Synthesis of the Diazadisilatitanacyclopentane $\mathrm{RSi(NH_2)NHTiMe(cp^*)NHSi(NH_2)R}$ ($\mathrm{R = PhNSiMe_3}$, $\mathrm{cp^* = \eta^5\text{-}C_5Me_5}$)

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Reaction of two equivalents of *N*-trimethylsilylaniline (**1**) with two equivalents of *n*-butyllithium, followed by subsequent treatment with $\mathrm{Si_2Cl_6}$ (**2**) leads to the formation of the tetrachlorodisilane $\mathrm{RSiCl_2SiCl_2R}$ (**3**) ($\mathrm{R = PhNSiMe_3}$). **3** is converted to $\mathrm{RSi(NH_2)_2Si(NH_2)_2R}$ (**4**) by reaction with liquid ammonia. **4** reacts with $\mathrm{cp^*TiMe_3}$ (**5**) ($\mathrm{cp^* = \eta^5\text{-}C_5Me_5}$) to yield the diazadisilatitanacyclopentane $\mathrm{RSi(NH_2)NHTiMe(cp^*)\text{-}NHSi(NH_2)R}$ (**6**). The crystal structure of **6** is reported.

Introduction

There are only three stable aminosilanes of the type $\mathrm{R^1Si(NH_2)_3}$ ($\mathrm{R^1}$ = 2,4,6-$\mathrm{Ph_3C_6H_2}$,[1] 2,6-*i*$\mathrm{Pr_2C_6H_3N\text{-}SiMe_3}$,[2] 2,4,6-*t*$\mathrm{Bu_3C_6H_2O}$[2]) known in the literature which contain three unsubstituted amino groups. In light of our experience with aminosilanes and the valence isoelectronic silanetriols,[3][4] we were interested in obtaining a stable aminodisilane containing four unsubstituted amino groups [$\mathrm{RSi(NH_2)_2Si(NH_2)_2R}$].

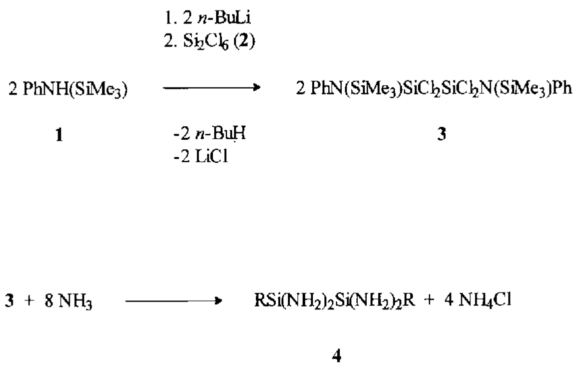
The aforementioned silanetriols and aminosilanes show interesting reactivity features.[5] Among other applications, silanetriols can be used to generate soluble zeolite precursors and titanium-containing heterocubanes,[6] while aminosilanes can be used to prepare titanium-containing heterocycles.[2] We report hereon the synthesis of 1,2-bis(*N*-trimethylsilylphenylamino)tetraaminodisilane.

Results and Discussion

A. Synthesis of $\mathrm{RSi(NH_2)_2Si(NH_2)_2R}$

The classical route for the synthesis of aminosilanes is the reaction of chlorosilanes with amines[7] or metal amides.[3] We have combined both of these methods to prepare substituted aminosilanes.[2] Due to its extreme moisture sensitivity, the *N*-trimethylsilylphenylamino lithium salt was generated in situ using $\mathrm{PhNHSiMe_3}$ (**1**) and *n*-butyllithium, and was subsequently reacted with hexachlorodisilane (**2**) to yield the tetrachlorodisilane (**3**). Finally, **3** was treated with liquid ammonia to give $\mathrm{RSi(NH_2)_2Si(NH_2)_2R}$ (**4**) (R = $\mathrm{PhNSiMe_3}$). The ammonia served both as the solvent and as an HCl acceptor to yield $\mathrm{NH_4Cl}$.

