

Synthesis of a Lewis Base Stabilized Dimer of N-Substituted Hydrosila Hydrazone and a Silaaziridine

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The dehydrohalogenation of a silicon(IV)-substituted diphenyl hydrazone derivative leads to a dimer of a N-substituted hydrosila hydrazone, which consists of a four-membered Si₂N₂ core and a hydrogen attached to each of the silicon atoms instead of giving a substituted hydrosilaneimine. The compound is obviously formed by dimerization of hydrosilaneimine. Moreover there are no straightforward synthetic methods known for the synthesis of silaaziridine. The preparation of such species would be of special importance for the development of a new field of silicon chemistry. The reaction of chlorosilylene, LSiCl, and PhCH=NPh resulted in a base-stabilized silaaziridine. All compounds were characterized by NMR spectroscopy, mass spectrometry, microanalysis, and X-ray structural analysis.

Introduction

The stable allotropes of the lighter p block elements such as nitrogen and oxygen possess triple and double bonds, respectively. Nitrogen has a ubiquitous nature to form double as well as triple bonds with carbon. Silicon, the congener of carbon, forms silane imine complexes,^{1–3} which constitute a vital area of research in the last two decades. However stable hydrosilaneimines, compounds with a Si=N double bond and one hydrogen attached to the silicon atom, are elusive and have been characterized only in an argon matrix.^{4,5} Moreover examples of silaaziridines, which are constituted of three-membered Si–N–C ring systems, are scant. The paucity of such compounds is largely related to their limited synthetic approach. In the case of silaaziridines, Brook et al. reported for the first time their synthesis using isocyanides and photochemically generated silenes.⁶ However, this method lacks generality. Moreover, silaaziridines have been proposed as reactive intermediates in thermal and photochemical silylene transfer reactions to imines, although the strained three-membered ring compounds were not isolated,

and instead rearranged products were obtained.^{7–9} In 2007 Woerpel et al. reported the synthesis of silaaziridine by applying silver triflate catalyzed silylene transfer from silacyclopropane to imines.¹⁰ The aziridines are used as precursors for the synthesis of N-containing heterocyclic compounds, which are important for producing drugs¹¹ and natural products.¹² Stable silaaziridine could be an alternative precursor for the synthesis of N,Si-containing heterocyclic compounds. Subsequently a facile synthesis of stable hydrosilaneimines and silaaziridines would be a real challenge for the synthetic chemist. Recently we were successful in isolating the previously reported stable chlorosilylene LSiCl (**1**) (L = PhC(N*t*Bu)₂)¹³ in high yield using LiN(SiMe₃)₂ as a dehydrohalogenating agent,¹⁴ which helped to carry out its versatile reactivities. Among them, one is the convenient synthesis of monosilaepoxide, which was formed by the reaction of **1** with ketones.¹⁵ The successful stabilization of monosilaoxirane by the benzamidinato ligand prompted us to probe the reaction of **1** with the >C=NR precursor. The question arises whether it will afford [1+2] cycloaddition compounds or oxidative addition products.

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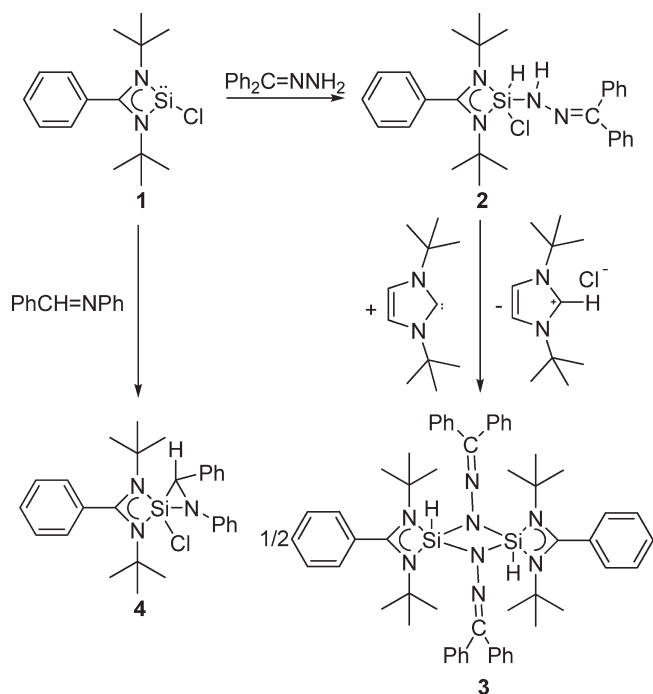
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Scheme 1. Preparation of Silicon(IV)-Substituted Diphenyl Hydrazone (2), N-Substituted Hydrosila Hydrazone (3), and Silaaziridine (4)



