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Synthesis, structures, and properties of novel aminodisilanes bearing bulky substituents: 1,2-bis(1,1,2-trimethylpropyl)-1,1,2,2-tetrakis(diethylamino)disilane and 1,2-di-tert-butyl-1,1,2,2-tetrakis(diethylamino)disilane ☆

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Abstract

Two novel tetraaminodisilanes, 1,2-bis(1,1,2-trimethylpropyl)-1,1,2,2-tetrakis(diethylamino)disilane (**1**) and 1,2-di-tert-butyl-1,1,2,2-tetrakis(diethylamino)disilane (**2**) were synthesized and X-ray crystallography analyses of these compounds were carried out. Reflecting the steric congestion, the Si–Si bonds are very long: 2.539(2) Å for bis(1,1,2-trimethylpropyl)disilane, and 2.4764(9) Å for di-tert-butyldisilane. UV spectra and oxidation potentials of several tetraaminodialkyldisilanes are compared and discussed. In addition, in the chlorination of **1** with HCl, 1,1,2,2-tetrachloro-1,2-bis(1,1,2-trimethylpropyl)disilane (**6**) was obtained with a 72% yield.

Keywords: Silicon; (Amino)disilane; Electronic spectra; X-ray diffraction; Chlorination

1. Introduction

Silicon compounds bearing amino groups have aroused the interest of chemists mainly in the theoretical field [1]. Recently Tamao et al. [2,3] have prepared the first stable silyllithiums taking advantage of the electronic properties of amino groups and their availability toward the synthesis of dimethyldisilane, starting from $MeSi(NEt_2)_2Cl$. Quite recently, Tamao et al. have found a systematic method for the preparation of (amino)(phenyl)disilanes and examined their electronic spectra in order to clarify the electronic effect of amino groups on the Ph–Si–Si system [4]. These preceding results have prompted us to make aminodisilanes bearing bulky groups. Since 1992, our group has reported the synthesis of octathexyloctasilacubane (thexyl or Tx denotes 1,1,2-trimethylpropyl group hereafter) [5] and its reaction [6] and showed the versatility of thexyl as a steric protection group. We herein report the synthesis of the stable 1,1,2,2-tetrakis(diethylamino)-1,2-dithexyldisilane (**1**) ($Tx_2Si_2(NEt_2)_4$) and 1,2-di-tert-butyl-1,1,2,2-tetrakis(diethylamino)disilane (**2**) (${}^tBu_2Si_2(NEt_2)_4$) and their X-ray crystallography analyses. Comparison of their UV and CV features with those of aminodisilanes with less bulky substituents connoted their distinct dependence on the bulkiness. In addition, the chlorination reaction of **1** was performed and 1,1,2,2-tetrachloro-1,2-dithexyldisilane (**6**) was obtained with a 72% yield.

2. Results and discussion

2.1. Preparations of $R_2Si_2(NEt_2)_4$

The aminodisilanes were prepared with a slight modification of the procedures reported by Tamao et al. [3] (Scheme 1). The reaction which introduces the amino groups into tetrachlorodisilanes did not afford tetraaminodisilanes, even for the least bulky dimethyl compound **5** [7]. Presumably the steric hindrance is too severe for the fourth diethylamino group to be introduced. Thus all **1–4** except 1,1,2,2,-tetrakis(diethyl-

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☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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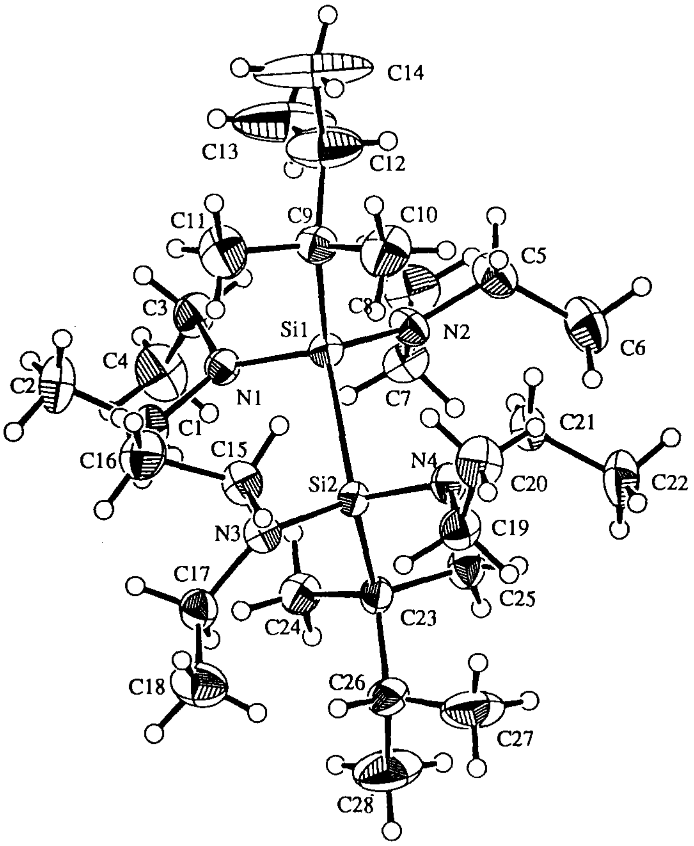


Fig. 1. ORTEPII drawing of 1. Thermal ellipsoids are drawn at the 30% probability level.

