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Silicon Azides

Neutral Lewis Base Adducts of Silicon Tetraazide**

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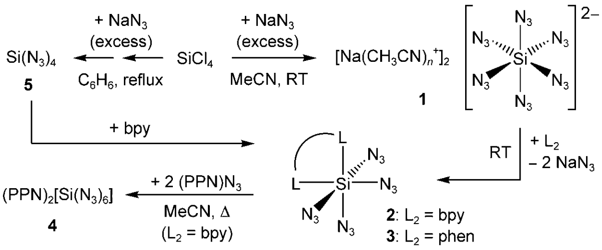
The field of binary main-group element azides[1] has enjoyed a renaissance in the last decade, leading to many fascinating compounds.[2] Binary azides of Group 14 elements are a class of rare, highly endothermic compounds. Their isolation and handling poses considerable challenges to experimentalists due to the combination of high energy content, excessive sensitivity and thermal lability.[3] Therefore, it is not surprising that to date only the primary explosive α-$Pb(N_3)_2$[4] and the ions $[C(N_3)_3]^+$[5] and $[E(N_3)_6]^{2-}$ (E = Si–Pb)[3,6,7] have been structurally characterized. Recently, the extremely hazardous compound $C(N_3)_4$ was isolated in tiny amounts and transformed into various organic products.[8] $Si(N_3)_4$ has been reported to be a violently explosive substance, which could not be obtained in pure form.[9] Experimental evidence for the presence of pure $Ge(N_3)_4$ is lacking,[10] and $Sn(N_3)_4$ and $Pb(N_3)_4$ are presently not known. Nitrogen-rich silicon compounds are of special interest due to their potential as a viable replacement for lead azide to avoid its deleterious environmental impact[11] and as precursors for new materials.[12] Herein we present the large-scale synthesis and full characterization of conveniently accessible, thermally stable, and highly energetic Lewis base adducts of $Si(N_3)_4$, and the safe synthesis and handling of solutions of pure $Si(N_3)_4$.



Scheme 1. Syntheses and reactions of $Si(N_3)_4$ and its Lewis base adducts. For an alternative synthesis of compound **4**, see Ref. [6].

Addition of $SiCl_4$ to a suspension of 7.3 equiv of NaN_3 in acetonitrile at room temperature afforded selectively the disodium salt of hexaazidosilicate (**1**; Scheme 1).[13] Evidence for the formation of **1** was provided by its selective chemical functionalization (see below) and the solution IR spectra, which displayed one strong $\nu_{asym}(N_3)$ absorption band at 2109 cm^{-1} and one weak $\nu_{sym}(N_3)$ absorption band at 1317 cm^{-1} after completion of the reaction. Both bands appear at the same positions as those reported for $(PPN)_2[Si(N_3)_6]$ (**4**; $PPN^+ = N(PPh_3)_2{}^+$).[6] Compound **1** forms colorless solutions in acetonitrile that are sensitive to hydrolysis but can be stored for several weeks under exclusion of air at −28 °C and used as stock for the syntheses of derivatives of $Si(N_3)_4$. Treatment of **1** with a slight excess of the Lewis bases 2,2′-bipyridine (bpy) and 1,10-phenanthroline (phen) afforded, after precipitation of NaN_3, exclusively the Lewis base adducts $[Si(N_3)_4(bpy)]$ (**2**) and $[Si(N_3)_4(phen)]$ (**3**), respectively (Scheme 1). After work-up and recrystallization from acetonitrile, compound **2** and the MeCN hemisolvate of **3** were isolated as colorless, analytically pure needles in 57–60 % yields (from $SiCl_4$). No explosions occurred during the repeated preparations of **2** and **3**·0.5 MeCN, which can be scaled-up to several grams of the desired compound. Both compounds are not sensitive to friction and are moderately soluble in CH_2Cl_2, THF, and MeCN. Although solutions of **2** and **3**·0.5 MeCN are rapidly hydrolyzed, releasing HN_3 and the Lewis bases (bpy or phen), the crystalline compounds can be stored and handled safely at ambient temperature under dry air. Under vacuum, compound **2** melts at 212 °C, whereas **3** decomposes upon melting at 215 °C.[14] The remarkable thermal stability of **2** and **3**·0.5 MeCN is surprising in view of their reactive nitrogen contents of 44–48 % and the extreme sensitiveness of $Si(N_3)_4$. The thermochemical properties of **2** and **3**·0.5 MeCN were studied in more detail by differential scanning calorimetry (DSC) and compared with those of the analogous germanium compounds $[Ge(N_3)_4(bpy)]$ (**2a**) and $[Ge(N_3)_4(phen)]\cdot 0.5\,MeCN$ (**3a**·0.5 MeCN).[13] Representative thermograms of **2** and **3**·0.5 MeCN are depicted in Figure 1. The thermogram of **2** reveals that melting at the extrapolated onset temperature $T_{on}^{ex} = 211\,°C$ (endothermic peak temperature $T_p^{endo} = 212\,°C$, $\Delta H_m = +110\,J\,g^{-1}$) is followed by a distinct decomposition process, which begins at $T_{on}^{ex} = 265\,°C$ ($T_p^{exo} = 294\,°C$), and liberates a large heat of decomposition ($\Delta H_d = -2.4\,kJ\,g^{-1}$). The germanium analogue **2a** shows a similar behavior.[13] In comparison, compound **3**·0.5 MeCN