Herein, we report on the synthesis of a stable base-stabilized Si_2N_2 core $[LSi(H)N(H)N=CPh_2]_2$ ($L = PhC(NtBu)_2$) (3) from the reaction of $LSiCl(H)N(H)N=CPh_2$ (2) with 1,3-bis(*tert*-butyl)imidazol-2-ylidene under HCl elimination. Here it is worth mentioning that compound 2 is obtained from the unprecedented oxidative addition of one of the N–H bonds of diphenyl hydrazone ($Ph_2C=N-NH_2$) to the silicon(II) center of the base-stabilized chlorosilylene, $LSiCl$ (1). Furthermore an efficient method is outlined for the synthesis of stable silaaziridine 4 by the reaction of 1 with *N*-benzylideneaniline ($PhCH=NPh$).

Results and Discussion

The reaction of chlorosilylene, $LSiCl$ (1), with diphenyl hydrazone in toluene leads to the silicon(IV)-substituted diphenyl hydrazone derivative $LSiCl(H)N(H)N=CPh_2$ (2) (Scheme 1). The reaction proceeds via the oxidative addition of one of the N–H bonds to the silicon(II) center. A similar reaction was observed when ammonia was reacted with the silylene $L'Si$ ($L' = CH\{(C=CH_2)(CMe)(2,6-tPr_2C_6H_3N)_2\}$).¹⁶ In contrast to the present results, when $L'Si$ was reacted with diphenyl hydrazone, there was exclusive formation of the [1+4] cycloaddition product.¹⁷ The different reactivity is mainly due to the difference in coordination numbers around the silicon atom of the two silylenes.

The formation of compound 2 was confirmed by elemental analysis, multinuclear NMR spectroscopy, and EI mass spectrometry. The 1H NMR spectrum of 2 shows resonances at δ 6.48 and 6.62 ppm for the Si–H and N–H proton, respectively, and both exhibit doublets with the same coupling constant ($^3J = 3$ Hz). The ^{29}Si NMR spectrum exhibits a

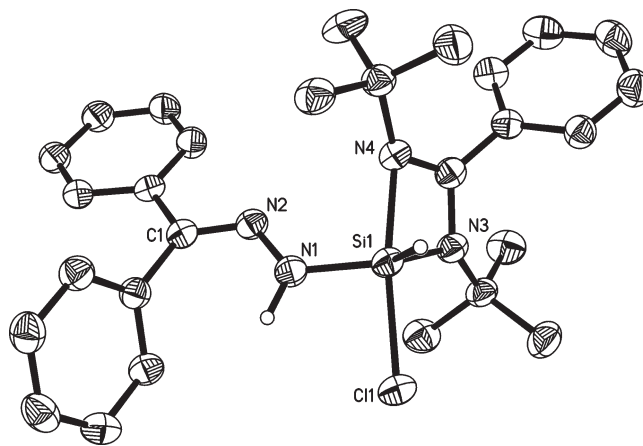


Figure 1. Molecular structure of 2. Thermal ellipsoids are shown at 50% probability. H atoms except on Si1 and N1 are omitted for clarity reasons. Selected bond distances (Å) and angles (deg): Si1–Cl1 2.2045(13), Si1–N1 1.722(3), N1–N2 1.364(3), Si1–N3 1.802(3); N2–N1–Si1 124.3(2), N1–Si1–Cl1 90.23(10).

doublet of doublets at $\delta -99.82$ ppm ($^1J(^{29}Si-^1H) = 299.45$ Hz, $^2J(^{29}Si-^1H) = 10.78$ Hz). Furthermore the solid-state structure of compound 2 was confirmed by single-crystal X-ray structural analysis.