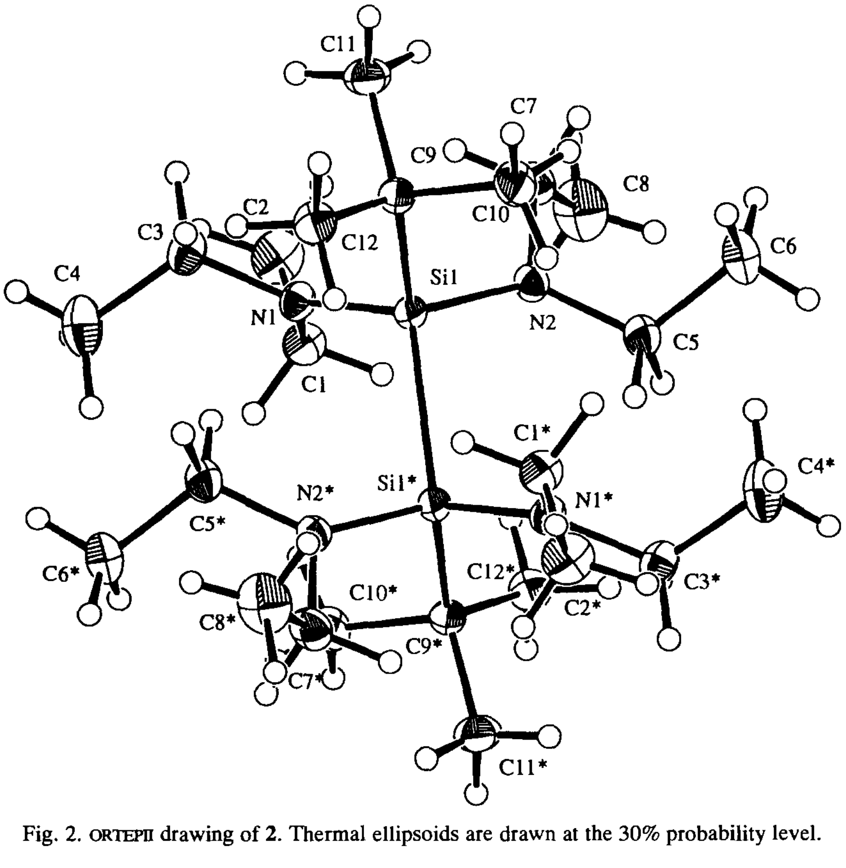
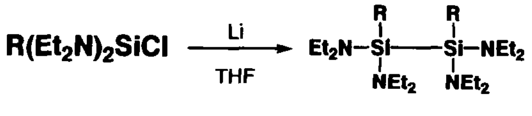


Fig. 2. ORTEPII drawing of 2. Thermal ellipsoids are drawn at the 30% probability level.

amino)-1,2-dimethyldisilane (**5**) were unknown and prepared for the first time. Against the fact that aminosilanes are apt to be hydrolyzed, **1** and **2** are surprisingly stable owing to the efficient protection with bulky thexyl or tert-butyl group. As expected, 1,1,2,2,-tetrakis(diethylamino)-1,2-diethyldisilane (**4**) and **5** decomposed simultaneously with a trace amount of water and gave cyclic siloxanes, while **1** and **2** survived even with the treatment with water. This obviates the careful handling, and recrystallization and their X-ray crystallography were made possible.

2.2. The structures and properties of tetraaminodisilanes

In Figs. 1 and 2, the ORTEP drawings of **1** and **2** are shown. Crystallographic data are shown in Table 1. Positional parameters, and selected bond distances and angles are given in Tables 2 and 3 for **1** and Tables 4 and 5 for **2** respectively. Both **1** and **2** crystallize in the $P\bar{1}$ space group, for **1** with two molecules per unit cell and for **2** with one molecule per unit cell. Compound **2** has a center of symmetry midway between the two silicon atoms, while **1** is asymmetrical. The unique features of these crowded molecules are mostly represented by the very long Si–Si bond lengths. In the thexyl-substituted compound **1**, the Si–Si distance is 2.539(2) Å and in the tert-butyl-substituted compound **2**, it is 2.4764(9) Å, and these values are much longer than the typical Si–Si bond length, 2.34 Å [8]. These distances apparently resulted from mutual repulsions between bulky thexyl or tert-butyl and diethylamino groups. It is noteworthy that there exists a large difference between the Si–Si lengths of **1** and **2** because of a slight change in the substituents. Also Si–C bonds are elongated considerably, the distances are 1.969(6) and 1.956(5) Å for **1** and 1.938(2) Å for **2**, while the usual Si–C bond length is 1.88 Å [8]. On the contrary, the Si–N bond lengths are mostly unaffected; the average length of 1.749 Å of **1** and 1.746 Å of **2** are both within the normal range 1.70–1.76 Å. The sums of bond angles around nitrogen atoms are 359.5° (N(1)), 359.8° (N(2)), 360.0° (N(3)) and 359.8° (N(4)) for **1** and 360.0° (N(1)) and 359.2° (N(2)) for **2**, showing that the geometry at nitrogen is nearly planar. The n orbital on nitrogen is thus assumed to be perpendicular to these planes; then the dihedral angles of Si–Si–N and C–N–C planes can be a measure of the degree of the n–σ interaction as Tamao et al. [4] claimed. For **1**, the observed angles are 25.7° (N(1)), 88.4° (N(2)), 72.2° (N(3)) and 34.5° (N(4)). For **2**, the angles are 79.6° (N(1)) and 17.9° (N(2)). In the case of $Ph_2Si_2(NEt_2)_4$, the corresponding values are reported to be 17°, 45°, 43° and 13° [4]. Interestingly, the angles for two nitrogen atoms (N(2) and N(3) for **1**, N(1) and N(1*) for **2**) are close to 90°, making the larger orbital overlap possible. The torsion angles of N–Si–Si–N are close to 180°; 172.0° for N(1)–Si(1)–Si(2)–N(4), 170.5° for N(2)–Si(1)–Si(2)–N(3); for **2**, the angles for N(1)–Si(1)–Si(1*)–N(1*) and N(2)–Si(1)–Si(1*)–N(2*) are both 180° because of symmetry. All these structural features are good support for strong n–σ interaction.