Scheme 1. Synthesis of **3**, **4** ($\mathrm{R = PhNSiMe_3}$)



$$\underset{\mathbf{1}}{2\ \mathrm{PhNH(SiMe_3)}} \xrightarrow[\substack{-2\ n\text{-BuH}\\ -2\ \mathrm{LiCl}}]{\substack{1.\ 2\ n\text{-BuLi}\\ 2.\ \mathrm{Si_2Cl_6}\ (\mathbf{2})}} \underset{\mathbf{3}}{2\ \mathrm{PhN(SiMe_3)SiCl_2SiCl_2N(SiMe_3)Ph}}$$

$$\mathbf{3} + 8\ \mathrm{NH_3} \longrightarrow \underset{\mathbf{4}}{\mathrm{RSi(NH_2)_2Si(NH_2)_2R}} + 4\ \mathrm{NH_4Cl}$$

3 is a colorless solid which melts at 63 °C, is stable at room temperature under an inert atmosphere, and is soluble in common organic solvents (*n*-hexane, diethyl ether, toluene, THF, dichloromethane). The IR spectrum exhibits three Si−Cl stretching vibrations (548, 523, 489 $\mathrm{cm^{-1}}$). The ^{29}Si-NMR spectrum of **3** shows a singlet ($\delta = -21.4$) in the same range as that of known 1,2-bis(amino)tetrachlorodisilanes of the type $\mathrm{R^2{}_2NSiCl_2SiCl_2NR^2{}_2}$ ($\mathrm{R^2}$ = Et: $\delta = -19.9$; $\mathrm{R^2}$ = *i*Pr: $\delta = -22.95$).[7]

4 is soluble in common organic solvents (*n*-hexane, diethyl ether, toluene, THF), forms colorless crystals which melt at 77 °C, and is stable under an inert atmosphere. The IR spectrum of **4** shows four N−H stretching vibrations (3452, 3409, 3389, 3355 $\mathrm{cm^{-1}}$). The Si−Cl stretching vibrations characteristic of $\mathrm{SiCl_2}$ moieties were no longer observed. The ^{1}H-NMR spectrum of **4** shows a singlet ($\delta = 0.15$) for the protons of the trimethylsilyl groups and a characteristic broad singlet ($\delta = 0.37$) for the amino protons (ratio of intensities 18:8). The ^{29}Si-NMR spectrum of **4** shows the presence of two singlets at $\delta = 4.77$ due to the trimethylsilyl groups and at $\delta = -28.3$ due to the aminosilyl

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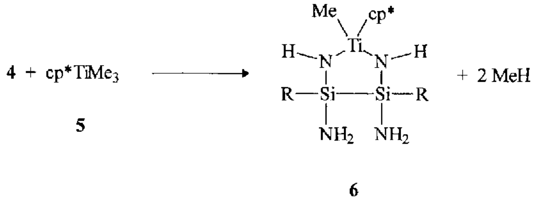
moieties respectively. This signal is shifted to higher field in comparison to that of **3** (Δδ = 6.9).

B. Synthesis and X-ray Crystal Structure of the Diazadisilatitanacyclopentane

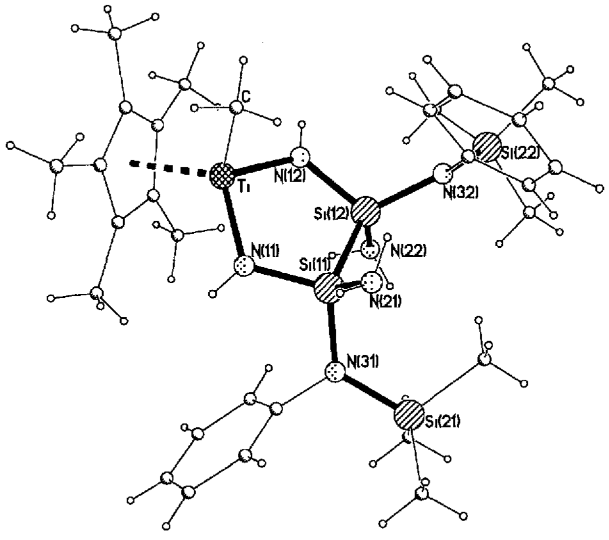
Reaction of **4** with an excess of cp*TiMe$_3$ (**5**) at room temperature yields the diazadisilatitanacyclopentane (**6**).

Scheme 2. Synthesis of **6** (R = PhNSiMe$_3$)



