

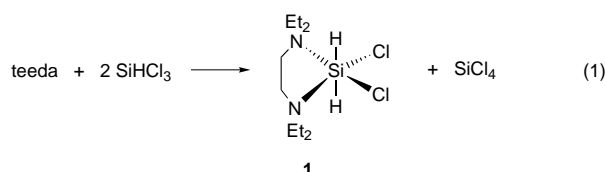
An unexpected redistribution of trichlorosilane. Synthesis, structure and bonding of (*N,N,N',N'*-tetraethylethylenediamine)dichlorosilane

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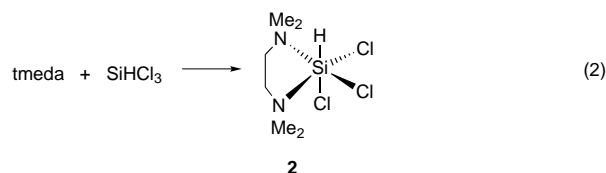
N,N,N',N'-Tetraethylethylenediamine (teeda) redistributes trichlorosilane to form the novel six-co-ordinate complex, (teeda)SiH₂Cl₂ and tetrachlorosilane.

Amid the abundance of amine-co-ordinated silanes¹ 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 SiH₃Cl, SiH₂Cl₂ and SiHCl₃ 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 olefins³ 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)SiH₂Cl₂ **1**,[‡] and tetrachlorosilane, equation (1).⁴



The addition of SiHCl₃ (22.9 g, 169 mmol) to a solution of teeda (7.2 g, 4.2 mmol) in dry CH₂Cl₂ (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 SiCl₄ 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 SiH₃Cl, SiH₂Cl₂ and SiHCl₃ and that 3-picoline (3-pic) forms two six-co-ordinate silicon compounds, SiH₂Cl₂(3-pic)₂ and [SiH₂(3-pic)₄]Cl₂.⁵

In contrast to the redistribution promoted by teeda, tmeda reacts with SiHCl₃ to give (tmeda)SiHCl₃ **2** exclusively, equation (2). Precipitation of this complex from CH₂Cl₂ is immediate and nearly quantitative. Complex **2** is sparingly soluble in CH₂Cl₂ and virtually insoluble in THF.



It was in our attempt to prepare a soluble diamine-trichlorosilane complex that we treated SiHCl₃ with teeda and found that the reaction takes a different course, *i.e.*, equation (1) and, in fact, **1** is soluble in CH₂Cl₂.

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 Shlegel⁸ for SiH₂Cl₂, 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. Coordination 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 SiH₂Cl₂ (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 ₂ Cl 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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[‡] Selected data for complex **1**: IR (cm⁻¹): ν(Si-H) 2178; NMR (CDCl₃): ¹H δ 1.13 (t, 12 H), 2.78 (s, 4 H), 2.91 (q, 8 H), 4.99 (s, 2 H); ¹³C δ 10.0, 47.57, 48.50; ²⁹Si 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 C₁₀H₂₆Cl₂N₂Si: C, 43.94; H, 9.59; N, 10.25%).

[§] Selected data for complex **2**: IR (cm⁻¹): 2128; NMR (CDCl₃): ¹H δ 2.68 (br, 12 H), 2.95 (br, 4 H), 4.92 (s, 1 H); ²⁹Si δ -145.6 (d, ¹J_{SiH} = 392 Hz) (Found: C, 26.68; H, 6.57; N, 11.0. Calc. for C₆H₁₇Cl₃N₂Si: C, 28.64; H, 6.81; N, 11.13%).

[¶] Crystal data for complex **1**: C₁₀H₂₆Cl₂N₂Si, *M* = 273.3, orthorhombic, space group *P*2₁2₁, *a* = 7.8230(5), *b* = 9.8720(10), *c* = 19.248(2) Å, *T* = 298 K, *Z* = 4, μ = 4.497 mm⁻¹, 1584 reflections measured, *R* = 0.0751, *R*' = 0.708. Crystal data for complex **2**: C₆H₁₇Cl₃N₂Si, *M* = 251.7, monoclinic, space group *P*2₁/*n*, *a* = 8.068(2), *b* = 12.670(3), *c* = 12.035(2) Å, β = 108.93(3)°, *T* = 298 K, *Z* = 4, μ = 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 ₂ Cl 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.