1: R = Tx ; 18%
2: R = *t*-Bu ; 12%
3: R = *i*-Pr ; 23%
4: R = Et ; 42%

Scheme 1.

Table 1
Summary of crystal data, data collection and refinement

	$Tx_2Si_2(NEt_2)_4$ (**1**)	t-$Bu_2Si_2(NEt_2)_4$ (**2**)
Crystal data		
Formula	$C_{28}H_{66}N_4Si_2$	$C_{24}H_{58}N_4Si_2$
Molecular weight	515.03	458.92
Crystal description	Colorless, prismatic	Colorless, prismatic
Crystal size (mm)	0.20×0.20×0.10	0.50×0.50×0.30
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.839(2)	9.571(2)
b (Å)	20.354(3)	9.849(3)
c (Å)	9.499(2)	9.489(3)
α (°)	93.35(2)	105.42(3)
β (°)	117.90(1)	108.56(2)
γ (°)	81.08(2)	110.98(2)
V (Å^3)	1660.5(5)	715.2(4)
Z	2	1
Data collection		
Diffractometer	Rigaku AFC7R	Rigaku AFC7S
Radiation (λ (Å))	Cu Kα (1.5418)	Mo Kα (0.7107)
μ (mm^{-1})	1.11	0.14
$2\theta_{max}$ (°)	120.1	55.0
Scan type	$\omega-2\theta$	$\omega-2\theta$
Scan width (°)	$1.37+0.30 \tan \theta$	$1.52+0.30 \tan \theta$
Number of reflections measured	5281	3480
Number of independent reflections	4937	3285
Number of observed reflections ($\lvert F_o \rvert \geqslant 3\sigma(F_o)$)	3312	2842
Refinement		
R	0.073	0.034
R_w	0.116	0.029
$(\Delta\rho)_{max}$ (electrons Å^{-3})	0.38	0.32
$(\Delta\rho)_{min}$ (electrons Å^{-3})	−0.27	−0.19

The steric congestion also implies unique physical properties. The UV spectra of **1–5** in hexane are shown in Fig. 3. These aminodisilanes show the absorption maxima as shoulders between 242 and 256 nm, and those of **2**–**5** were close each other [9]. On the contrary, λ_{max} of **1** was 256 nm and more than 10 nm longer than those of others. Presumably this difference can be attributed to the longer Si–Si length of **1** due to the steric hindrance in addition to the electronical effect of the thexyl groups which withdraw electron to weaken Si–Si bond. Usually, when the Si–Si bonds suffer strain, λ_{max} of those compounds are known to move to a longer wavelength [10]. However, hexaalkyldisilanes do not show absorption maxima over 200 nm; even for very bulky hexa-tert-butyldisilane [11] it has not been possible to discuss with simple models. These tetraaminodisilanes can be good models which indicate the relationship of absorption maxima and structure of disilanes. As in the case of (amino)(phenyl)disilanes [4], no solvent effects were observed this time; thus λ_{max} of **1** in methanol was 256 nm ($\varepsilon = 5000$).

The oxidation potentials of **1**–**3** are depicted in Fig. 4 [12]. Hexamethyldisilane was measured as a reference. From these results, some interesting features are seen. Firstly, as expected, the effect of amino groups is large and there is a large gap between hexamethyldisilane and **3**. Secondly, only **1** has a unique oxidation potential while **2** and **3** showed similar values. We consider that these can be attributed to the structural and electronic features as in the case of UV spectra.

There exists a large difference between **1** and **2** for the values of both λ_{max} and the oxidation potential, and this could be attributed to the difference of highest occupied molecular orbital (HOMO) levels of these compounds. Presumably the bond elongation by steric and electronical effects raises the HOMO level of **1**. Considering the fact that a more branched thexyl group makes the HOMO level higher, we could say the n–σ interaction between nitrogen and silicon–silicon bond exists most plausibly. The results of X-ray structure also indicated the possibility of spatial interaction of orbitals. However, the exact description of the orbital interaction can be outlined with calculation and photochemistry. Further investigations are now in progress.

2.3. Chlorination reaction

We found that **1** can be converted to 1,1,2,2-tetrachloro-1,2-dithexyldisilane (**6**) as in the case of diethylaminodisilanes [3]. Thus the treatment of **1** with dry HCl gas in benzene reached completion at room temperature in 10 min. Filtration followed by bulb-to-bulb distillation was done and the yield was 72%. Tetra-