6 is stable at room temperature under an inert atmosphere and is soluble in common organic solvents (*n*-hexane, toluene, diethyl ether, THF). Single crystals of **6** were obtained from *n*-hexane. **6** forms yellow cubic crystals which decompose at 110°C. Four N–H stretching vibrations (3463, 3432, 3385, 3343 cm^{-1}) were observed in the IR spectrum of **6** and the ^{1}H-NMR spectrum shows a singlet (δ = 0.19) for the protons of the two trimethylsilyl groups, a broad signal (δ = 0.08 to 0.28) for the four protons of the unsubstituted amino groups, and a broad singlet (δ = 5.98) for the two protons of the titanium-bonded amino groups (ratio of intensities 18:4:2). The proton signal for the titanium-bonded amino groups is shifted to lower field in comparison to that of the unsubstituted amino groups in **6** (Δδ = 5.8), in **4** (Δδ = 5.61), and those of the known diaminosilatitanacyclobutane (Δδ = 5.64).[2] The structure of **6** was fully elucidated by an X-ray crystal structure analysis and is shown in Figure 1. The coordination around Ti is tetrahedral if the centroid of the cp* ring is considered as a coordination site, with the other three sites being occupied by the C atom from the methyl group and by the N11 and N12 atoms to form a five-membered ring. The diazadisilatitanacyclopentane ring has an envelope conformation with the N12 atom deviating by 0.395(6) Å from the mean plane through the other four atoms. The arrangement gives a roughly eclipsed conformation of the substituents at the two vicinal Si atoms. In order to minimize the steric hindrance of the substituents, the Si atoms adopt the same configuration (*R,R* or *S,S*). It was not possible to calculate the positions for the two NH$_2$ moieties, because they are neither perfectly trigonal nor perfectly tetrahedral. The hydrogens at N21 and N22 were found in plausible positions in the difference electron density map and in the refinement plausible thermal parameters were obtained. The values of the Ti–N, Si–Si, and Si–N bond lengths in **6** are very similar to those found in Ti(–NMe–SiMe$_2$–SiMe$_2$–MeN–)$_2$, in which two five-membered TiNSiSiN rings are present: Ti–N = 1.902(6) and 1.909(6) Å, Si–Si = 2.355(3) Å and Si–N = 1.732(6) and 1.734(6) Å.[8] This is the only other structurally characterized compound with a comparable ring structure. It is noteworthy that here the N–Ti–N bite angle [107.1(2)°] is larger than in **6** [100.2(3)°].

Figure 1. View of the molecular structure of the complex **6** together with the atomic numbering system[a]



[a] Selected bond lengths [Å] and angles [°] for **6**: Ti–N(11) 1.915(7), Ti–N(12) 1.903(7), Ti–cp* (centroid) 2.051 (12), Si(11)–N(21) 1.718(7), Si(11)–N(11) 1.717(6), Si(11)–N(31) 1.742(7), Si(11)–Si(12) 2.356(4), Si(12)–N(12) 1.727(7), Si(12)–N(22) 1.730(7), Si(12)–N(32) 1.741(7), N(12)–Ti–N(11) 100.2(3), N(11)–Si(11)–Si(12) 98.2(3), N(12)–Si(12)–Si(11) 99.5(3), Si(11)–N(11)–Ti 118.0(4), Si(12)–N(12)–Ti 119.0(4), .

In summary, we have prepared a disilane containing four NH$_2$ groups for the first time. This tetraaminodisilane reacts with cp*TiMe$_3$ with elimination of methane to yield a diazadisilatitanium compound. Bearing in mind our earlier studies on the reactions of silanetriols and triaminosilanes using different organometallic moieties, it may be possible to generate a range of novel compounds by this method. Investigations in this area are currently under way.

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Experimental Section

General: All reactions were carried out under nitrogen using Schlenk-type glassware and a drybox. Solvents were dried and distilled under nitrogen prior to use. The following instruments were used for the characterization of compounds: Bruker AM 200 NMR spectrometer (^{1}H, 200 MHz), Bruker AC 250 NMR spectrometer (^{1}H, 250 MHz; ^{13}C, 63 MHz; ^{29}Si, 50 MHz), tetramethylsilane as the external standard; BIO-RAD Digilab FTS 7 IR spectrometer; Bruker AM 200 MS spectrometer, Bruker MSL 400 MS spectrometer; Bühler SPA-1 (for melting points). The starting materials hexachlorodisilane,[9] *N*-trimethylsilylaniline[10] and cp*TiMe$_3$[11] were prepared by literature methods.

