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Chemical and Structural Features of NMe_2Et Adducts of the Silanimines $Me_2Si{=}NSi\mathit{t}Bu_3$ and $\mathit{t}Bu_2Si{=}NSiCl\mathit{t}Bu_2$

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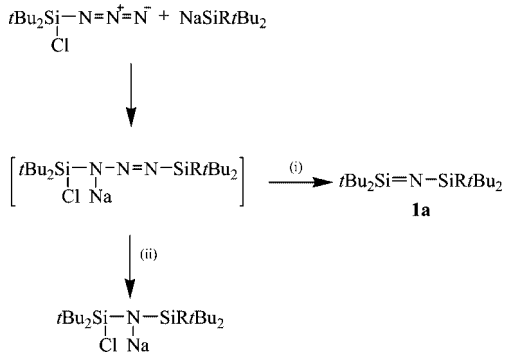
In contrast to $\mathit{t}Bu_2SiN(Li)SiX\mathit{t}Bu_2$ (X = Cl, *t*Bu), the silyl amide $Me_2SiClN(Li)Si\mathit{t}Bu_3$ is unstable towards LiCl elimination, which means that the silanimine donor adduct $Me_2Si{=}NSi\mathit{t}Bu_3{\cdot}NMe_2Et$ can be synthesized in high yield from the reaction of $Me_2SiClN(H)Si\mathit{t}Bu_3$ with *n*BuLi in the presence of NMe_2Et. The silanimine adduct $\mathit{t}Bu_2Si{=}NSiCl\mathit{t}Bu_2{\cdot}NMe_2Et$, with bulky *t*Bu substituents at the unsaturated Si center, is accessible by treating the donor-free silanimine $\mathit{t}Bu_2Si{=}NSiCl\mathit{t}Bu_2$ with NMe_2Et. X-ray quality crystals of the silanimine amine adduct $Me_2Si{=}NSi\mathit{t}Bu_3{\cdot}NMe_2Et$ (monoclinic, $P2_1/n$) were grown from pentane at –25 °C. During thermolysis of the adducts $Me_2Si{=}NSi\mathit{t}Bu_3{\cdot}NMe_2Et$ and $\mathit{t}Bu_2Si{=}NSiCl\mathit{t}Bu_2{\cdot}NMe_2Et$ in NMe_2Et as solvent a Stevens rearrangement takes place to produce $EtN(Me)CH_2SiMe_2N(H)Si\mathit{t}Bu_3$ and $EtN(Me)CH[Me_2SiN(H)Si\mathit{t}Bu_3]_2$, and $EtN(Me)CH_2Si\mathit{t}Bu_2N(H)SiCl\mathit{t}Bu_2$, respectively. In contrast, the thermolysis of $Me_2Si{=}NSi\mathit{t}Bu_3{\cdot}NMe_2Et$ in vacuo gives the silanimine dimer $(Me_2SiNSi\mathit{t}Bu_3)_2$ (monoclinic, $P2_1/n$) in 80 % yield. The benzophenone imine $Ph_2C{=}NSi\mathit{t}Bu_3$ (triclinic, $P\bar{1}$) was obtained from the Wittig-like reaction of $Me_2Si{=}N{-}Si\mathit{t}Bu_3$ with Ph_2CO.

Introduction

Ab initio calculations have shown that the silanimine $H_2Si{=}NSiH_3$ possesses an almost linear Si–N–Si skeleton with a short Si=N double bond and a short Si–N single bond.[1] Moreover, these calculations reveal a negative charge of 1.71 on the N center of $H_2Si{=}NSiH_3$. It is interesting to note that in the solid state the stable, substituted silanimine $\mathit{t}Bu_2Si{=}N{-}Si\mathit{t}Bu_3$, which contains bulky *t*Bu groups,[2] features nearly the same Si=NSi skeleton as that calculated for $H_2Si{=}NSiH_3$. Obviously only electronic effects, namely the difference in electronegativity between Si and N, determine the molecular structure of this type of silanimine (Scheme 1).

Silanimines are highly reactive compounds therefore their syntheses should be carried out under mild conditions. We have found that at low temperature in the weakly polar solvent Bu_2O the reaction of the silyl azide $\mathit{t}Bu_2SiClN_3$ with the silanides $\mathit{t}Bu_3SiNa$ and $\mathit{t}Bu_2PhSiNa$, respectively, in a 1:1 stoichiometry, leads cleanly to the silanimines $\mathit{t}Bu_2Si{=}NSi\mathit{t}Bu_3$ [**1a**(*t*Bu)] and $\mathit{t}Bu_2Si{=}NSiPh\mathit{t}Bu_2$ [**1a**(Ph)].[2,3] In contrast, when $\mathit{t}Bu_2ClSiN_3$ is treated with $\mathit{t}Bu_3SiNa$ in the polar solvent tetrahydrofuran, the sodium amide $\mathit{t}Bu_2Si{-}ClN(Na)Si\mathit{t}Bu_3$ is formed rather than the silanimine **1a**(*t*Bu).[4] As reported earlier, LiCl elimination of silyl amides can also be carried out at higher temperatures in vacuo to give silanimines.[5] As we noted previously, the silanimine $\mathit{t}Bu_2Si{=}NSiCl\mathit{t}Bu_2$ [**1a**(Cl)] can be synthesized by a [3+2] cycloreversion reaction.[6] Surprisingly, in the thermolysis of the silatetrazoline **2**(Cl) the silanimine **1a**(Cl) and the silyl azide $\mathit{t}Bu_3SiN_3$ are produced, as shown in Scheme 2.[6,7]



Scheme 1. (i) $–N_2$, –NaCl, Bu_2O (R = *t*Bu, Ph); (ii) $–N_2$, thf (R = *t*Bu).

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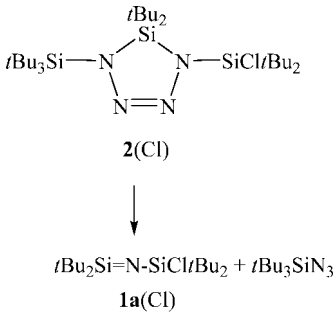


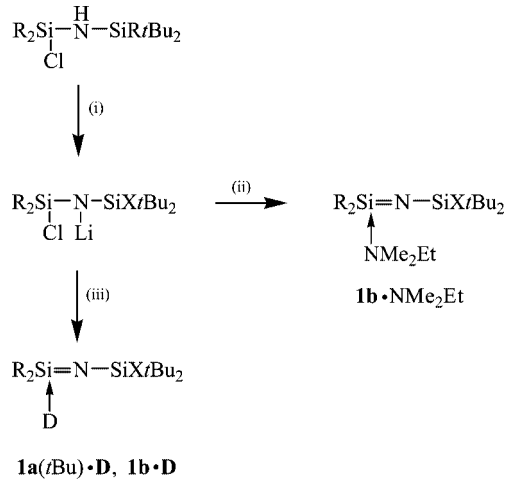
Scheme 2.

In this paper, the syntheses and thermolysis reactions of the silanamine aminates Me$_2$Si=NSi*t*Bu$_3$·NMe$_2$Et and *t*Bu$_2$Si=NSiCl*t*Bu$_2$·NMe$_2$Et are described. We also report the crystal structures of the silanimine aminate Me$_2$Si=NSi*t*Bu$_3$·NMe$_2$Et, the silanimine dimer (Me$_2$SiN-Si*t*Bu$_3$)$_2$, the benzophenone imine Ph$_2$C=NSi*t*Bu$_3$, and the silylamine *t*Bu$_2$SiClN(H)Si*t*Bu$_3$.

