared to the distance calculated by Gordon *et al.*[9] for uncomplexed $SiHCl_3$, the Si–H bond length (1.363 Å) is shorter ($\Delta = 0.09$ Å), the Si–Cl(2) bond is longer ($\Delta = 0.11$ Å) as is the Si–Cl(1) bond ($\Delta = 0.17$ Å).

The structures of six-co-ordinate ethylenediamine complexes of dichlorosilane with *cis*-Cl and *trans*-Cl were minimized at the MP2/CEP-31G* level of theory using effective core potentials (ECP's).[15] The MP4 energies and MP2 frequencies were also computed with the same basis set. The computed structures are qualitatively consistent with the crystal data, including the less than 180° H–Si–H bond angle. Additional calculations were done to study the degree of d orbital participation in bonding with hypervalent silicon. Reported Mulliken Population analyses are based on Hartree–Fock calculations with the CEP-31G* (ECP split-valence with polarization) basis set. The overlap populations of silicon d functions with the hydrogen s functions did not change significantly from four- to six-co-ordinate silicon (Table 4). This is consistent with the findings of Gordon *et al.*[16] for six-co-ordinate silicon species of the type SiF_6^{2-} and SiH_6^{2-}.

For SiH_2Cl_2, the Si–H bond character from Si was 30.6% s, 57.8% p, and 11.6% d. For (en)SiH_2Cl_2 with *cis*-Cl the Si–H bond character was 40.9% s, 47.4% p, and only 11.7% d. The *trans*-Cl case showed Si–H bond character as 31.0% s, 57.5% p, and 11.4% d.[14]

For comparison, SiH_4 was 24.1% s, 65.2% p, and 10.7% d while CH_4 showed 25.7% s, 72.0% p, and 2.3% d. The change in s character was far more significant for the dichloro case than for the trichloro case upon complexation (Table 4). This can also be seen as a greater change in the $^1J_{SiH}$ coupling constant (Table 3).

The higher s character of the Si–H bond should explain the greater Si–H coupling constant observed in the ^{29}Si NMR spectra. The $^1J_{SiH}$ coupling constant of **1** is greater than the largest previously reported value of 381.7 Hz for $HSiF_3$.[17] The large upfield chemical shift in the ^{1}H and ^{29}Si NMR spectra may be explained by the co-ordination of two σ-donor nitrogens to the silicon atom. The slightly shorter Si–H bond length in both crystal structure and theoretical calculations and higher calculated s character of **1** compared to **2** can explain the higher Si–H stretching frequency in **1**.

Isomers of (en)SiH_2Cl_2 were found to show stabilization of the *trans*-Cl isomer over the *cis*-Cl by 3.8 kcal mol^{-1} and 3.0 kcal mol^{-1} (cal = 4.184 J) for MP2 and MP4 calculations (including zero point vibrational corrections) respectively. This small stabilization leads us to believe that the observation of (en)SiH_2Cl_2 with *cis*-Cl is due to kinetic rather than thermodynamic effects.

Complex **1** is a potential synthetic equivalent of SiH_2Cl_2 and functions as a safe and convenient source of this compound. Upon treatment with PhMgCl, **1** generates Ph_2SiH_2 in 75% yield, equation (3). Complex **1** *cis*-Cl also undergoes ligand exchange to form **3** *cis*-Cl,[||] equation (4). A noteworthy

$$(\text{teeda})\text{SiH}_2\text{Cl}_2 + \text{PhMgCl} \longrightarrow \text{Ph}_2\text{SiH}_2 \qquad (3)$$

$$(\text{teeda})\text{SiH}_2\text{Cl}_2 + \text{tmeda} \longrightarrow \underset{\mathbf{3}}{(\text{tmeda})\text{SiH}_2\text{Cl}_2} + \text{teeda} \qquad (4)$$

aspect of this process is that the configuration about silicon is unchanged.

Acknowledgements

Financial support from the National Science Foundation and Dow Corning Corporation is gratefully acknowledged. The authors thank David Atwood and Kyli Martin for help in determination of the crystal structures of complexes **1** and **2**.

[||] Selected data for complex **3**: IR (cm^{-1}): 2197; NMR ($CDCl_3$): ^1H δ 2.51 (s, 12 H), 2.81 (s, 4 H), 5.00 (s, 2 H) (Found: C, 33.61; H, 8.07; N, 13.15. Calc. for $C_6H_{18}Cl_2N_2Si$: C, 33.18; H, 8.35; N, 12.90%).

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Received 8*th January* 1998; *Communication* 8/00240A