Synthesis of **3**: To a solution of 49.61 g (300 mmol) of *N*-trimethylsilylaniline in 150 ml of *n*-hexane was added 140 ml (336 mmol) of a solution of 2.4 M *n*-butyllithium in *n*-hexane. The reaction mixture was heated under reflux during the addition of *n*-butyllithium. After the addition was complete, the reaction mixture was heated under reflux for 3 h. The solution of the lithium amide generated in situ was cooled to −78°C and a solution of 72.60 g (270 mmol) of hexachlorodisilane in 20 ml diethyl ether was added over a period of 1 h. After warming up to room temperature over a period of 14 h, the reaction mixture was heated under reflux for 3 h. After cooling to room temperature, the lithium chloride formed was removed by filtration through Celite and washed three times with 50 ml of *n*-hexane. The solvent was removed in vacuo. The residue was extracted with 100 ml of *n*-hexane and stored at −80°C. The product precipitated as a colourless solid and was isolated by filtration and dried in vacuo. Yield 82.2 g (52%) **3**, m.p. 63°C (*n*-hexane). − IR (KBr): $\tilde{\nu}$ = 548 (Si−Cl), 523 (Si−Cl), 489 cm^{-1} (Si−Cl). − ^{1}H NMR (250 MHz, CDCl$_3$): δ = 0.11 (s, 18 H, CH$_3$), 6.98−7.15 (m, 10 H, aromatic H). − ^{13}C NMR (CDCl$_3$): δ = 1.8 (CH$_3$), 126.0 (*o*-C$_6$H$_5$), 129.1 (*p*-C$_6$H$_5$), 130.5 (*m*-C$_6$H$_5$), 141.9 (*ipso*-C$_6$H$_5$). − ^{29}Si NMR (CDCl$_3$): δ = −21.4 (SiCl$_2$), 13.4 (SiMe$_3$). − MS (EI, 70 eV); *m/z* (%): 526 (47) [M$^+$], 212 (100) [Ph(SiMe$_2$)NSiCl$^+$]. − $C_{18}H_{28}Cl_4N_2Si_4$ (526.59): calcd. C 41.06, H 5.36, Cl 26.93, N 5.32, Si 21.33; found C 41.3, H 5.6, Cl 26.2, N 5.3, Si 21.0.

Synthesis of **4**: 9.63 g (18 mmol) of **3** were dissolved in 100 g of liquid ammonia at −78°C. The reaction mixture was slowly warmed, during which it started refluxing at −30°C. The reaction mixture was maintained at this temperature for 8 h. The solution was allowed to warm up to room temperature over a period of 14 h during which liquid ammonia evaporated. The residue was extracted with 100 ml of *n*-hexane and the ammonium chloride formed was removed by filtration. The filtrate was concentrated to about 40 ml and stored at −20°C. The colourless crystals formed were isolated by filtration and dried in vacuo. Yield 7.1 g (86%) **4**, m.p. 77°C (*n*-hexane). − IR (KBr, Nujol): $\tilde{\nu}$ = 3452 (N−H), 3409 (N−H), 3389 (N−H), 3355 cm^{-1} (N−H). − ^{1}H NMR (250 MHz, C$_6$D$_6$): δ = 0.15 [s, 18 H, Si(CH$_3$)$_3$], 0.37 (br. s, 8 H, NH$_2$), 6.90−7.13 (m, 10 H, aromatic H). − ^{13}C NMR (C$_6$D$_6$): δ = 2.9 [Si(CH$_3$)$_3$], 123.8 (*o*-C$_6$H$_5$), 128.8 (*p*-C$_6$H$_5$), 130.6 (*m*-C$_6$H$_5$), 148.0 (*ipso*-C$_6$H$_5$). − ^{29}Si NMR (C$_6$D$_6$): δ = −28.3 [Si(NH$_2$)$_2$], 4.77 (SiMe$_3$). − MS (EI, 70 eV); *m/z* (%): 448 (35) [M$^+$], 399 (100) [M$^+$ − 3NH$_2$ − H], 284 (93) [M$^+$ − PhNSiMe$_3^+$], 224 (24) [M$^+$]. − $C_{18}H_{36}N_6Si_4$ (448.87): calcd. C 48.17, H 8.08, N 18.72, Si 25.03; found C 48.9, H 7.7, N 16.7, Si 25.4.