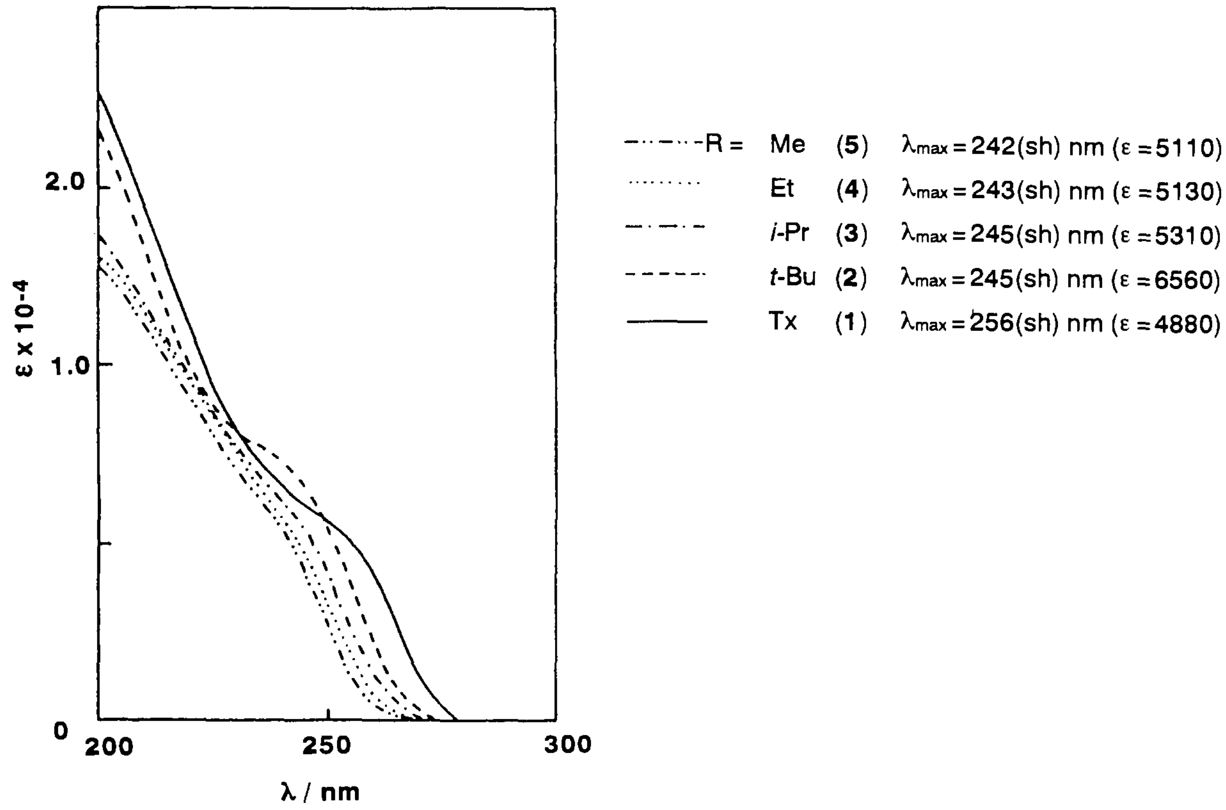


Fig. 3. UV spectra of **1**–**5** in hexane.

Table 2
Fractional atomic coordinates and equivalent isotropic thermal parameters for **1**

Atom	x	y	x	B_{eq} (Å^2)
Si(1)	0.0556(2)	0.30660(7)	0.2706(2)	3.42(3)
Si(2)	−0.0001(1)	0.18858(7)	0.1918(1)	3.17(3)
N(1)	0.0870(5)	0.3127(2)	0.4679(5)	3.73(10)
N(2)	−0.0996(5)	0.3683(2)	0.1626(5)	4.3(1)
N(3)	0.1417(5)	0.1263(2)	0.3180(5)	3.80(10)
N(4)	−0.0069(5)	0.1740(2)	0.0054(5)	4.0(1)
C(1)	0.1491(7)	0.2557(3)	0.5756(6)	4.7(1)
C(2)	0.3023(8)	0.2582(4)	0.7256(7)	6.6(2)
C(3)	0.0744(8)	0.3754(3)	0.5465(7)	5.3(2)
C(4)	−0.0243(10)	0.3775(4)	0.6311(9)	7.2(2)
C(5)	−0.1241(8)	0.3968(3)	0.0123(8)	5.8(2)
C(6)	−0.2841(9)	0.3918(4)	−0.1315(9)	7.7(2)
C(7)	−0.2254(6)	0.3930(3)	0.2025(7)	4.9(1)
C(8)	−0.2511(8)	0.4674(3)	0.2210(10)	6.7(2)
C(9)	0.2412(6)	0.3232(3)	0.2573(7)	4.4(1)
C(10)	0.2478(8)	0.2910(4)	0.1117(9)	7.0(2)
C(11)	0.3779(8)	0.2877(4)	0.3995(9)	7.3(2)
C(12)	0.2687(10)	0.3956(4)	0.260(1)	9.4(3)
C(13)	0.245(2)	0.4424(5)	0.359(2)	14.7(6)
C(14)	0.416(2)	0.4026(5)	0.254(2)	17.7(7)
C(15)	0.2933(6)	0.1113(3)	0.3221(7)	4.7(1)
C(16)	0.4337(7)	0.1076(4)	0.4842(9)	6.3(2)
C(17)	0.1270(6)	0.0862(3)	0.4321(7)	4.7(1)
C(18)	0.1407(9)	0.0127(4)	0.403(1)	7.3(2)
C(19)	0.0386(7)	0.1094(3)	−0.0483(7)	4.8(1)
C(20)	0.1560(8)	0.1102(4)	−0.1085(8)	6.3(2)
C(21)	−0.0733(7)	0.2257(3)	−0.1184(7)	4.8(1)
C(22)	−0.2132(8)	0.2110(4)	−0.2727(7)	6.7(2)
C(23)	−0.1994(6)	0.1830(3)	0.1858(6)	3.8(1)
C(24)	−0.1977(6)	0.2091(3)	0.3415(7)	4.7(1)
C(25)	−0.3201(6)	0.2309(3)	0.0525(7)	4.8(1)
C(26)	−0.2515(6)	0.1111(3)	0.1500(7)	5.0(1)
C(27)	−0.286(1)	0.0862(4)	−0.014(1)	9.2(3)
C(28)	−0.388(1)	0.1061(5)	0.177(1)	10.2(3)