Results and Discussion

Syntheses

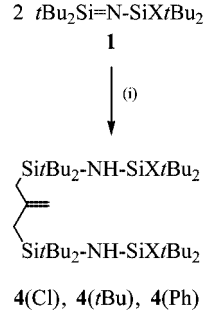
The silyl amides *t*Bu$_2$SiClN(Li)SiX*t*Bu$_2$ (X = Cl, *t*Bu) can be cleanly prepared from the precursor silylamines *t*Bu$_2$SiClN(H)SiX*t*Bu$_2$ (X = Cl, *t*Bu) [**3**(Cl), **3**(*t*Bu)] and alkyllithium reagents like MeLi or *n*BuLi. The NMR spectra of *t*Bu$_2$SiClN(Li)SiX*t*Bu$_2$ (X = Cl, *t*Bu) reveal that elimination of LiCl does not take place in the presence of thf or Et$_2$O at ambient or lower temperatures, whereas the silyl amide Me$_2$SiClN(Li)Si*t*Bu$_3$ eliminates LiCl at low temperature in Et$_2$O. An important factor influencing LiCl elimination of these silyl amides appears to be the degree of steric crowding around the unsaturated silicon center. In earlier reports we described the synthesis of several donor adducts of the silanimines **1a**(*t*Bu) and Me$_2$Si=NSi*t*Bu$_3$ (**1b**),[8,9] and we found that donor adducts of the silanimines **1a**(*t*Bu) and **1b** can be generated by reaction of the silyl amides *t*Bu$_2$SiClN(Li)Si*t*Bu$_3$ and Me$_2$SiClN(Li)Si*t*Bu$_3$, respectively, with CF$_3$SO$_3$SiMe$_3$.[8,9] In this paper we describe a synthesis that does not require CF$_3$SO$_3$SiMe$_3$ by which the silanimine aminate **1b**·NMe$_2$Et can be produced in large amounts. The silanimine amine adduct **1b**·NMe$_2$Et was synthesized from the reaction of Me$_2$SiClN(H)Si*t*Bu$_3$ with *n*BuLi in the presence of NMe$_2$Et at –78 °C in Et$_2$O. X-ray quality crystals of **1b**·NMe$_2$Et (monoclinic, $P2_1/n$) were grown from a pentane solution at –25 °C (Scheme 3). The adduct of silanimine **1a**(Cl) with NMe$_2$Et, which possesses a bulky *t*Bu substituent at the unsaturated Si center, is accessible by treating the donor-free silanimine **1a**(Cl) with NMe$_2$Et.



Scheme 3. (i) +RLi, –RH; (ii) +NMe$_2$Et, –LiCl (R = Me, X = *t*Bu); (iii) +CF$_3$SO$_3$SiMe$_3$, +D (D = thf, Et$_2$O, NEt$_3$), –Me$_3$SiCl, –CF$_3$SO$_3$Li (R = Me, *t*Bu; X = *t*Bu).

Reactivity of Me$_2$Si=NSi*t*Bu$_3$·NMe$_2$Et and *t*Bu$_2$Si=NSiCl*t*Bu$_2$·NMe$_2$Et

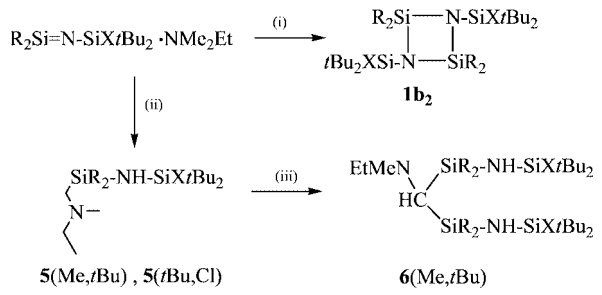
Thermolysis of the donor-free silanimines **1a**(Cl), **1a**(*t*Bu), and **1a**(Ph) in [D$_6$]benzene at ambient temperature gave the compounds **4**(Cl), **4**(*t*Bu), and **4**(Ph), respectively, as isolable products (Scheme 4).[6,10] The formation of these products can be explained by an ene reaction of isobutene with two molecules of the silanimine. Obviously, the *t*Bu-substituted silanimines **1a**(Cl), **1a**(*t*Bu), and **1a**(Ph) are the source of isobutene at ambient temperature. Thus, these silanimines undergo a β-elimination reaction to form isobutene, which reacts twice with the undegraded silanimines to give the corresponding ene reaction products.



Scheme 4. (i) +CH$_2$=C(CH$_3$)$_2$ (X = Cl, *t*Bu, Ph).

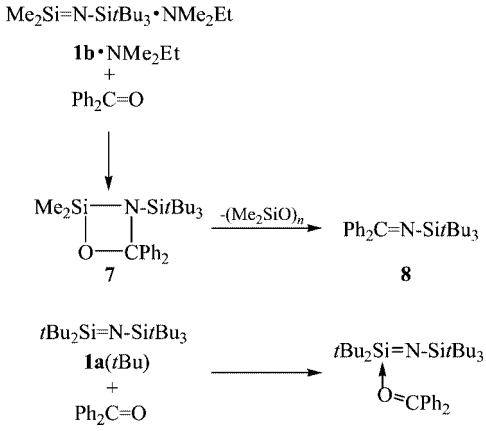
In contrast to the degradation reaction of donor-free silanimines **1a**(Cl), **1a**(*t*Bu), and **1a**(Ph), during thermolysis of the silanimine amine adducts **1a**(Cl)·NMe$_2$Et and **1b**·NMe$_2$Et in dimethylethylamine as solvent a Stevens rearrangement takes place to produce EtN(Me)CH$_2$Si-Me$_2$N(H)Si*t*Bu$_3$ [**5**(Me,*t*Bu)] and EtN(Me)CH[Me$_2$SiN(H)-Si*t*Bu$_3$]$_2$ [**6**(Me,*t*Bu)], and EtN(Me)CH$_2$Si*t*Bu$_2$N(H)-SiCl*t*Bu$_2$ [**5**(*t*Bu,Cl)], respectively. A similar reaction was observed in the thermolysis of the pyridine adduct of **1a**(Ph).[11] It is interesting to note that the thermolysis reaction of **1b**·NMe$_2$Et leads to two products [80% **5**(Me,*t*Bu) and 20% **6**(Me,*t*Bu) in NMe$_2$Et; 10% **5**(Me,*t*Bu) and 90%

6(Me,*t*Bu) in [D_6]benzene; Scheme 5]. The thermolysis of **1b**·NMe_2Et in vacuo gives the silanimine dimer (Me_2SiN-$SitBu_3$)$_2$ (**1b$_2$**) in 80% yield. The silylamines **5**(Me,*t*Bu) and **6**(Me,*t*Bu) were produced as side products in this reaction, as shown in Scheme 5. The silanimine dimer **1b$_2$** was characterized by X-ray crystallography (see below).



Scheme 5. (i) in vacuo (R = Me, X = *t*Bu); (ii) R = Me, X = *t*Bu; R = *t*Bu, X = Cl; (iii) +$Me_2SiNSitBu_3$ (R = Me, X = *t*Bu).

Generally, the reactivity of the silanimine–NMe_2Et adducts of **1a**(Cl) and **1b** resemble those of the corresponding donor-free silanimines. In earlier reports we discussed the reactivity of the silanimines **1a**(Cl) and **1b** in detail.[6,8] In contrast to the reaction of **1a**(*t*Bu) with benzophenone, in which a stable silanimine adduct is formed due to steric hindrance,[12] the silanimine **1b**·NMe_2Et reacts with benzophenone to produce benzophenone imine **8**, via the oxaazasilacyclobutane **7**, by a Wittig-like reaction, as depicted in Scheme 6. The benzophenone imine **8** was obtained in 53% yield. X-ray quality crystals of this compound were obtained by sublimation at 105 °C/0.001 mbar.



Scheme 6.