Synthesis of **6**: A solution of 0.90 g (2.01 mmol) of **4** in 20 ml of diethyl ether was added at room temperature to 0.92 g (4.03 mmol) of cp*TiMe$_3$ in 20 ml of diethyl ether. The solution was stirred for 48 h, and the solvent was removed in vacuo. The resulting yellow oil was crystallized from 15 ml of *n*-hexane at −20°C to give bright yellow crystals which were isolated by filtration and dried in vacuo. Yield 1.2 g (89%) **6**, m.p. 110°C (dec., *n*-hexane). Single crystals for X-ray structure analysis were obtained from *n*-hexane. − IR (KBr, Nujol): $\tilde{\nu}$ = 3463 (N−H), 3432 (N−H), 3385 (N−H), 3343 cm^{-1} (N−H). − ^{1}H NMR (200 MHz, C$_6$D$_6$): δ = 0.08−0.28 (br., 4 H, SiNH$_2$), 0.19 [s, 9 H, Si(CH$_3$)$_3$], 0.54 (s, 3 H, TiCH$_3$), 1.76 (s, 15 H, C$_{10}$H$_{15}$), 5.98 (br.s, 2 H, TiNH), 6.88−7.22 (m, 10 H, aromatic H). − ^{13}C NMR (C$_6$D$_6$): δ = 2.7 [Si(CH$_3$)$_3$], 2.9 [Si(CH$_3$)$_3$], 11.8 (TiCH$_3$), 37.0 [C$_5$(*C*H$_3$)$_5$], 119.7 [*C*$_5$(CH$_3$)$_5$], 123.4 (*o*-C$_6$H$_5$), 123.6 (*o*-C$_6$H$_5$), 128.8 (*p*-C$_6$H$_5$), 128.9 (*p*-C$_6$H$_5$), 129.7 (*m*-C$_6$H$_5$), 130.6 (*m*-C$_6$H$_5$), 148.4 (*ipso*-C$_6$H$_5$), 148.5 (*ipso*-C$_6$H$_5$). − ^{29}Si NMR (C$_6$D$_6$): δ = −20.4 (SiNHTi), −19.8 (SiNHTi), 4.3 (SiMe$_3$), 4.6 (SiMe$_3$). − MS (EI, 70 eV); *m/z* (%): 646 (5) [M$^+$ + 2 H], 629 (31) [M$^+$ − Me], 479 (100) [M$^+$ − Ph − Me − SiMe$_3$]. − $C_{29}H_{52}N_6Si_4Ti$ (644.99): calcd. C 54.00, H 8.31, N 13.03, Si 17.42, Ti 7.42; found C 53.4, H 7.8, N 12.6, Si 16.8, Ti 6.6.

X-ray Structure Determination of **6**: All crystals were of very poor quality. Dimensions of the crystal used for the analysis were: 0.18 × 0.25 × 0.35 mm. The crystallographic data are summarized in Table 1. The intensity data were collected at room temperature using a Siemens AED diffractometer, using the graphite-monochromated Cu-K_α radiation and the θ-2θ scan technique. 5730 reflections were measured (with θ in the range 3−60°) of which 5474 were independent and included in the structure refinement. A correction for absorption was applied (maximum and minimum values for the transmission coefficient were 1.000 and 0.732)[12]. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2), with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced in the geometrically calculated positions and refined riding on their parent atoms, excepting those at the nitrogen atoms which were found but not refined. The refinement converged at wR_2 = 0.2867 for all data and 395 variables [R_1 = 0.0962 for 2306 reflections with $I > 2\sigma(I)$; min./max. residual electron density: −0.493/0.438 eÅ^{-3}]. The SHELXS-86 and SHELXL-93 systems of computer programs were used.[13] Details are compiled in Table 1.[14]

Table 1. Crystal data and structure refinement for **6**

Empirical formula	$C_{29}H_{52}N_6Si_4Ti$
Formula weight	645.03
Temperature	293(2) K
Wavelength	1.54184 Å
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 12.659(5) Å
	b = 24.730(8) Å
	c = 13.247(5) Å
	β = 116.93(2) °
Volume	3697(2) Å^3
Z	4
Density (calculated)	1.159 Mg/m^3
Absorption coefficient	3.403 mm^{-1}
F(000)	1384
Crystal size	0.18 × 0.25 × 0.35 mm
θ range for data collection	3 to 60 °
Index ranges	$-14 \leq h \leq 11$, $-27 \leq k \leq 17$, $-14 \leq l \leq 14$
Reflections collected	5730
Independent reflections	5474
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	5454/0/395
Goodness-of-fit on F^2	1.162
Final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0962, $wR2$ = 0.2279
R indices (all data)	$R1$ = 0.1688, $wR2$ = 0.2867
Largest diff. peak and hole	0.44 and −0.48 eÅ^{-3}

[a] $R_1 = \Sigma|F_o - F_c|/\Sigma(F_o)$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2]$; $P = [\max(F_o^2,0) + 2F_c^2]/3$.

☆ Dedicated to Professor *Gottfried Huttner* on the occassion of his 60th birthday.

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[14] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (internat.) +44 (0)1223/336-033, e-mail: deposit@chemcrys.cam.ac.uk], by quoting the deposition number CCDC-100519.

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