$B_{eq} = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Table 3
Selected bond lengths (Å) and angles (°) for **1**

Bond lengths			
Si(1)–Si(2)	2.539(2)	Si(1)–N(1)	1.751(4)
Si(1)–N(2)	1.747(4)	Si(1)–C(9)	1.969(6)
Si(2)–N(3)	1.747(4)	Si(2)–N(4)	1.750(4)
Si(2)–C(23)	1.956(5)		
Bond angles			
Si(2)–Si(1)–N(1)	104.9(2)	Si(2)–Si(1)–N(2)	114.5(2)
Si(2)–Si(1)–C(9)	111.3(2)	N(1)–Si(1)–N(2)	106.1(2)
N(1)–Si(1)–C(9)	110.3(2)	N(2)–Si(1)–C(9)	109.4(2)
Si(1)–Si(2)–N(3)	115.1(2)	Si(1)–Si(2)–N(4)	108.2(2)
Si(1)–Si(2)–C(23)	106.6(2)	N(3)–Si(2)–N(4)	105.3(2)
N(3)–Si(2)–C(23)	109.8(2)	N(4)–Si(2)–C(23)	112.0(2)
Si(1)–N(1)–C(1)	122.2(3)	Si(1)–N(1)–C(3)	124.2(4)
Si(1)–N(2)–C(5)	122.5(4)	Si(1)–N(2)–C(7)	124.5(4)
Si(2)–N(3)–C(15)	121.2(4)	Si(2)–N(3)–C(17)	125.7(3)
Si(2)–N(4)–C(19)	124.9(4)	Si(2)–N(4)–C(21)	121.8(3)
Si(1)–C(9)–C(10)	111.6(4)	Si(1)–C(9)–C(11)	105.7(4)
Si(1)–C(9)–C(12)	118.0(4)	Si(2)–C(23)–C(24)	110.1(3)
Si(2)–C(23)–C(25)	105.8(3)	Si(2)–C(23)–C(26)	114.9(4)

Table 4
Fractional atomic coordinates and equivalent isotropic thermal parameters for **2**

Atom	x	y	z	B_{eq} (Å^2)
Si(1)	0.37929(5)	0.44060(5)	0.36229(5)	2.166(9)
N(1)	0.3208(2)	0.5769(1)	0.3115(1)	2.63(3)
N(2)	0.2028(1)	0.2993(1)	0.3582(1)	2.62(3)
C(1)	0.2200(2)	0.6313(2)	0.3750(2)	3.34(4)
C(2)	0.0591(3)	0.6059(3)	0.2442(3)	4.53(6)
C(3)	0.3691(2)	0.6503(2)	0.2074(2)	3.41(4)
C(4)	0.4481(3)	0.8329(3)	0.2799(4)	5.04(7)
C(5)	0.2088(2)	0.2202(2)	0.4684(2)	3.33(4)
C(6)	0.1316(3)	0.0373(2)	0.3866(3)	4.42(5)
C(7)	0.0348(2)	0.2287(2)	0.2210(2)	3.51(4)
C(8)	−0.1011(3)	0.2253(3)	0.2730(4)	5.44(7)
C(9)	0.4239(2)	0.3313(2)	0.1935(2)	2.59(3)
C(10)	0.4150(3)	0.1783(2)	0.2131(3)	3.67(5)
C(11)	0.2886(3)	0.2742(3)	0.0192(2)	3.74(5)
C(12)	0.5977(2)	0.4244(2)	0.2059(2)	3.39(4)

$B_{eq} = \frac{8}{3}\pi^2[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha]$.

Table 5
Selected bond lengths (Å) and angles (°) for **2**

Bond lengths			
Si(1)–Si(1*)	2.4764(9)	Si(1)–N(1)	1.748(1)
Si(1)–N(2)	1.743(1)	Si(1)–C(9)	1.938(2)
Bond angles			
Si(1*)–Si(1)–N(1)	114.87(5)	Si(1*)–Si(1)–N(2)	108.38(5)
Si(1*)–Si(1)–C(9)	110.48(5)	N(1)–Si(1)–N(2)	105.25(6)
N(1)–Si(1)–C(9)	109.29(6)	N(2)–Si(1)–C(9)	108.26(7)
Si(1)–N(1)–C(1)	121.9(1)	Si(1)–N(1)–C(3)	124.5(1)
Si(1)–N(2)–C(5)	124.7(1)	Si(1)–N(2)–C(7)	120.7(1)
Si(1)–C(9)–C(10)	106.1(1)	Si(1)–C(9)–C(11)	112.6(1)
Si(1)–C(9)–C(12)	115.8(1)		

chlorodisilane (**6**) can be handled in the air; however, it slowly decomposes with a trace amount of water.