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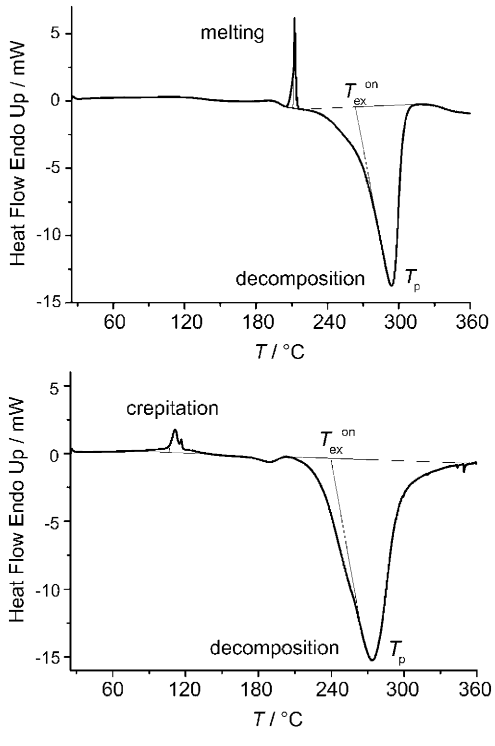

Figure 1. DSC thermograms (5 K min^{-1}) of **2** (top) and **3**·0.5 MeCN (bottom).

releases first the solvent molecules at $T_{on}^{ex}=106\,°C$ ($T_p^{endo}=111\,°C$) and then decomposes at $T_{on}^{ex}=239\,°C$ ($T_p^{exo}=274\,°C$), releasing slightly less energy ($\Delta H_d=-2.3\,kJ\,g^{-1}$).[15] The heat of decomposition of an explosive, ΔH_d [kJ g^{-1}], can serve as an estimate for its heat of explosion, Q_E [kJ g^{-1}] (Q_E of some explosives: hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) 5.4, 2,4,6-trinitrotoluene (TNT) 4.3, picric acid 4.2, $Pb(N_3)_2$ 1.6)[16a–c] and helps to evaluate the energy content of **2** and **3**·0.5 MeCN. The heats of decomposition of both silicon azides are larger than that of NaN_3 (ca. $-0.8\,kJ\,g^{-1}$)[16d] and $Pb(N_3)_2$, but lower than that of the classical explosive RDX ($-4.5\,kJ\,g^{-1}$).[16e]

Compounds **2** and **3**·0.5 MeCN were characterized by elemental analyses, IR spectroscopy, multinuclear NMR spectroscopy, and single-crystal X-ray diffraction (Figures 2 and 3).[13] The molecular structures reveal the presence of distorted-octahedral λ^6 silicon complexes.[17] The distortion of the coordination polyhedron results mainly from the bite angle of the chelating ligands bpy (81.20(6)°) and phen (81.81(5)°).