Single crystals of 2 were obtained from a hot saturated *n*-hexane solution at room temperature after one day. Compound 2 crystallizes in the triclinic space group $P\bar{1}$, with one monomer in the asymmetric unit as illustrated in Figure 1. Surprisingly, 2 is monomeric in the solid state, and what is even more striking, the NH group is not involved in any kind of hydrogen bonding. Compound 2 is stable in the solid state as well as in solution for a longer period of time without any decomposition under an inert atmosphere. The coordination polyhedron around the silicon atom features a distorted tetragonal-pyramidal geometry. The silicon is attached to two nitrogen atoms from the backbone of the chelating ligand, the nitrogen atom from the diphenyl hydrazone moiety, the Cl atom, and a hydrogen atom. The N1–N2 bond length is 1.364(3) Å, which is indicative of a N–N single bond. A noteworthy feature of compound 2 is the Si(H)NH moiety (Si1–N1 1.722(3) Å). The Si–N1 bond length can be compared with the slightly shorter Si–N bond lengths than that in $RSi(NH_2)_3$ ($R = 2,4,6-Ph_3C_6H_2$ av 1.709(7) Å,¹⁸ $R = 2,6-tPr_2C_6H_3-NSiMe_3$ av 1.709(2) Å,¹⁹ and $R = 2,4,6-tBuC_6H_2O$ av 1.692(6) Å).¹⁹

Compound 2 exhibits a Si–H as well as a N–H bond, which both are potential proton donors for the elimination of HCl. This would occur from either the 1,1 or 1,2 position while adding a proton scavenger (such as amine, *N*-heterocyclic carbene). In the case of 1,1 HCl elimination there would be the formation of $LSiN(H)N=CPh_2$, while 1,2 HCl elimination would lead to the substituted hydrosilaneimine derivative $LSi(H)=NNCPh_2$. In the literature there are protocols on both the formation of silylene compounds by

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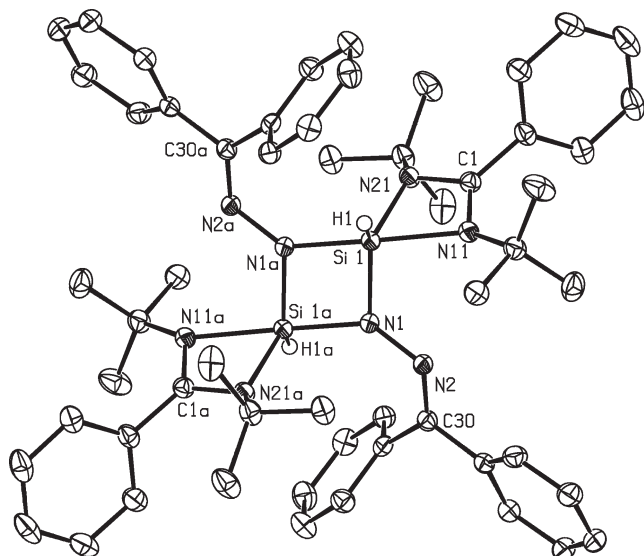


Figure 2. Molecular structure of **3**. Thermal ellipsoids are shown at 50% probability. H atoms except on those on silicon are omitted for clarity reasons. Selected bond lengths [Å] and angles [deg]: Si1–N11 2.0280(11), Si1–N21 1.8306(10), Si1–N1 1.7521(10), Si1–H 1.350; N11–Si1–N21 68.18(4), N11–Si1–N1 99.17(5), Si1–N1–Si1a 99.66(5).

1,1 HCl elimination^{20,21} and the formation of compounds with Si=N bonds by 1,2 HCl elimination.²² The reaction of compound **2** with an equivalent amount of 1,3-bis-(*tert*-butyl)imidazol-2-ylidene²³ leads only to N-substituted hydrosila hydrazone as a dimer of composition [LSi(H)–NN=CPh₂]₂ (**3**) in good yield (Scheme 1) instead of forming the hydrosilaneimine derivative LSi(H)=NNCPh₂. This is in contrast to the reaction of LSiHCl₂ with the same carbene,¹⁴ which yields exclusively LSiCl.