NMR Spectra

When considering the ^{29}Si NMR spectra of the silanimines of the type $R_2Si(1)=NSi(2)R_3$ and their donor adducts, certain general trends can be observed. As is to be expected for the unsaturated Si centers of silanimines, the ^{29}Si signals of these nuclei are shifted extremely downfield whereas the silanimine donor adducts show signals for the unsaturated Si center that are shifted upfield, as listed in Table 1. Due to anisotropy effects the signals of both Si atoms of $R_2Si(1)=NSi(2)R_3$ are shifted upfield. The linearity of the silanimine $R_2Si(1)=NSi(2)R_3$ skeleton [Si(1)–N–Si(2) angle] is therefore recognizable by the ^{29}Si NMR shift of the Si(2) center. If a strong donor is coordinated to the silanimine the skeleton deviates more from linearity than if a weak one is bonded. In this case, the signal of the Si(2) center will be shifted further downfield than the Si(2) signal of a weak adduct. Therefore, the strength of a silanimine donor can be measured by the ^{29}Si NMR shift of Si(2) of these adducts. In contrast to **1b**, the silanimines **1a**(Cl) and **1a**(*t*Bu) form weaker adducts with NMe_2Et than with thf.[6,9] As shown in Table 1, this trend can also be seen in their ^{29}Si NMR spectra.

Table 1. ^{29}Si NMR shifts (in C_6D_6 if not indicated otherwise) of silanimines $R_2Si(1)=NSi(2)R_3$.

	δ^{29}Si(1)	δ^{29}Si(2)	Ref.
$tBu_2Si(1)=NSi(2)tBu_3$	78.4	–7.7	[2]
$tBu_2Si(1)=NSi(2)PhtBu_2$	81.8	–13.1	[3]
$tBu_2Si(1)=NSi(2)CltBu_2$	3.0	3.0	[6]
$Me_2Si(1)=NSi(2)tBu_3$·NMe_2Et	–8.9	–10.3	–
$tBu_2Si(1)=NSi(2)CltBu_2$·NMe_2Et	–3.4	–6.4	–
$Me_2Si(1)=NSi(2)tBu_3$·THF	–4.4	–11.1	[2]
$tBu_2Si(1)=NSi(2)tBu_3$·THF	1.1	–14.7	[2]
$tBu_2Si(1)=NSi(2)CltBu_2$·THF	2.9	–5.2	[6]
$Me_2Si(1)=NSi(2)tBu_3$·Et_2O	–1.5[a]	–11.1[a]	[8]
$tBu_2Si(1)=NSi(2)CltBu_2$·Et_2O	–0.2[a]	–6.5[a]	[6]

[a] Recorded in Et_2O.

It is interesting to note that in contrast to the NMR spectra of the donor-free silanimine **1a**(Cl),[6] which reveal only one signal set for both silyl groups, the NMR spectra of its NMe_2Et complex show signals that can be assigned to two different silyl groups.

Structure of $Me_2Si=NSitBu_3$·NMe_2Et

Figure 1 shows the molecular structure of the silanimine amine adduct **1b**·NMe_2Et (monoclinic, $P2_1/n$); selected bond lengths and angles are listed in the figure caption.

As shown in Table 2, the silanimine amine adduct **1b**·NMe_2Et has an Si–N–Si angle smaller than 180° and smaller than those in the donor-free silanimines **1a**(*t*Bu), and **1a**(Ph) and in the corresponding thf adduct **1b**·thf [**1a**(*t*Bu): Si–N–Si 177.8(2)°; **1a**(Ph): Si–N–Si 168.34(16)° and 172.95(18)°; **1b**·thf: Si–N–Si 161.0(6)° and 161.5(6)°; **1b**·NMe_2Et: Si–N–Si 156.44(10)°]. The Si=N double bond in **1b**·NMe_2Et [1.6036(13) Å] is somewhat longer than those of the donor-free silanimines **1a**(*t*Bu) and **1a**(Ph) and the corresponding thf adduct **1b**·thf [**1a**(*t*Bu): Si=N 1.568(3) Å; **1a**(Ph): Si=N 1.573(3) Å; **1b**·thf: Si=N 1.574(10) and 1.588(9) Å]. As depicted in Table 2, the N–Si single bonds in the silanimines **1a**(*t*Bu), **1a**(Ph), and in the silanimines adducts **1b**·NMe_2Et and **1b**·thf, however, are remarkably shorter than those found in related supersilylated nitrogen compounds [e.g. **1b$_2$**, **3**(*t*Bu), and **8**; Table 3]. Due to the higher Lewis acidity of silanimines in comparison to that of silenes, the distance between the unsaturated Si center

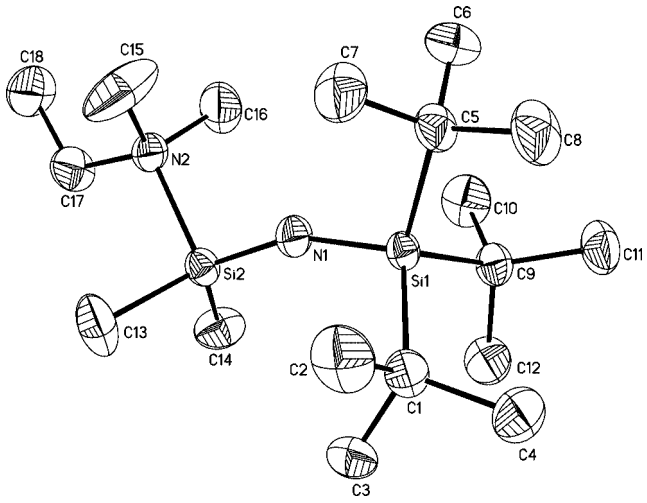


Figure 1. Thermal ellipsoid plot of $Me_2Si{=}NSi\textit{t}Bu_3{\cdot}NMe_2Et$ (**1b**·NMe_2Et) showing the atomic numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si(1)–N(1) 1.6600(13), Si(1)–C(1) 1.951(2), Si(1)–C(5) 1.954(2), Si(1)–C(9) 1.956(2), N(1)–Si(2) 1.6036(13), Si(2)–C(14) 1.868(2), Si(2)–C(13) 1.868(2), Si(2)–N(2) 1.9694(14); N(1)–Si(1)–C(1) 110.06(7), N(1)–Si(1)–C(5) 107.52 (7), C(1)–Si(1)–C(5) 110.15 (8), N(1)–Si(1)–C(9) 110.05(7), C(1)–Si(1)–C(9) 109.55(8), C(5)–Si(1)–C(9) 109.49(7), Si(2)–N(1)–Si(1) 156.44(10), N(1)–Si(2)–C(14) 119.27(10), N(1)–Si(2)–C(13) 119.38 (9), N(1)–Si(2)–N(2) 105.13 (6), C(14)–Si(2)–N(2) 101.73(8), C(13)–Si(2)–N(2) 102.11(10), C(16)–N(2)–Si(2) 107.97(12), C(15)–N(2)–Si(2) 107.4(2), C(17)–N(2)–Si(2) 112.98(11), N(2)–C(17)–C (18) 117.3 (2).

and the amine N atom in **1b**·NMe_2Et (1.969 Å) is shorter than that in the adduct $Me_2Si{=}C(SiMe_2Ph)_2{\cdot}NMe_2Et$ (1.988 Å).[13]

Structure of the Silanimine Dimer ($Me_2SiNSi\textit{t}Bu_3)_2$

X-ray quality crystals of the silanimine dimer ($Me_2SiNSi\textit{t}Bu_3)_2$ (**1b$_2$**) were grown from a benzene solution at ambi-