3. Experimental section

Fourier transform NMR spectra were obtained with a JEOL model α-500 (^{1}H at 500.00 MHz, ^{13}C at 125.65

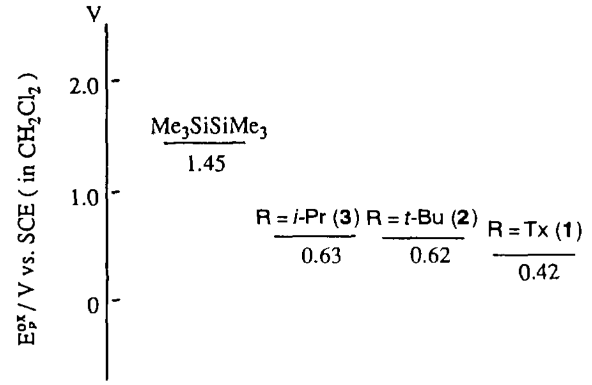


Fig. 4. Oxidation potentials of **1**–**3** and hexamethyldisilane.

MHz and ^{29}Si at 99.25 MHz). Chemical shifts are reported relative to $SiMe_4$ and residual solvent peaks were used for standards. For ^{29}Si NMR, $SiMe_4$ was used for the external standard. Electron impact (EI) mass spectrometry (MS) was performed with a JEOL JMS-D300. IR spectra were measured with a JASCO A-102 spectrometer and polystyrene film was used for standard. UV and visible spectra were taken on a JASCO Ubest-50 spectrometer with an FDD-395 floppy disk unit. Analytical high performance liquid chromatography (HPLC) was done with JASCO 875UV/880PU and UV-970/880PU instruments with a Chemco 1.6 × 250(w) 5-ODS-H column. Preparative HPLC was carried out using a JAI LC-908 with Chemco 20 × 250(w) 7-ODS-H column. Gas–liquid chromatography was conducted with Ohkura GC-103 with 1% and 10% KF-96 on a Celite 545sk packed glass column. Cyclic voltammograms were recorded using a Hokuto-Denko Ltd. HB-104 function generator and HA-301 potentiostat. A conventional three-electrode configuration was used, with a platinum electrode of 1.5 mm diameter as a working electrode, a platinum counter-electrode, and a saturated calomel electrode as a reference. Tetrabutylammonium perchlorate, 0.1 mol l^{-1} in dichloromethane, was used as the supporting electrolyte.

All the solvents used in the reaction were purified with reported methods. Tetrahydrofuran (THF) and ether were purified by distillation from benzophenone ketyl just before use. Hexane was distilled from LAH. Methanol and THF for HPLC were distilled once and degassed by ultrasonic apparatus. All the reactions were carried out under an argon atmosphere unless otherwise noted. Anhydrous Na_2SO_4 and $MgSO_4$ were used as drying agents in the process of work-up.

3.1. *Preparation of bis(diethylamino)thexylchlorosilane*

To a mixture of thexyltrichlorosilane [13] (6.60 g, 30.0 mmol), triethylamine (9.2 ml, 66 mmol) and dry THF (30 ml) was added a solution of diethylamine (6.4 ml, 60 mmol) in THF (5 ml) at 0.°C over 30 min. Then the mixture was refluxed and stirred for 14 days. The resulting solution was diluted with hexane, and the salt generated was filtered with a glass filter funnel under an inert atmosphere. The filtrate was concentrated and the residue was distilled under reduced pressure to give 1,2-bis(diethylamino)thexylchlorosilane (yield, 4.51 g (50%); boiling point (b.p.), 94.5°C (4.5 Torr)). ^{1}H NMR ($CDCl_3$): δ 0.91 (d,$J = 6.9$ Hz, 6H), 0.99 (s, 6H), 1.02 (t, $J = 7.0$ Hz, 12H), 1.90 (sept, $J = 6.9$ Hz, 1H), 2.95 (q, $J = 7.0$ Hz, 8H) ppm. ^{13}C NMR ($CDCl_3$): δ 13.49, 18.43, 20.84, 29.40, 33.22, 38.45 ppm. ^{29}Si NMR ($CDCl_3$): δ −7.21 ppm. IR (NaCl plate): ν 2970, 2856, 1465, 1378, 1202, 1161, 1023, 938 cm^{-1}. MS (30 eV, %); *m/z* 292 (M^+, 7), 207 (base). Anal. Found: C, 57.53; H, 11.47; N, 9.61. $C_{14}H_{33}N_2SiCl$. Calc.: C, 57.38; H, 11.37; N, 9.56%.

3.2. *Preparation of bis(diethylamino)-tert-butylchlorosilane*

Introduction of two diethylamino groups was achieved in the presence of triethylamine (9.2 ml, 66 mmol) and diethylamine (6.4 ml, 60 mmol) with tert-butyltrichlorosilane (5.75 g, 30 mmol) under reflux in THF for 10 days (yield, 6.04 g (76%); b.p., 78.5°C (4.4 Torr)). ^{1}H NMR ($CDCl_3$): δ 1.02 (t, $J = 6.8$ Hz, 12H), 1.03 (s, 9H), 2.91 (sext, $^2J = 14.0$ Hz, $^3J = 6.8$ Hz, 4H), 2.94 (sext, $^2J = 14.0$ Hz, $^3J = 6.7$ Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 13.89, 22.28, 27.11, 38.33 ppm. ^{29}Si NMR ($CDCl_3$): δ −12.16 ppm. IR (NaCl plate) 2970, 2940, 2860, 1470, 1393, 1376, 1342, 1293, 1207, 1103, 1055, 1023, 940, 923 cm^{-1}. MS (70eV, %): *m/z* 264 (M^+, 14), 56 (base). Exact mass. Found: 264.1777. $C_{12}H_{29}N_2SiCl$ Calc.: 264.1789.