The mean Si–N$_\alpha$ bond length of the axial azido groups (**2** 1.856 Å, **3**·0.5 MeCN 1.850 Å) is slightly longer than that of the equatorial azido groups (**2** 1.825 Å, **3**·0.5 MeCN 1.834 Å; Table 1).[18] The same trend is found for the calculated Si–N$_{azide}$ bond lengths of **2** and **3** at the BP/TZVPP level of theory (Table 1), and can be rationalized by the delocalized orbital model used to describe the bonding in hexacoordinate compounds of main group elements[19] in combination with Bent's rule.[20] The mean Si–N$_\alpha$(azide) bond lengths in **2** (1.841 Å) and **3**·0.5 MeCN (1.842 Å) are considerably longer than that of $Si(N_3)_4$ (**5**; $Si{-}N_{calcd}=1.735$ Å) and other tetracoordinate azidosilanes (1.760(3)–1.814(2) Å),[21] but shorter than that of $[Si(N_3)_6]^{2-}$ in **4** (1.871 Å).[6] Furthermore, the difference Δ(NN) between the mean N$_\alpha$–N$_\beta$ and N$_\beta$–N$_\gamma$ bond lengths in **2** (7.5 pm) and **3**·0.5 MeCN (7.7 pm) is smaller than that of **5** ($\Delta(NN)_{calcd}=9.0$ pm) or HN_3 (10.9 pm),[22] but larger than that of $[Si(N_3)_6]^{2-}$ (5.7 pm). All of these bonding parameters suggest that the polarity of the Si–N$_\alpha$(azide) bond increases in the series $Si(N_3)_4 < [Si(N_3)_4(L_2)]$ (L_2 = bpy, phen) $< [Si(N_3)_6]^{2-}$. Additional support for this trend is provided by the solution IR and ^{14}N NMR spectra. The IR spectra of **2** and **3**·0.5 MeCN in acetonitrile solution show three intense absorption bands at 2151, 2126, and 2116 cm^{-1} (**2**) and 2150, 2126, and 2118 cm^{-1} (**3**), which by comparison with the calculated IR spectra can be assigned to the A and two B symmetric $\nu_{asym}(N_3)$ modes of the C_2 minimum structures (Table 1).[13] The values of the $\nu_{asym}(N_3)$ vibrational frequencies of **2** and **3**·0.5 MeCN are in between those of **5** (2170 cm^{-1} in benzene)[13] and $[Si(N_3)_6]^{2-}$ (**4**; 2109 cm^{-1} in acetonitrile),[6] confirming the Si–N$_\alpha$(azide) bond polarity trend mentioned above. The solution $^{14}N\{^1H\}$ NMR spectra of

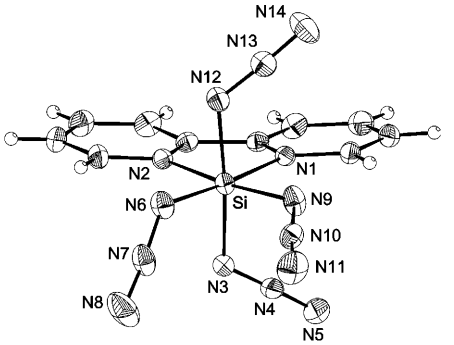

Figure 2. Diamond plot of the molecular structure of **2** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Si–N1 1.969(1), Si–N2 1.943(2), Si–N3 1.864(2), Si–N6 1.818(2), Si–N9 1.833(2), Si–N12 1.848(2), N3–N4 1.211(2), N6–N7 1.220(2), N9–N10 1.207(2), N12–N13 1.207(2), N4–N5 1.136(2), N7–N8 1.134(2), N10–N11 1.136(2), N13–N14 1.142(2); Si-N3-N4 120.6(1), Si-N6-N7 123.9(1), Si-N9-N10 123.2(1), Si-N12-N13 123.3(1), N1-Si-N2 81.20(6), N6-Si-N9 97.00(7).

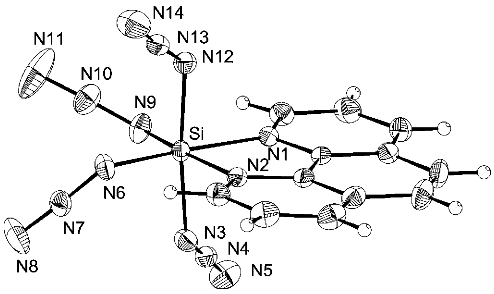

Figure 3. Diamond plot of the molecular structure of **3** (thermal ellipsoids set at 50% probability). Selected bond lengths [Å] and angles [°]: Si–N1 1.962(1), Si–N2 1.976(1), Si–N3 1.860(1), Si–N6 1.828(1), Si–N9 1.839(1), Si–N12 1.840(1), N3–N4 1.214(2), N6–N7 1.215(2), N9–N10 1.207(2), N12–N13 1.217(2), N4–N5 1.140(2), N7–N8 1.139(2), N10–N11 1.135(2), N13–N14 1.134(2); Si-N3-N4 121.15(9), Si-N6-N7 121.7(1), Si-N9-N10 120.3(1), Si-N12-N13 121.17(9), N1-Si-N2 81.81(5), N6-Si-N9 97.76(6).