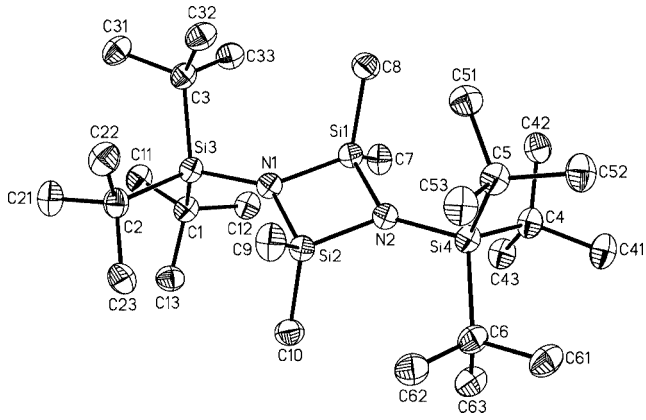


Figure 2. Thermal ellipsoid plot of the silanimine dimer ($Me_2SiNSi\textit{t}Bu_3)_2$ (**1b$_2$**) showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: N(1)–Si(2) 1.764(2), N(1)–Si(3) 1.774(2), N(1)–Si(1) 1.778(2), N(2)–Si(2) 1.761(2), N(2)–Si(1) 1.774(2), N(2)–Si(4) 1.775(2), Si(1)–C(8) 1.866(3), Si(1)–C(7) 1.873(3), Si(1)–Si(2) 2.4690(9), Si(2)–C(10) 1.867(3), Si(2)–C(9) 1.868(3), Si(3)–C(3) 1.950(3), Si(3)–C(2) 1.959(3), Si(3)–C(1) 1.961(3), Si(4)–C(4) 1.950(3), Si(4)–C(5) 1.955(3), Si(4)–C(6) 1.956(3); Si(2)–N(1)–Si(3) 133.53(12), Si(2)–N(1)–Si(1) 88.38(9), Si(3)–N(1)–Si(1) 137.98(12), Si(2)–N(2)–Si(1) 88.60(9), Si(2)–N(2)–Si(4) 132.76(12), Si(1)–N(2)–Si(4) 138.42(12), N(2)–Si(1)–N(1) 91.07(9), N(2)–Si(1)–C(8) 115.47(11), N(1)–Si(1)–C(8) 116.19(11), N(2)–Si(1)–C(7) 115.82(11), N(1)–Si(1)–C(7) 116.13(11), C(8)–Si(1)–C(7) 102.84(13), C(8)–Si(1)–Si(2) 128.81(9), C(7)–Si(1)–Si(2) 128.35(10), N(2)–Si(2)–N(1) 91.95(10), N(2)–Si(2)–C(10) 113.80(11), N(1)–Si(2)–C(10) 110.43(11), N(2)–Si(2)–C(9) 111.06(11), N(1)–Si(2)–C(9) 113.78(11), C(10)–Si(2)–C(9) 113.95(13), C(10)–Si(2)–Si(1) 122.43(9), C(9)–Si(2)–Si(1) 123.62(10), N(1)–Si(3)–C(3) 106.58(11), N(1)–Si(3)–C(2) 112.06(10), C(3)–Si(3)–C(2) 108.62(11), N(1)–Si(3)–C(1) 110.50(10), C(3)–Si(3)–C(1) 110.47(11), C(2)–Si(3)–C(1) 108.59(11), N(2)–Si(4)–C(4) 107.12(10), N(2)–Si(4)–C(5) 110.42(10), C(4)–Si(4)–C(5) 110.06(11), N(2)–Si(4)–C(6) 111.54(11), C(4)–Si(4)–C(6) 108.80(11), C(5)–Si(4)–C(6) 108.88(11).

Table 2. Bond lengths [Å] and angles [°] of silanimines.

	1b·NMe_2Et	**1b**·thf[2]	**1a**(Ph)[11]	**1a**($\textit{t}$Bu)[2]	$H_2Si{=}NSiH_3$[1]
Si=N	1.6036(13)	1.588(9)/1.574(10)	1.573(2)/1.573(3)	1.568(3)	1.549[a]
Si–N	1.6600(13)	1.654(9)/1.667(10)	1.695(2)/1.690(3)	1.695(3)	1.688[a]
Si–N–Si	156.44(10)	161.5(5)/161.0(6)	168.34(16)/172.95(18)	177.8(2)	175.6[a]

[a] Calculated.

Table 3. Bond lengths [Å] and angles [°] of supersilylated nitrogen compounds (av. = average value).

	N–Si$\textit{t}Bu_3$	N–SiR_2	Si–N–E (E = Si, C, N, M)	Si–$C_{\textit{t}Bu}$ (av.)
$(\textit{t}Bu_3SiNSiMe_2)_2$ (**1b$_2$**)	1.775(2) av.	1.769(2) av.	135.67(12) av.	1.955(3)
$\textit{t}Bu_3SiN(H)ClSi\textit{t}Bu_2$ [**3**($\textit{t}$Bu)]	1.729(6) av.	1.694(7) av.	160.5(5) av.	1.931(8)
$\textit{t}Bu_3SiN{=}CPh_2$ (**8**)	1.721(4) av.	–	154.3(3) av.	1.922(4)
$\textit{t}Bu_2Si{=}NSi\textit{t}Bu_3{\cdot}\textit{t}BuMe_2SiN_3$[7]	1.815(2) av.	1.789(2) av.	153.0(3) av.	1.940(3)
$O(\textit{t}Bu_2SiHNSi\textit{t}Bu_3)_2$[14]	1.750(1)	1.772(1)	157.13(6)	1.947(3)
$\textit{t}Bu_3SiN(H)SiMesCH_2C_6H_2Me_2$[15]	1.770(8)	1.729(8)	145.5(5)	1.866(12)
$\textit{t}Bu_3SiNC\textit{t}Bu^+$ [16]	1.822	–	179.0	1.902
$\textit{t}Bu_3SiN(H)N(H)Si\textit{t}Bu_3$[17]	1.760(3)	–	120.6(2)	1.932(3)
$\textit{t}Bu_3SiN(H)N{=}NSi\textit{t}Bu_3$[18]	1.790(8) av.	–	124.9(7) av.	1.95(1)
$\textit{t}Bu_3SiN(SnMe_3)N{=}NSi\textit{t}Bu_3$[18]	1.82(2) av.	–	119.1(15) av.	1.922(4)
$\textit{t}Bu_3SiNHM$[19] (M = Ti, V, Zr, Ta, W)	1.723(9)–1.758(4)	–	160.9(3)–166.6(5)	1.92(1)–1.94(1)
$\textit{t}Bu_3SiNM_2$[19] (M = Ti, V, Zr, Ta, W)	1.719(14)–1.778(3)	–	164.1(2)–176.3(2)	1.93(3)–1.95(1)

ent temperature. It crystallizes in the monoclinic space group $P2_1/n$. As depicted in Figure 2, the central core of **1b$_2$** is a planar four-membered ring. The corners of this four-membered ring are alternately occupied by two Si and two N atoms [Si–N–Si (av) 88.49(9)°; N–Si–N 91.51(10)°]. The Si–N bond lengths of **1b$_2$** are longer than those of the silanimines **1a**(*t*Bu), **1a**(Ph), **1b**·thf, and **1b**·NMe_2Et, and those of the silylamine **3**(*t*Bu) (see Tables 2 and 3).

Structure of the Benzophenone Imine $Ph_2C{=}NSitBu_3$

X-ray quality crystals of the benzophenone imine **8** were obtained by sublimation at 105 °C/0.001 mbar. It crystallizes in the triclinic space group $P\bar{1}$. It is interesting to note that the solid-state structure features three independent molecules in the asymmetric unit. As depicted in Figure 3, the C=N–Si skeleton deviates much more from linearity [C–N–Si 154.6(3)°, 154.9(3)°, and 153.5(3)°] than the Si=N–Si skeleton of **1a**(*t*Bu). The structure of **8** contains a C=N double bond [1.253(4), 1.263(5), and 1.261(5) Å] and, in comparison with the silanimine **1a**(*t*Bu), a longer Si–N single bond, as shown in Tables 2 and 3 [**1a**(*t*Bu): N–Si*t*Bu$_3$ 1.695(3) Å; **8**: N–Si*t*Bu$_3$ 1.722(3), 1.720(3), and 1.721(4) Å; Figure 3].