3 is a yellow solid soluble in benzene, toluene, diethyl ether, and THF, respectively, and shows no decomposition on exposure to dry air. **3** was characterized by multinuclear spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis. The ¹H NMR spectrum of **3** exhibits a singlet (δ 4.86 ppm) that can be assigned to the Si–H proton, accompanied by two ²⁹Si satellite resonances. The ²⁹Si NMR spectrum exhibits a doublet resonance (δ –96.65 ppm) with a coupling constant of $J(^{29}\text{Si}–\text{H}) = 286.18$ Hz. Suitable crystals for X-ray structural analysis were obtained from a hot saturated THF solution of **3** after storing this solution overnight at room temperature. **3** crystallizes in the monoclinic space group $P2_1/n$, with one-half molecule of **3** in the asymmetric unit and one slightly disordered THF molecule. **3** exists as a dimer in the solid state (Figure 2). There are no classical intermolecular hydrogen bonds observed in the crystal lattice. Geometry criteria suggest one attractive C–H \cdots N hydrogen bond

each. The coordination polyhedron around the silicon atom comprises two nitrogen atoms from the supporting ligand, one hydrogen atom, and two nitrogen atoms of the hydrazone moiety, featuring a distorted trigonal-bipyramidal geometry. The axial positions are occupied by two nitrogen atoms. The axial substituents include an angle of 80.34° with the silicon atom. The distorted trigonal-bipyramidal architecture includes different Si–N bond distances for axial and equatorial substituents. The Si–N bond lengths in the equatorial positions (Si1–N1 1.752 Å and Si1–N21 1.831 Å) are shorter than that in the axial positions (Si–N11 2.028 Å). In summary, compound **3** represents a stable crystalline compound with three four-membered rings that are connected through silicon atoms, and it exhibits at each silicon center a terminal-bound hydrogen atom.

After the successful synthesis of an N-substituted hydrosila hydrazone, we turned our attention to the synthesis of silaaziridine. From the retrosynthetic point of view, the silaaziridines can be prepared by reacting either silene with nitrene or, alternatively, silaimine with carbene, or imine with silylene. The preparation of stable silene^{24–26} and silaimine^{1–3} is limited, although nowadays there are numerous reports on stable silylenes.^{27,28} For developing a new route to stable silaaziridines we employed the reaction of stable silylenes with imines. Finally it is noteworthy that in all the known silaaziridines the silicon atom binds to either carbon or silicon. So far no compounds are available where heteroatoms are attached to silicon.

The addition of *N*-benzylideneaniline (PhCH=NPh) to a solution of **1** in toluene leads to compound **4** (Scheme 1). The colorless solution was evaporated, and the residue extracted with hot *n*-hexane to yield colorless crystals of **4** in 88% yield. The exact mechanism for the formation of **4** is unknown, but two mechanistic pathways can be envisioned. Either an electrophilic attack of **1** could occur at the imine nitrogen of *N*-benzylideneaniline to give a sila ylide, or alternatively, a nucleophilic attack of **1** to the imine carbon of *N*-benzylideneaniline might be possible to result in a charge-separated species. Both pathways can lead to compound **4** after successive ring closure. Compound **4** is well soluble in benzene, toluene, THF, and diethyl ether and shows no decomposition on exposure to dry air. **4** was characterized by ¹H and ²⁹Si NMR spectroscopy, EI mass spectrometry, elemental analysis, and X-ray structural analysis.

The ¹H NMR spectrum of **4** exhibits a singlet resonance (δ 4.07 ppm) that can be assigned to the C–H proton of the three-membered silaaziridine ring. The ²⁹Si NMR spectrum exhibits a singlet resonance (δ –131.35 ppm) consistent with a neutral pentacoordinate silicon.²⁶ Single crystals of **4** were obtained from a saturated hot *n*-hexane solution after one day. Compound **4** crystallizes in the triclinic space group $P\bar{1}$, with two molecules in the asymmetric unit. Interestingly, the