Table 1: Comparison of selected experimental and calculated bond lengths [Å], IR vibrational frequencies [cm^{-1}], and ^{14}N NMR chemical shifts [ppm] of the compounds **2**–**5** and $SiCl_{(4-n)}(N_3)_n$ ($n=1$–3).[a]

	$Si\text{-}N_{bpy/phen}$	$(Si\text{-}N_\alpha)_{ax}$[b]	$(Si\text{-}N_\alpha)_{äq}$[b]	$(N_\alpha\text{-}N_\beta)_{ax}$	$(N_\alpha\text{-}N_\beta)_{äq}$	$(N_\beta\text{-}N_\gamma)_{ax}$	$(N_\beta\text{-}N_\gamma)_{äq}$	$\Delta(NN)_{ax}$[c] $\Delta(NN)_{äq}$	$\nu_{asym}(N_3)$[d]	$\delta(^{14}N)$[e]		
										$(N_\alpha)_{ax}$ $(N_\alpha)_{äq}$	$(N_\alpha)_{ax}$ $(N_\alpha)_{äq}$	$(N_\alpha)_{ax}$ $(N_\alpha)_{äq}$
2 (exp.)	1.969(1)	1.864(2)	1.818(2)	1.211(2)	1.220(2)	1.136(2)	1.134(2)	7.0	2151, 2126,	−302	−141	−205
	1.943(2)	1.848(2)	1.833(2)	1.207(2)	1.207(2)	1.142(2)	1.136(2)	7.9	2116			
2 (calcd)[f]	2.050	1.860	1.826	1.219	1.223	1.150	1.146	6.9	2202, 2187,	−287.4	−136.5	−190.8
								7.7	2169, 2166	−298.2	−139.6	−191.8
3 (exp.)	1.962(1)	1.860(1)	1.828(1)	1.214(2)	1.215(2)	1.140(2)	1.139(2)	7.9	2150, 2126,	−300	−141	−204
	1.976(1)	1.840(1)	1.839(1)	1.217(2)	1.207(2)	1.134(2)	1.135(2)	7.4	2118			
3 (calcd)[f]	2.079	1.855	1.824	1.224	1.228	1.155	1.151	6.9	2202, 2187,	−288.6	−136.6	−190.8
								7.7	2169, 2167	−298.6	−139.2	−192.3

		$Si\text{-}N_\alpha$	$N_\alpha\text{-}N_\beta$	$N_\beta\text{-}N_\gamma$	$\Delta(NN)$	$\nu_{asym}(N_3)$	N_α	N_β	N_γ
4 (exp.)[g]	–	1.866(1)	1.198(2)	1.144(2)	5.4	2109	−297	–	−215
		1.881(1)	1.201(2)	1.144(2)	5.7				
		1.867(1)	1.207(2)	1.146(2)	6.1				
4 (calcd)h]	–	1.902	1.205	1.161	4.4	2190, 2186	−284.8	−133.3	−216.7
5 (exp.)	–	–	–	–		2170	−320	−150	−189
5 (calcd)[i,j]	–	1.735	1.230	1.140	9.0	2223, 2217	−308.0	−145.8	−182.0
$SiCl(N_3)_3$[i,j]	–	1.731	1.229	1.140		2237, 2224	−302.1	−145.9	−180.1
$SiCl_2(N_3)_2$[i,j]	–	1.732	1.230	1.140		2233, 2223	−296.4	−146.2	−177.7
$SiCl_3(N_3)$[i,j]	–	1.735	1.230	1.140		2226	−288.2	−146.0	−176.3