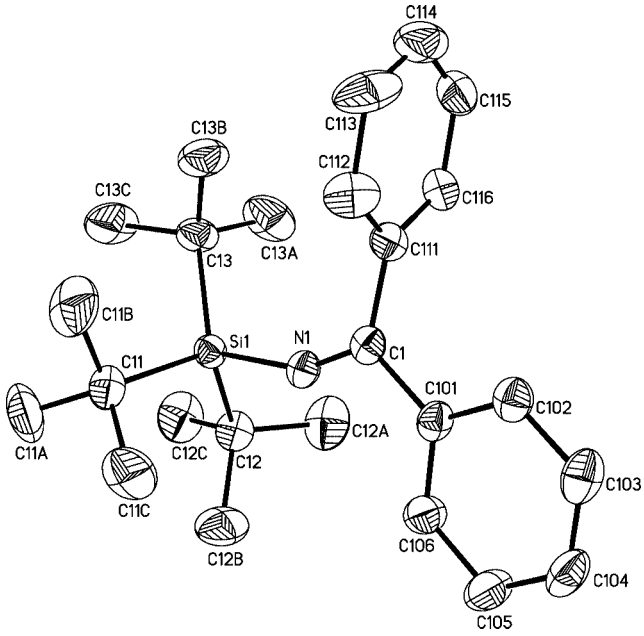


Figure 3. Thermal ellipsoid plot of one of three independent molecules in the asymmetric unit of $Ph_2C{=}NSitBu_3$ (**8**) showing the atom numbering scheme. The displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Si(1)–N(1) 1.722(3), Si(1)–C(11) 1.919(4), Si(1)–C(13) 1.922(4), Si(1)–C(12) 1.929(4), N(1)–C(1) 1.253(4), C(1)–C(101) 1.510(5), C(1)–C(111) 1.512(5); N(1)–Si(1)–C(11) 102.30(18), N(1)–Si(1)–C(13) 116.02(18), C(11)–Si(1)–C(13) 112.1(2), N(1)–Si(1)–C(12) 101.14(18), C(11)–Si(1)–C(12) 113.6(2), C(13)–Si(1)–C(12) 111.1(2), C(1)–N(1)–Si(1) 154.6(3), N(1)–C(1)–C(101) 119.8(4), N(1)–C(1)–C(111) 123.9(4), C(101)–C(1)–C(111) 116.2(4).

Structure of the Silylamine $tBu_2SiClN(H)Sitbu_3$

The solid-state structure of the silylamine $tBu_2SiClN(H)$-Si*t*Bu$_3$ [**3**(*t*Bu)] (triclinic, $P\bar{1}$) shows two symmetrically independent molecules in the unit cell. As shown in Table 3, **3**(*t*Bu) possesses Si–N–Si angles of 164.2(5)° and 158.5(5)°, respectively, which can be compared to the values for **1a**(*t*Bu) [177.8(2)°], **1a**(Ph) [172.95(18)°], **1b**·thf [161.0(6)° and 161.5(6)°], and **1b**·NMe_2Et [156.44(10)°]. The Si(Cl)–N bond [av. 1.694(7) Å] in **3**(*t*Bu) lies in the range of the N–Si*t*Bu$_3$ bond lengths for the supersilyl-substituted silanimines **1a**(*t*Bu), **1a**(Ph), **1b**·thf, and **1b**·NMe_2Et but is shorter than the Si–N single bonds of the silanimine dimer **1b$_2$** and the benzophenone imine **8** (Table 3). On the other hand, the length of the N–Si*t*Bu$_3$ bond in **3**(*t*Bu) is similar to those found in the silanimine dimer **1b$_2$** and the benzophenone imine **8**. Both molecules of **3**(*t*Bu) show large thermal displacements, resulting in distorted structural parameters and a large difference density. The molecular structure of **3**(*t*Bu) shows that the N–H groups are extremely shielded by the *t*Bu groups and are not involved in hydrogen bonding (Figure 4 and Table 4).

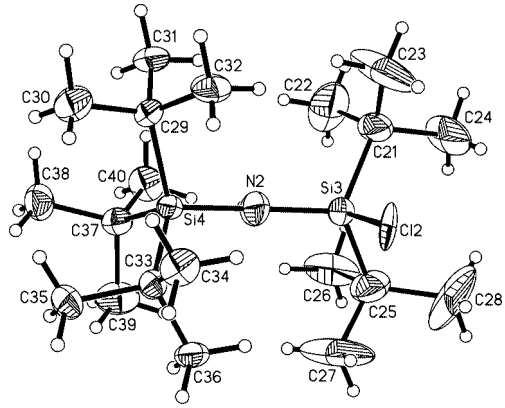


Figure 4. Thermal ellipsoid plot of one of the two independent molecules in the asymmetric unit of the silylamine $tBu_2SiClN(H)$ Si*t*Bu$_3$ [**3**(*t*Bu)]. The displacement ellipsoids are drawn at the 30% probability level. Selected bond lengths [Å] and angles [°]: Si(4)–N(2) 1.733(6), Si(4)–C(29) 1.918(7), Si(4)–C(33) 1.925(7), Si(4)–C(37) 1.935(8), Cl(2)–Si(3) 2.293(3) Si(3)–N(2) 1.679(7), Si(3)–C(25) 1.851(9), Si(3)–C(21) 1.908(9); Si(3)–N(2)–Si(4) 164.2(5), N(2)–Si(4)–C(29) 109.5(3), N(2)–Si(4)–C(33) 111.2(3), C(29)–Si(4)–C(33) 110.8(3), N(2)–Si(4)–C(37) 102.8(4), C(29)–Si(4)–C(37) 110.5(3), C(33)–Si(4)–C(37) 111.9(3), N(2)–Si(3)–C(25) 114.6(4), N(2)–Si(3)–C(21) 112.3(4), C(25)–Si(3)–C(21) 114.3(5), N(2)–Si(3)–Cl(2) 101.9(3), C(25)–Si(3)–Cl(2) 105.1(4), C(21)–Si(3)–Cl(2) 107.3(5).

Conclusions

In summary, we have shown that in contrast to tBu_2SiN-(Li)Si*X*t*Bu*$_2$ (X = Cl, *t*Bu), the silyl amide $Me_2SiClN(Li)$-Si*t*Bu$_3$ is unstable towards LiCl elimination, which means that the silanimine aminate **1b**·NMe_2Et can be synthesized in high yield from the reaction of $Me_2SiClN(H)Sitbu_3$ with *n*BuLi in the presence of NMe_2Et. The silanimine adduct **1a(Cl)·NMe$_2$Et**, which possesses the bulky *t*Bu substituent

Table 4. Crystallographic data and further details of the structure determination of **1b**·NMe_2Et, **1b$_2$**, **3**(*t*Bu), and **8**.