3.3. *Preparation of bis(diethylamino)isopropylchlorosilane*

This compound was obtained with a 80% yield in a similar manner under reflux for 7 h (b.p., 82.4°C (6.5 Torr)). ^{1}H-NMR ($CDCl_3$): δ 1.01 (t, $J = 7.0$ Hz, 12H), 1.04 (d, $J = 7.0$ Hz, 6H), 1.13 (m, 1H), 2.89 (sext, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, 4H), 2.89 (sext, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 14.39, 15.69, 17.45, 38.45 ppm. ^{29}Si NMR ($CDCl_3$): δ −11.94 ppm. IR (NaCl plate): ν 2960, 2930, 2860, 1460, 1372, 1340, 1290, 1204, 1163, 1100, 1056, 1023, 997, 937, 922 cm^{-1}. MS (70 eV, %): *m/z* 250 (M^+, 43), 56 (base). Exact mass. Found: 250.1658. $C_{11}H_{27}N_2SiCl$ Calc.: 250.1632.

3.4. *Preparation of bis(diethylamino)ethylchlorosilane*

This compound was obtained with a 42% yield in a similar manner at room temperature for 89 h (b.p., 86.0°C (9.0 Torr)). ^{1}H NMR ($CDCl_3$): δ 0.80 (q, $J = 7.3$ Hz, 2H), 0.99 (t, $J = 7.0$ Hz, 12H), 1.29 (t, $J = 7.3$ Hz, 3H), 2.87 (q, $J = 7.0$ Hz, 8H) ppm. ^{13}C NMR ($CDCl_3$): δ 6.79, 8.62, 14.72, 38.67 ppm. ^{29}Si NMR ($CDCl_3$) δ −8.30 ppm. IR (NaCl plate): ν 2970, 2940, 2880, 1460, 1374, 1342, 1293, 1208, 1169, 1100, 1058, 1027, 958, 937, 926 cm^{-1}. MS (30 eV, %): *m/z* 236 (M^+, 58), 164 (base).

3.5. *Synthesis of 1,1,2,2,-tetrakis(diethylamino)-1,2-dithexyldisilane (1)*

To a suspension of lithium dispersion (0.11 g, 15 mmol) in dry THF (5 ml) was added bis(diethylamino) thexylchlorosilane (1.0 g, 3.4 mmol) at room temperature. The reaction mixture was stirred at room temperature for 63 h. The crude product was recrystallized from EtOH to afford white crystals of **1** (yield, 157 mg (18%); m.p. 244–246°C). ^{1}H NMR (C_6D_6): δ 0.97 (d, $J = 6.7$ Hz, 12H), 1.01 (t, $J = 7.0$ Hz, 24H), 1.12 (s, 12H), 1.97 (sept, $J = 6.9$ Hz, 2H), 2.95 (sext, $^2J = 13.9$ Hz, $^3J = 6.8$ Hz, 8H), 3.05 (sext, $^2J = 14$ Hz, $^3J = 7.0$ Hz, 8H) ppm. ^{13}C NMR (C_6D_6): δ 13.04, 19.34, 23.12, 31.55, 33.88, 39.49 ppm. ^{29}Si NMR (C_6D_6): δ -2.25 ppm. IR (NaCl plate): ν 2975, 2940, 2880, 1463, 1377, 1195, 1175, 1019, 920 cm^{-1}. MS (30 eV, %): m/z 429 (M-Tx, 1), 257 (base). Anal. Found: C, 64.77; H, 12.95; N, 10.79. $C_{28}H_{66}N_4Si_2$ Calc.: C, 65.28; H, 12.94; N, 10.88%.

3.6. Synthesis of 1,1,2,2,-tetrakis(diethylamino)-1,2-di-tert-buthyldisilane (2)

Synthesis was done in a similar way at room temperature for 13.5 days. Recrystallization from acetone gave white crystals (yield, 12%, m.p., 237–239°C). ^{1}H NMR (C_6D_6): δ 1.07 (t, $J = 7.0$ Hz, 24H), 1.21 (s, 18H), 3.07 (nonet, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, 16H) ppm. ^{13}C NMR (C_6D_6): δ 13.34, 24.90, 30.45, 38.88 ppm. ^{29}Si NMR (C_6D_6): δ -1.68 ppm. IR (NaCl plate): ν 2970, 2930, 2860, 1477, 1460, 1380, 1294, 1195, 1170, 1045, 1023, 917 cm^{-1}. MS (30 eV, %): m/z 401 (M $-{}^t$Bu, 8), 229 (base). Anal. Found: C, 62.10; H, 12.86; N, 11.99. $C_{24}H_{58}N_4Si_2$ Calc.: C, 62.79; H, 12.76; N, 12.21%.

3.7. Synthesis of 1,1,2,2,-tetrakis(diethylamino)-1,2-di-isopropyldisilane (3)

Synthesis was done in a similar way at room temperature for 12 days. Recrystallization from acetone gave white crystals (yield, 23%; m.p., 114°C (sublimed)). ^{1}H NMR (C_6D_6): δ 1.07 (t, $J = 7.0$ Hz, 24H), 1.11–1.20 (m, 2H), 1.26 (d, $J = 6.9$ Hz, 12H), 3.02 (sext, $^2J = 13.9$ Hz, $^3J = 6.9$ Hz, 8H), 3.05 (sext, $^2J = 14.0$ Hz, $^3J = 7.0$ Hz, 8H) ppm. ^{13}C NMR (C_6D_6): δ 14.00, 18.96, 19.57, 39.05 ppm. ^{29}Si NMR (C_6D_6): δ -4.80 ppm. IR (NaCl plate): ν 2960, 2860, 1460, 1370, 1344, 1288, 1203, 1168, 1107, 1062, 1023, 995, 912 cm^{-1}. MS (30 eV, %): m/z 430 (M$^+$, 4), 215 (base). Anal. Found: C, 61.12; H, 12.81; N, 12.93. $C_{22}H_{54}N_4Si_2$ Calc.: C, 61.31; H, 12.65; N, 13.00%.