[a] All calculations were at the BP/TZVPP level of theory unless otherwise stated; NMR chemical shift calculations by the GIAO/MBPT(2) method. [b] $(Si-N_\alpha)_{ax}$ and $(Si-N_\alpha)_{eq}$ are the Si–N bond lengths of the azido groups in the "axial" and "equatorial" positions, respectively (Ref. [18]). [c] $\Delta(NN)_{ax}$ and $\Delta(NN)_{eq}$ is the difference in pm between the mean N_α–N_β and N_β–N_γ bond lengths of the axial and equatorial azido groups in **2** and **3**, respectively. [d] Experimental and calculated, unscaled IR vibrational frequencies of the antisymmetric N_3 stretching modes [cm^{-1}]. [e] Experimental and calculated ^{14}N NMR chemical shifts relative to CH_3NO_2. [f] C_2-Symmetric minimum structures of **2** and **3**. [g] Ref. [6]. [h] S_6-Symmetric minimum structure of $Si(N_3)_6^{2-}$ (RI-BP86/TZVPP). [i] Calculated bond lengths and vibrational frequencies of **5** (S_4 symmetry), $SiCl(N_3)_3$, (C_3 symmetry), $SiCl_2(N_3)_2$ (C_1 symmetry; average bond lengths are given) and $SiCl_3(N_3)$ (C_S symmetry). [j] Calculated average $^{14}N_\alpha$, $^{14}N_\beta$, and $^{14}N_\gamma$ chemical shifts of the C_1 symmetric structures.

2 and **3**·0.5 MeCN show only one set of three broad singlet signals for the N_α, N_β, and N_γ atoms of the azido groups at $\delta = -302$, -141, and -205 ppm (**2**) and -300, -141, and -204 ppm (**3**).[13] A comparison of the ^{14}N NMR chemical shifts of **2**, **3**·0.5 MeCN, **4**, and **5** reveals a downfield shift of the N_α resonances in the series **5** (-320 ppm) / **2** and **3**·0.5 MeCN (-302 and -300 ppm) / **4** (-297 ppm) and an upfield shift of the N_γ resonances, **5** (-189 ppm) / **2** and **3**·0.5 MeCN (-205 and -204 ppm) / **4** (-215 ppm). These trends are verified by the GIAO-MBPT(2) ^{14}N NMR chemical shift calculations[13] and provide further evidence for the increasing polarity of the $Si-N_\alpha$(azide) bonds in the series $Si(N_3)_4 < [Si(N_3)_4(L_2)]$ ($L_2 =$ bpy, phen) $< [Si(N_3)_6]^{2-}$.

The IR and ^{1}H NMR spectra do not provide any evidence for a dissociation of the hexacoordinate complexes to $Si(N_3)_4$ and bpy (phen) in solution at ambient temperature. In comparison, the electron impact mass spectra show only intense signals of the $[bpy]^+$ or $[phen]^+$ and $[Si(N_3)_4]^+$ ions and fragments thereof. This suggests that **2** and **3** dissociate in the gas phase to **5** and the bases bpy and phen, respectively. Further evidence for the thermodynamic instability of **2** in the gas phase is provided by the DFT calculations at the B3LYP/TZVPP level of theory, which predict that dissociation of **2** to give **5** and bpy is an exergonic process at 298 K ($\Delta G^0_{diss}(298) = -32.5$ kJ mol^{-1}). A comparison with the $\Delta G^0_{diss}(298)$ values of $[SiX_4(bpy)]$ (X = F, Cl, Br) shows that the gas-phase stability of **2** lies in between that of the fluoro and the chloro complex ($\Delta G^0_{diss} = -9.3$ and -72.8 kJ mol^{-1}, respectively).[13]

Whereas the bidentate N-heterocyclic bases bpy and phen react rapidly with **1** in acetonitrile, no reaction of **1** with pyridine or *N,N,N',N'*-tetramethylethylenediamine was observed in acetonitrile. This result indicates that the reaction equilibrium $[Si(N_3)_6]^{2-} + 2L \rightleftarrows [Si(N_3)_4L_2] + 2N_3^-$ depends strongly on the Lewis base L. The equilibrium depends also on the nature of the cation, as shown by the reaction of **2** with two equiv of $(PPN)N_3$, which leads to the selective formation of **4** either in THF at ambient temperature or in acetonitrile after gentle heating (Scheme 1). All of these observations imply that **1** is of limited use as a starting material for the preparation of Lewis base adducts of $Si(N_3)_4$. Therefore, the synthesis of $Si(N_3)_4$ was attempted and for this purpose the reaction of $SiCl_4$ with excess NaN_3 in refluxing benzene was reinvestigated.[9a,23] Monitoring of the reaction progress by ^{14}N NMR spectroscopy revealed a slow conversion in the absence of an azido group transfer catalyst, which led to an equilibrium mixture containing three products in the approximate ratio 1.8:2.9:1.[13] The products were identified to be the azidosilanes $SiCl_2(N_3)_2$, $SiCl(N_3)_3$, and $Si(N_3)_4$ (**5**) upon comparison of their ^{14}N NMR chemical shifts with those calculated for $SiCl_{(4-n)}(N_3)_n$ using the GIAO/MBPT(2) method (Table 1). No further change of the composition of the reaction mixture occurred after heating for 120 h in refluxing benzene. However, the Cl/N_3 exchange reaction could be driven to completion after filtration of the reaction mixture from NaN_3/NaCl and reheating with a new batch of NaN_3 for additional 120 h (Scheme 1). Exclusive formation of