	1b·NMe_2Et	**1b$_2$**	**3**(*t*Bu)	**8**
Empirical formula	$C_{18}H_{44}N_2Si_2$	$C_{28}H_{66}N_2Si_4$	$C_{20}H_{46}ClNSi_2$	$C_{25}H_{37}NSi$
Color	colorless	colorless	colorless	yellow
Formula weight	344.73	543.19	392.21	379.65
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a [Å]	10.431(2)	8.8953(4)	8.7999(18)	8.4950(10)
b [Å]	17.361(2)	25.2188(9)	15.954(7)	16.830(2)
c [Å]	12.664(2)	14.8096(7)	18.366(6)	26.592(3)
α [°]	90	90	94.16(3)	105.598(4)
β [°]	97.80(2)	90.632(4)	100.41(3)	97.122(4)
γ [°]	90	90	98.26(4)	101.089(4)
V [Å^3], Z	2272.1(6), 4	3322.0(2), 4	2496.8(14), 4	3530.9(7), 6
$D_{calcd.}$ [Mg m^{-3}]	1.008	1.086	1.043	1.071
μ(Mo-K_α) [mm^{-1}]	0.157	0.198	0.253	0.109
F(000)	776	1216	872	1248
Crystal size [mm^3]	0.4 × 0.4 × 0.8	0.49 × 0.29 × 0.27	0.50 × 0.19 × 0.10	0.31 × 0.14 × 0.12
Diffractometer	Stoe-IPDS-II	Stoe-IPDS-II	Siemens Smart CCD	Siemens Smart CCD
θ-range [°]	2.00–28.00	1.59–25.35	1.13–30.73	0.81–25.03
Index ranges	$-13 \le h \le 10$	$-10 \le h \le 10$	$-12 \le h \le 12$	$-10 \le h \le 10$
	$0 \le k \le 21$	$-30 \le k \le 30$	$-22 \le k \le 22$	$-20 \le k \le 20$
	$-15 \le l \le 16$	$-17 \le l \le 17$	$-27 \le l \le 28$	$-31 \le l \le 31$
No. of reflections collected	6319	82992	31799	34387
No. of independent reflections	4619	6085	13016	12390
R(int)	0.0203	0.1395	0.0787	0.1345
Absorption correction	empirical	empirical	empirical	empirical
No. of data/restraints/parameter	4619/0/375	6085/0/307	13016/0/433	12390/0/730
Goodness of fit on F^2	1.063	1.104	1.772	0.958
Final R indices [$I > 2\sigma(I)$], R_1, wR_2	0.0351, 0.0940	0.0565, 0.1431	0.1502, 0.3527	0.0763, 0.1171
Largest diff. peak/hole [e Å^{-3}]	0.276/–0.203	0.474/–0.371	2.045/–0.700	0.241/–0.271

on the unsaturated Si center, is accessible by treating the donor-free silanimine **1a**(Cl) with NMe_2Et.

In contrast to the degradation reaction of the donor-free silanimines **1a**(Cl), **1a**(*t*Bu), and **1a**(Ph), a Stevens rearrangement takes place in the thermolysis of the silanimine amine adducts **1a**(Cl)·NMe_2Et and **1b**·NMe_2Et in dimethylethylamine to produce $EtN(Me)CH_2SiMe_2N(H)SitBu_3$ and $EtN(Me)CH[Me_2SiN(H)SitBu_3]_2$, and $EtN(Me)CH_2Si$-$tBu_2N(H)SiCltBu_2$, respectively. The thermolysis of **1b**·NMe_2Et in vacuo gives the silanimine dimer **1b$_2$** in 80% yield. In contrast to the reaction of **1a**(*t*Bu) with benzophenone, in which a stable silanimine adduct is formed, the silanimine amine complex **1b**·NMe_2Et reacts with benzophenone to produce benzophenone imine **8**, via oxaazasilacyclobutane **7**, by a Wittig-like reaction. Due to the anisotropy effect the ^{29}Si NMR spectra of silanimines of the type $R_2Si(1){=}NSi(2)R_3$ reveal upfield-shifted signals for both Si nuclei, therefore the linearity of the silanimine skeleton can be determined from the ^{29}Si shift of the Si(2) center.

Experimental Section

General Remarks: All experiments were carried out under dry nitrogen or argon with strict exclusion of air and moisture using standard Schlenk techniques. $tBu_2Si{=}NSiCltBu_2$,[6] tBu_2SiFH,[20] tBu_2SiClH,[20] and $Me_2SiClN(H)SitBu_3$[8] were prepared according to literature procedures. All other starting materials were purchased from commercial sources and used without further purification. The solvents were distilled from sodium/benzophenone (benzene, toluene, tetrahydrofuran, diethyl ether) or Na/Pb alloy (pentane, hexane, heptane) prior to use. C_6D_6 was dried with molecular sieves and stored under dry nitrogen. The NMR spectra were recorded with a Jeol FX 90, a Jeol GSX 270, a Bruker AM 250, a Bruker DPX 250, or a Bruker Avance 400 spectrometer. The ^{29}Si NMR spectra were recorded using the INEPT pulse sequence with empirically optimized parameters for polarization transfer from the *t*Bu substituents.

Synthesis of $tBu_2SiClN(H)SitBu_3$ [3(*t*Bu)]: This compound was prepared according to a literature procedure.[4] X-ray quality crystals of **3**(*t*Bu) were grown from benzene at ambient temperature. Selected data: thermal decomposition of **3**(*t*Bu) occurs at 113 °C. ^{1}H NMR (C_6D_6, internal TMS): δ = 1.19 (s, 18 H, tBu_2SiCl), 1.21 (s, 27 H, tBu_3Si) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 23.6 (3 C, CMe_3), 24.5 (2 C, CMe_3), 29.3 (6 C, CMe_3), 31.3 (9 C, CMe_3) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, external TMS): δ = 8.4 ($SitBu_3$), 16.0 ($SiCltBu_3$) ppm. $C_{20}H_{46}ClNSi$ (392.22): calcd. C 61.25, H 11.82, N 3.57; found C 62.02, H 12.05, N 3.18. EI MS: *m*/*z* (%) 334 (100) $[M - tBu]^+$.

Synthesis of $tBu_2Si(H)NH_2$: tBu_2SiClH (10.05 g, 56.2 mmol) was added to 10 mL of liquid NH_3 at –60 °C and stirred for 6 h. After heating to room temperature the reaction product was distilled at 93 °C/100 Torr: Yield: 5.72 g (68%). ^{1}H NMR (C_6D_6, internal TMS): δ = 0.97 (s, 18 H, tBu_2Si), 4.03 (br., HSi) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 18.9 (CMe_3), 27.7 (CMe_3) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, external TMS): δ = 7.1 ppm ($SitBu_2$). $C_8H_{21}NSi$ (159.35): calcd. C 60.30, H 13.28, N 8.78; found C 59.13, H 13.14, N 8.02. EI MS: *m*/*z* (%) 159 (13) $[M]^+$, 102 (100) $[M - tBu]^+$.

Synthesis of $tBu_2Si(H)N(H)SiHtBu_2$: A mixture of $LiNH_2$ (4.60 g, 200 mmol) and tBu_2SiFH (16.20 g, 100 mmol) in tetrahydrofuran (100 mL) was refluxed for 24 h. After addition of methanol

(40 mL), all volatile compounds were removed in vacuo and the residue was extracted into 150 mL of pentane. After filtration, the solvent was removed in vacuo to give tBu$_2$Si(H)N(H)SiHtBu$_2$ as a colorless oil: Yield: 10.93 g (72%). B.p. 58 °C/0.01 mbar. ^{1}H NMR (C_6D_6, internal TMS): δ = 1.07 (s, 36 H, tBu$_2$Si), 4.23 (d, HSi) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 20.6 (*C*Me$_3$), 28.5 (C*Me$_3$*) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = 7.0 ppm (SitBu$_2$). $C_{16}H_{39}NSi_2$ (301.67): calcd. C 63.70, H 13.03, N 4.64; found C 63.04, H 12.95, N 4.72. EI MS: *m*/*z* (%) 301 (5) [M]$^+$, 244 (100) [M – tBu]$^+$.