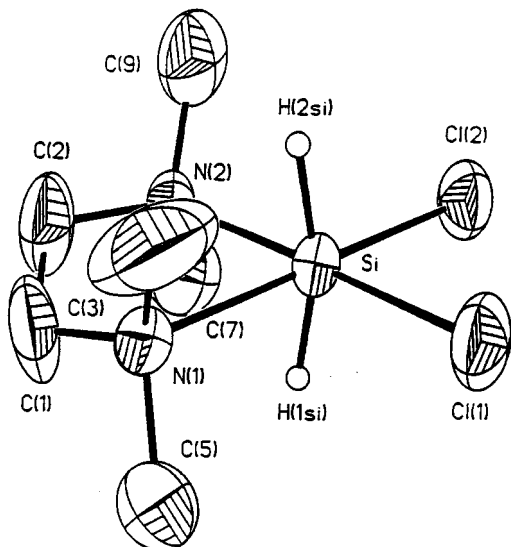


Fig. 1 An ORTEP⁶ plot of compound **1** (four terminal methyl groups are omitted for clarity). Selected bond distances (Å) and angles (°): Si–H(1) 1.266(57), Si–H(2) 1.341(61), Si–Cl(1) 2.223(4), Si–Cl(2) 2.233(4), Si–N(1) 2.134(8), Si–N(2) 2.126(8); H(1)–Si–H(2) 163.4(40), N(1)–Si–N(2) 84.8(3)

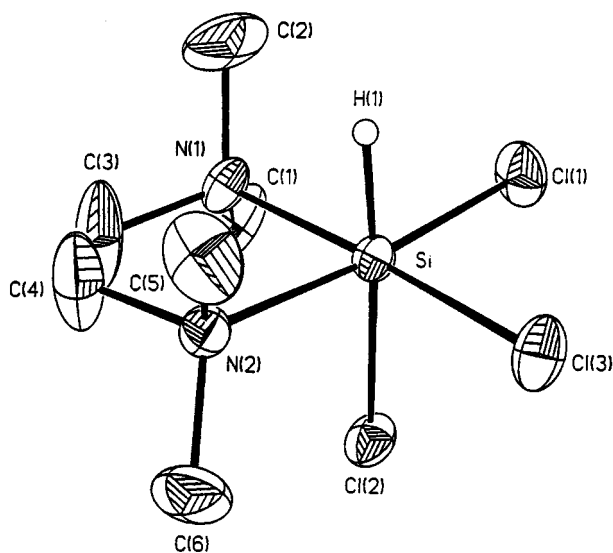


Fig. 2 An ORTEP plot of compound **2**. Selected bond distances (Å) and angles (°): Si–H(1) 1.363(30), Si–Cl(1) 2.205(2), Si–Cl(2) 2.152(2), Si–Cl(3) 2.202(2), Si–N(1) 2.087(5), Si–N(2) 2.075(4); H(1)–Si–Cl(2) 175.5(15), N(1)–Si–N(2) 85.0(2)

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 SiHCl₃, 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

Table 3 IR and NMR* data of silanes

Silane	$\nu(\text{Si-H})/\text{cm}^{-1}$	$\delta(^1\text{H})/\text{ppm}$	$\delta(^{29}\text{Si})/\text{ppm}$	$^1J(^{29}\text{Si-H})/\text{Hz}$
SiH ₂ Cl 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 CDCl₃, internal standard Si(CH₃)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 ₃ Cl	26.6	61.2	12.1
SiH ₂ Cl ₂	30.6	57.8	11.6
(en)SiH ₂ Cl ₂ ^a	40.9	47.4	11.7
(en)SiH ₂ Cl 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.

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 SiF₆²⁻ and SiH₆²⁻.

For SiH₂Cl₂, the Si–H bond character from Si was 30.6% s, 57.8% p, and 11.6% d. For (en)SiH₂Cl₂ 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

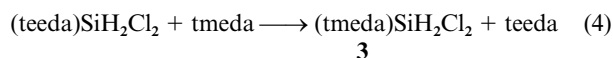
For comparison, SiH₄ was 24.1% s, 65.2% p, and 10.7% d while CH₄ showed 25.7% s, 72.0% p, and 2.3% d. The change in s character was far more significant for the dichloro case than for the trichloro case upon complexation (Table 4). This can also be seen as a greater change in the $^1J_{\text{SiH}}$ coupling constant (Table 3).

The higher s character of the Si–H bond should explain the greater Si–H coupling constant observed in the ²⁹Si NMR spectra. The $^1J_{\text{SiH}}$ coupling constant of **1** is greater than the largest previously reported value of 381.7 Hz for HSiF₃.¹⁷ The large upfield chemical shift in the ¹H and ²⁹Si 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)SiH₂Cl₂ 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)SiH₂Cl₂ with *cis*-Cl is due to kinetic rather than thermodynamic effects.

Complex **1** is a potential synthetic equivalent of SiH₂Cl₂ and functions as a safe and convenient source of this compound. Upon treatment with PhMgCl, **1** generates Ph₂SiH₂ in 75% yield, equation (3). Complex **1** *cis*-Cl also undergoes ligand exchange to form **3** *cis*-Cl, equation (4). A noteworthy



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

Acknowledgements

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|| Selected data for complex **3**: IR (cm⁻¹): 2197; NMR (CDCl₃): 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 C₆H₁₈Cl₂N₂Si: C, 33.18; H, 8.35; N, 12.90%).

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