$Si(N_3)_4$ was confirmed by chemical functionalization with bpy to afford selectively the Lewis base adduct **2** in 91% yield. $Si(N_3)_4$ was characterized by ^{29}Si NMR spectroscopy ($\delta_{Si} = -74.0$ ppm) and ^{14}N NMR spectroscopy ($\delta = -320$ (N_α), -150 (N_β), and -189 ppm (N_γ)). The experimental ^{14}NMR chemical shifts compare well with the calculated values (Table 1).[13] Quantum-chemical calculations at the BP/TZVPP level of theory suggest furthermore that $Si(N_3)_4$ has a S_4 symmetric minimum structure (Table 1).[13] Finally, the IR spectrum of $Si(N_3)_4$ in benzene displays one strong $\nu_{asym}(N_3)$ absorption band at 2170 cm^{-1} and one $\nu_{sym}(N_3)$ absorption band of medium intensity at 1328 cm^{-1}.[13]

The high-energy content of **2** and **3** combined with their favorable properties in storage and handling let us suggest that Lewis-base adducts of $Si(N_3)_4$ are promising highly energetic materials, which may become an attractive replacement of lead azide, given that silicon is abundant, cheap, and environmentally harmless. In this respect, the safe and convenient synthesis of solutions of pure $Si(N_3)_4$ is a major progress, which opens up a new route to nitrogen-rich silicon compounds taking advantage of the synthetic potential of the azido group.[24]

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[13] The Supporting Information contains the syntheses and the analytical and the spectroscopic data of **1**, **2**, **3**·0.5 MeCN, and **5**. It also contains selected FTIR and NMR spectra of the compounds, the crystallographic data of **2** and **3**·0.5 MeCN, the DSC thermograms of **2**, **3**·0.5 MeCN and of the analogous germanium compounds $[Ge(N_3)_4(bpy)]$ (**2a**) and $[Ge(N_3)_4(phen)]$·0.5 MeCN (**3a**·0.5 MeCN), a summary of the DSC results, and the results of the extensive DFT and GIAO-MBPT(2) calculations of **2**, **3**, and $SiCl_{(4-n)}(N_3)_n$ ($n = 0$–4).

[14] Upon rapid heating in sealed capillary tubes under vacuum compound **2** detonates at around 293 °C, while **3** explodes at lower temperatures (261–282 °C).

[15] No melting of **3**·0.5 MeCN was detected by DSC (5 K min^{-1}) before decomposition in contrast to the analogous germanium compound **3a**·0.5 MeCN. However, heating of **3**·0.5 MeCN in sealed capillary tubes under vacuum revealed that decomposition of **3** begins upon melting at 215 °C.

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[17] For an overview on higher-coordinate silicon compounds, see: O. Seiler, C. Burschka, S. Metz, M. Penka, R. Tacke, *Chem. Eur. J.* **2005**, *11*, 7379, and references therein.

[18] The term "axial" is used to denote the position of the two azido groups N3-N4-N5 and N12-N13-N14 in **2** and **3**·0.5 MeCN, which are *trans*-disposed. The term "equatorial" is used for the remaining azido groups N6-N7-N8 and N9-N10-N11.

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[21] a) S. S. Zigler, K. J. Haller, R. West, M. S. Gordon, *Organometallics* **1989**, *8*, 1656; b) M. Denk, R. K. Hayashi, R. West, *J. Am. Chem. Soc.* **1994**, *116*, 10813.

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[23] According to Ref. [9a], attempts to obtain pure $Si(N_3)_4$ from the reaction of $SiCl_4$ with excess NaN_3 in the presence of an azido group transfer catalyst failed. Fractional sublimation of the resulting $[SiCl_{(4-n)}(N_3)_n]$ compounds did not lead to chlorine-free products and was hampered by the explosivity of $Si(N_3)_4$.

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