Note: tBu$_2$Si(H)N(H)SiHtBu$_2$ can also be synthesized from tBu$_2$Si(H)NHLi and tBu$_2$SiFH in tetrahydrofuran by heating.

Synthesis of tBu$_2$SiClN(H)SiCltBu$_2$ [3(Cl)]: A mixture of *N*-chlorosuccinimide (23.79 g, 178.1 mmol) and tBu$_2$Si(H)N(H)SiHtBu$_2$ (9.775 g, 32.4 mmol) in CCl_4 (75 mL) was refluxed for 48 h. After filtration, the solvent was removed in vacuo and the obtained solid reaction product was sublimed at 60 °C/10^{-4} Torr: Yield: 9.36 g (80%). ^{1}H NMR (C_6D_6, internal TMS): δ = 1.12 (s, 36 H, tBu$_2$Si) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 23.4 (*C*Me$_3$), 28.1 (C*Me$_3$*) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = 17.9 ppm (SitBu$_2$). $C_{16}H_{37}Cl_2NSi_2$ (370.56): calcd. C 51.86, H 10.06, N 3.78; found C 50.74, H 9.89, N 3.42. EI MS: *m*/*z* (%) 369 (1) [M]$^+$, 312 (100) [M – tBu]$^+$.

Synthesis of the Silanimine Adduct tBu$_2$Si=NSiCltBu$_2$·NMe$_2$Et [1a(Cl)·NMe$_2$Et]: NMe$_2$Et (2 mL) was added to a solution of tBu$_2$Si=NSiCltBu$_2$ (0.8 mmol) in 5 mL of benzene. After removing all volatile compounds in vacuo **1a**(Cl)·NMe$_2$Et was obtained as a colorless solid. ^{1}H NMR (C_6D_6, internal TMS): δ = 1.18 (s, 18 H, tBu$_2$SiCl), 1.46 (s, 18 H, tBu$_2$Si), 0.63 (t, ^3J = 7.2 Hz, 3 H, CH$_3$), 2.89 (q, ^3J = 7.2 Hz, 2 H, NCH$_2$), 2.11 (s, 6 H, NMe$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 9.7 (CH$_3$), 25.3 (*C*Me$_3$), 25.7 (*C*Me$_3$), 30.3 (C*Me$_3$*), 31.8 (C*Me$_3$*), 44.8 (NCH$_2$), 52.9 (NMe$_2$) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = –6.4 (SiCltBu$_2$), –3.4 (SitBu$_2$) ppm.

Synthesis of the Silanimine Adduct Me$_2$Si=NSitBu$_3$·NMe$_2$Et (1b·NMe$_2$Et): *n*BuLi (7.89 mmol) in hexane (5.1 mL) was added to a solution of Me$_2$SiClN(H)SitBu$_3$ (2.43 g, 7.89 mmol) and 10 mL of NMe$_2$Et in 50 mL of Et$_2$O at –78 °C and stirred for 4 h. After heating to room temperature the volatile compounds were removed in vacuo and the solid reaction product was extracted into 30 mL of pentane. After filtration, single crystals of **1b**·NMe$_2$Et were obtained from the pentane filtrate at –25 °C. Yield: 1.47 g (54%). ^{1}H NMR (C_6D_6, internal TMS): δ = 0.12 (s, 6 H Me$_2$Si), 0.32 (t, 3 H, CH$_3$), 1.45 (s, 27 H, tBu$_3$Si), 1.77 (s, 6 H, NMe$_2$), 2.50 (q, 2 H, NCH$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 1.9 (Me$_2$Si), 6.5 (CH$_3$), 24.5 (*C*Me$_3$), 32.1 (C*Me$_3$*), 41.5 (NCH$_2$), 51.0 (NMe$_2$) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = –8.9 (Me$_2$Si), –10.3 (SitBu$_3$) ppm.

Synthesis of the Silanimine Dimer (Me$_2$SiNSitBu$_3$)$_2$ (1b$_2$): Compound **1b**·NMe$_2$Et (0.608 g, 1.76 mmol) was heated at 120 °C in vacuo (0.01 mbar) for 4 h, then the obtained solid was extracted into 10 mL of benzene. **1b$_2$** was crystallized from this solution at ambient temperature. Yield: 0.382 g (80%). The NMR spectra of the mother liquid show the signals of **1b$_2$** and small signals which can be assigned to **5**(Me,*t*Bu) and **6**(Me,*t*Bu). Selected data for **1b$_2$**: m.p. 268 °C. ^{1}H NMR (C_6D_6, internal TMS): δ = 0.79 (s, 12 H Me$_2$Si), 1.23 (s, 54 H, tBu$_3$Si) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 12.1 (Me$_2$Si), 23.8 (*C*Me$_3$), 32.6 (C*Me$_3$*) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = 7.4 (Me$_2$Si), 4.6 (SitBu$_3$) ppm. $C_{28}H_{66}N_2Si_4$ (543.18): calcd. C 61.91, H 12.95, N 5.16; found C 61.28, H 12.62, N 5.09.

Thermolysis of the Silanimine Adduct Me$_2$SiNSitBu$_3$·NMe$_2$Et (1b·NMe$_2$Et): A solution of **1b·NMe$_2$Et** (0.168 g, 0.487 mmol) in 0.8 mL of NMe$_2$Et was heated at 135 °C for 30 h. The NMR (^{1}H, ^{13}C, ^{29}Si) spectra showed the signals of **5**(Me,*t*Bu) (80%) and **6**(Me,*t*Bu) (20%). After removing all volatile compounds at room temp. and 0.001 mbar, colorless **5**(Me,*t*Bu) was distilled at 70 °C/0.001 mbar from the obtained mixture. Analytically pure **6**(Me,*t*Bu) remained as the distillation residue.

5(Me,*t*Bu): ^{1}H NMR (C_6D_6, internal TMS): δ = 0.26 (s, 6 H Me$_2$Si), 0.96 (t, ^1J = 7.1 Hz, 3 H, CH$_3$), 1.20 (s, 27 H, tBu$_3$Si), 1.74 (s, 2 H, SiCH$_2$N), 2.15 (s, 3 H, NCH$_3$), 2.30 (q, ^1J = 7.1 Hz, 2 H, NCH$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 3.64 (Me$_2$Si), 13.3 (CH$_3$), 23.0 (*C*Me$_3$), 30.7 (C*Me$_3$*), 45.4 (NCH$_3$), 50.2 (NCH$_2$Si), 55.7 (NCH$_2$) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = –3.7 (Me$_2$Si), 6.4 (SitBu$_3$) ppm. $C_{18}H_{44}N_2Si_2$ (344.74): calcd. C 62.71, H 12.87, N 8.13; found C 63.01, H 12.14, N 8.52. EI MS: *m*/*z* (%) 344 (7) [M]$^+$, 287 (100) [M – tBu]$^+$.

6(Me,*t*Bu): M.p. 116 °C. ^{1}H NMR (C_6D_6, internal TMS): δ = 0.41 (s, 6 H MeSi), 0.44 (s, 6 H MeSi), 1.06 (t, ^1J = 7.1 Hz, 3 H, CH$_3$), 1.20 (s, 54 H, tBu$_3$Si), 1.76 (s, 1 H, Si$_2$CHN), 2.49 (s, 3 H, NCH$_3$), 2.81 (q, ^1J = 7.1 Hz, 2 H, NCH$_2$) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 6.1 (MeSi), 6.2 (MeSi), 14.7 (CH$_3$), 23.0 (*C*Me$_3$), 30.9 (C*Me$_3$*), 44.0 (NCH$_3$), 53.6 (NCHSi$_2$), 54.0 (NCH$_2$) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = –1.6 (Me$_2$Si), 6.7 (SitBu$_3$) ppm. $C_{32}H_{77}N_3Si_4$ (616.33): calcd. C 62.36, H 12.60, N 6.80; found C 62.00, H 12.83, N 6.65. EI MS: *m*/*z* (%) 615 (3) [M]$^+$, 558 (100) [M – tBu]$^+$.