3.8. Synthesis of 1,1,2,2,-tetrakis(diethylamino)-1,2-diethyldisilane (4)

This compound was obtained as an pale yellow oil with 42% yield. The reaction was done at room temperature for 6.5 days. ^{1}H NMR (C_6D_6): δ 0.84 (q, $J = 7.8$ Hz, 4H), 1.07 (t, $J = 7.0$ Hz, 24H), 1.16 (t, $J = 7.8$ Hz, 6H), 2.99 (q, $J = 7.0$ Hz, 16H) ppm. ^{13}C NMR (C_6D_6): δ 8.44, 10.80, 14.90, 39.54 ppm. ^{29}Si NMR (C_6D_6): δ -11.35 ppm. IR (NaCl plate): ν 2960, 2925, 2870, 1454, 1368, 1339, 1285, 1198, 1170, 1097, 1048, 1019, 919 cm^{-1}. MS (30 eV, %): m/z 402 (M$^+$, 25), 201 (base). Exact mass. Found: 402.3563. $C_{20}H_{50}N_4Si_2$ Calc.: 402.3574.

1,1,2,2,-Tetrakis(diethylamino)-1,2-dimethyldisilane (**5**) was prepared by the reported method [3].

3.9. X-ray crystallographic analysis of 1

Colorless prismatic crystals of **1** were obtained from acetone by slow evaporation. A crystal specimen of dimensions 0.20 × 0.20 × 0.10 mm was mounted on a glass fiber and used for data collection on an Rigaku AFC7R diffractometer using graphite-monochromated Cu Kα radiation and a 12 kW rotating anode generator. Cell parameters were refined by the least-squares method using 14 reflections in the range $50.08° < 2\theta < 50.95°$. Intensity data were collected in the range of $2\theta < 120.1°$ by the ω–2θ scan technique at 20 ± 1°C. The space group $P\bar{1}$ was determined from no systematic absences. 4937 unique reflections were collected. 3312 non-zero observed reflections ($|F_o| \geqslant 3\sigma(F_o)$) were obtained and corrected for Lorentz polarization and empirical absorption based on a ψ scan. The structure was solved by direct methods (SHELXS86 [14]) using DIRDIF92 Fourier techniques [15]. Non-hydrogen atoms were found from subsequent Fourier syntheses and refined by the full-matrix least-squares method. All hydrogen atoms were included but not refined. Final R and R_w values are 0.073 and 0.116 respectively [16]. All calculations were carried out by teXsan [17] with a SiliconGraphics INDY computer.

3.10. X-ray crystallographic analysis of 2

Colorless prismatic crystals of **2** were obtained from isopropyl alcohol by slow evaporation. A crystal specimen of dimensions 0.50 × 0.50 × 0.30 mm was mounted in a glass capillary, and used for data collection on an Rigaku AFC7S diffractometer using graphite-monochromated Mo Kα radiation. Cell parameters were refined by the least-squares method using 14 reflections in the range $54.74° < 2\theta < 54.96°$. Intensity data were collected in the range of $2\theta < 55.0°$ by the ω–2θ scan technique at 20 ± 1°C. Based on a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$. 3285 unique reflections were collected. 2842 non-zero observed reflections ($|F_o| \geqslant 3\sigma(F_o)$) were obtained and corrected for Lorentz polarization and empirical absorption based on a ψ scan. The structure was solved by SHELXS86 [14] with DIRDIF92 Fourier techniques [15]. Non-hydrogen atoms were found from subsequent Fourier syntheses and refined anisotropically by the full-matrix least-squares method. All hydrogen atoms were refined isotropically. Final R and R_w values are 0.034 and 0.029, respectively. All calculations were carried out by teXsan [17] with a SiliconGraphics INDY computer.

3.11. Synthesis of 1,1,2,2,-tetrachloro-1,2-dithexyldisilane (6)

Tetrakis(diethylamino)dithexyldisilane **1** (235 mg, 0.46 mmol) was dissolved in benzene (2 ml). HCl gas was bubbled for 10 min followed by Ar gas bubbling. Dry hexane (3 ml) was added and the salt generated was filtered. The resulting mixture was distilled with a bulb-to-bulb apparatus (oven temperature, 220°C; 1.0 Torr) to obtain 124 mg (74%) of tetrachlorodisilane (**6**). ^{1}H NMR (C_6D_6): δ 0.88 (d, $J = 6.9$ Hz, 12H), 1.10 (s, 12H), 2.08 (sept, $J = 6.9$ Hz, 2H) ppm. ^{13}C NMR (C_6D_6): δ 18.73, 19.73, 33.71, 33.83 ppm. ^{29}Si NMR (C_6D_6): δ 19.13 ppm. MS (30 eV, %): m/z 366 (M^+, 1), 283 (2), 213 (4) 113 (7), 85 (Tx, base). Exact mass. Found: 366.0327. $C_{12}H_{26}Cl_4Si_2$ Calc.: 366.0327.

4. Supplementary material available

Tables of anisotropic thermal parameters, atomic coordinates and isotropic thermal parameters involving H atoms, bond lengths and angles for **1** and **2**, are also available from the authors.

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