Remark: A solution of **1b**·NMe$_2$Et (0.025 g, 0.073 mmol), 0.1 mL of NMe$_2$Et and 1 mL of C_6D_6 was heated at 120 °C for 24 h. The NMR (^{1}H, ^{13}C, ^{29}Si) spectra showed the signals of **5**(Me,*t*Bu) (10%) and **6**(Me,*t*Bu) (90%).

Thermolysis of the Silanimine Adduct tBu$_2$Si=NSiCltBu$_2$·NMe$_2$Et [1a(Cl)·NMe$_2$Et]: A solution of **1a**(Cl)·NMe$_2$Et (0.5 mmol) in 2 mL of NMe$_2$Et was stored for 2 weeks at ambient temperature. The NMR (^{1}H, ^{13}C, ^{29}Si) spectra showed only the signals of **5**(*t*Bu,Cl). ^{1}H NMR (C_6D_6, internal TMS): δ = 0.96 (t, ^1J = 7.33 Hz, 3 H, CH$_3$), 1.14 (s, 18 H, tBu$_2$Si), 1.23 (s, 18 H, tBu$_2$Si), 2.06 (s, 3 H, NCH$_3$), 2.15 (q, ^1J = 7.33 Hz, 2 H, NCH$_2$), 2.35 (s, 2 H, SiCH$_2$N) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 13.1 (CH$_3$), 23.3 (*C*Me$_3$), 23.6 (*C*Me$_3$), 28.7 (C*Me$_3$*), 29.5 (C*Me$_3$*), 39.2 (NCH$_2$Si), 45.1 (NCH$_3$), 53.7 (NCH$_2$) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = 17.5 (tBu$_2$SiCl), 0.6 (SitBu$_2$) ppm. EI MS: *m*/*z* (%) 334 (43) [M – tBu]$^+$, 166 (100) [Me$_2$SiNHSiClMe$_2$]$^+$.

Note: A solution of **1a**(Cl)·NMe$_2$Et (0.134 g, 0.329 mmol) in 0.6 mL of C_6D_6 was stored at ambient temperature for a week. The NMR (^{1}H, ^{13}C, ^{29}Si) spectra showed the signals of **5**(*t*Bu,Cl).

Reaction of the Silanimine Adduct Me$_2$Si=NSitBu$_3$·NMe$_2$Et (1b·NMe$_2$Et) with Ph$_2$CO: A solution of Ph$_2$C=O (0.275 g, 1.50 mmol) in 10 mL of Et$_2$O was added to a solution of **1b**·NMe$_2$Et (0.520 g, 1.51 mmol) in 10 mL of Et$_2$O at –78 °C. The NMR (^{1}H, ^{13}C, ^{29}Si) spectra showed the signals of Ph$_2$C=NSitBu$_3$ (**8**) and other compounds containing Me$_2$SiO groups.[8] After removing all volatile compounds in vacuo (0.001 mbar), single crystals of **8** were obtained by sublimation at 105 °C/0.001 mbar. Yield: 0.301 g (53%). M.p. 98 °C. ^{1}H NMR (C_6D_6, internal TMS): δ = 1.18 (s, 27 H, tBu$_3$Si), 7.08 (m, 6 H, *o*/*p*-Ph), 7.387 (m, 4 H, *m*-Ph) ppm. ^{13}C{^{1}H} NMR (C_6D_6, internal TMS): δ = 23.7 (*C*Me$_3$), 30.9 (C*Me$_3$*), 128.26 (*m*/*o*-Ph), 128.29 (*m*/*o*-Ph), 129.3 (*p*-Ph), 143.3 (*i*-Ph), 170.3 (C=N) ppm. ^{29}Si{^{1}H} NMR (C_6D_6, external TMS): δ = –4.9 ppm (SitBu$_3$). $C_{19}H_{39}NSi_2$ (379.66): calcd. C 79.01, H 9.81, N 3.69; found C 78.54, H 9.65, N 3.72. EI MS: *m*/*z* (%) 322 (100)

$[M - tBu]^+$. IR: $\nu_{C=N}$ = 1692 cm^{-1}. UV/Vis: λ_{max} = 401 nm (ε_{401} = 7.48 $M^{-1}cm^{-1}$).

Lithiation of $tBu_2SiClN(H)SiXtBu_2$ (X = Cl, *t*Bu) [3(Cl), 3(*t*Bu)]: A solution of RLi [X = Cl(thf): RLi = 3.16 mmol of *n*BuLi in 2 mL of hexane and 10 mL of thf; X = Cl(thf): RLi = 1.93 mmol of MeLi in 3 mL of Et_2O; X = Cl(Et_2O): RLi = 1.05 mmol of *n*BuLi in 0.7 mL of hexane and 10 mL of Et_2O] was added to a solution of $tBu_2SiClN(H)SiXtBu_2$ (in 10 mL of thf, X = Cl, 1.162 g, 3.14 mmol; in 6 mL of thf, X = *t*Bu, 0.756 g, 1.93 mmol; in 10 mL Et_2O, X = Cl, 0.385 g, 1.05 mmol) at –78 °C. After removing the solvent, the silylated amides $tBu_2SiClN(Li)SiXtBu_2$ (X = Cl, *t*Bu) were obtained as colorless solids. The NMR spectra of the reaction solution showed only the signals of the silylated amides $tBu_2SiClN(Li)SiXtBu_2$ (X = Cl, *t*Bu).

$tBu_2SiClNLi(thf)SiCltBu_2$: ^1H NMR (C_6D_6, internal TMS): δ = 1.32 (m, 4 H, CH_2), 1.36 (s, 36 H, tBu_2Si), 3.47 (m, 4 H OCH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 24.8 (CMe_3), 25.2 (CH_2), 28.9 (CMe_3), 68.7 (OCH_2) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, external TMS): δ = 4.8 ppm ($SitBu_2$).

$tBu_2SiClNLi(thf)SitBu_3$: ^1H NMR (C_6D_6, internal TMS): δ = 1.17 (m, 4 H, CH_2), 1.32 (s, 27 H, tBu_3Si), 1.44 (s, 18 H, tBu_2Si), 3.35 (s, 8 H OCH_2) ppm.

tBu_2SiCl-NLi(Et_2O)$SiCltBu_2$: ^1H NMR (C_6D_6, internal TMS): δ = 0.904 (t, 6 H, CH_3), 1.315 (s, 36 H, tBu_2Si), 3.181 (q, 4 H OCH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6, internal TMS): δ = 14.8 (CH_3), 24.8 (CMe_3), 29.0 (CMe_3), 65.8 (OCH_2) ppm. $^{29}Si\{^1H\}$ NMR (C_6D_6, external TMS): δ = 5.5 ppm ($SitBu_2$).

Note: Treatment of one equivalent of $tBu_2SiClN(Li)SiXtBu_2$ (X = Cl, *t*Bu) with one equivalent of MeOH leads quantitatively to the formation of **3**(Cl) and **3**(*t*Bu).

X-ray Crystallographic Study: Data collection was performed with either a Stoe-IPDS-II diffractometer or a Siemens CCD three-circle diffractometer. Empirical absorption correction was performed with MULABS[21] and SADABS,[22] structure solution by direct methods,[23] and structure refinement by full-matrix least-squares on F^2 with SHELXL-97.[24] Hydrogen atoms were placed at ideal positions and refined with fixed isotropic displacement parameters using a riding model.

CCDC-602102 (for **1b**·NMe_2Et), -602101 (for **1b$_2$**), -609530 [for **3**(*t*Bu)], and -609686 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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