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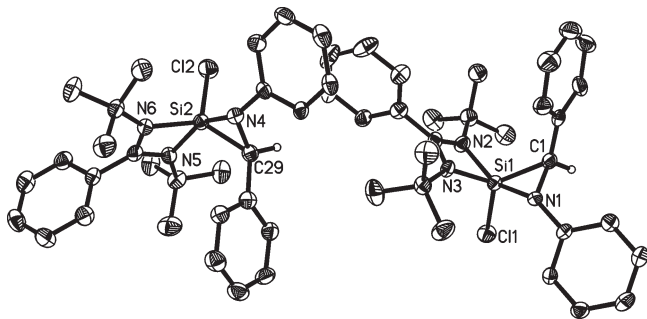


Figure 3. Molecular structure of **4** shows the two different isomers in the asymmetric unit. Thermal ellipsoids are shown at 50% probability. H atoms except on C1 and C29 are omitted for clarity reasons. Selected bond lengths [Å] and angles [deg]: Si1–Cl1 2.0800(17), Si1–N1 1.733(4), Si1–C1 1.858(4), Si1–N2 1.914(4); N1–Si1–C1 49.58(16), N1–Si1–Cl1 105.35(13), N2–Si1–N3 70.89(15).

unit cell contains two different isomers. C1 and C29 exhibit chirality that is distinct in the two cases. The hydrogens at these carbon atoms were found and refined freely with respect to the location but constrained with respect to the displacement parameters. X-ray crystal structure analysis afforded the structure as illustrated in Figure 3. Compound **4** is stable in the solid state as well as in solution for a longer period of time without any decomposition under inert atmosphere. The coordination polyhedron around the silicon atom features a distorted trigonal-bipyramidal geometry, with the chlorine atom at an axial position. The silicon is attached to two nitrogen atoms from the backbone of the chelating ligand, one carbon and one nitrogen atom from the imine moiety, and a chlorine atom. The three nitrogen atoms are in equatorial positions, whereas the carbon is in between an equatorial and axial position, giving rise to the distortion. The composition of **4** was also confirmed by mass spectrometry and elemental (C, H, N) analysis. The most intense peak in the EI mass spectrum appeared at $m/z = 475 [M]^+$.

Conclusions

In summary, we have demonstrated that base-stabilized chlorosilylene, $LSiCl$, allows for a convenient oxidative addition reaction of one of the N–H bonds of phenyl hydrazone under the formation of a silicon(IV)-substituted hydrazone derivative. The latter undergoes a 1,2 HCl elimination by a N-heterocyclic carbene to generate a stable N-substituted hydrosila hydrazone as a dimer that contains a chain of three four-membered rings, and in the spirocyclic structure each Si atom is part of two four-membered rings and a hydrogen atom on silicon. Moreover we have shown a convenient method for an efficient synthesis of a stable silicon–heteroatom (chlorine, nitrogen) bound silaaziridine. The latter is prone to further functionalization and might have a similar impact on organic chemistry to that realized for carbon–heteroatom-bound aziridines.²⁹

Experimental Section

General Procedures. All manipulations were performed under a dry and oxygen-free atmosphere (N_2) using standard Schlenk

techniques or inside a MBraun MB 150-GI glovebox maintained at or below 1 ppm of O_2 and H_2O . All solvents were distilled from Na/benzophenone prior to use. The starting material **1** was prepared using a literature procedure.¹⁴ Other chemicals were purchased and used as received. 1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a Bruker Avance DRX instrument and referenced to the deuterated solvent in the case of the 1H and ^{13}C NMR and $SiMe_4$ for the ^{29}Si NMR spectra. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. EI-MS were measured on a Finnigan Mat 8230 or a Varian MAT CH5 instrument. Melting points were measured in sealed glass tubes with a Büchi melting point B 540 instrument.

Synthesis of 2. A solution of $Ph_2C=NNH_2$ (0.19 g, 1 mmol) in toluene (10 mL) was added to a toluene solution (35 mL) of **1** (0.29 g, 1 mmol) at $-78^\circ C$. The reaction mixture was allowed to warm slowly to room temperature and stirred for 12 h at this temperature. After that all volatiles were removed under vacuum. The residue was dissolved in *n*-hexane (45 mL), and the solution was warmed and filtered over a Celite pad. The resulting solution was kept overnight at room temperature to afford colorless crystals of **2**. Yield: 0.39 g, 80%. Mp: $138–140^\circ C$. 1H NMR (500 MHz, C_6D_6): δ 7.85–7.84, 7.18–6.84 (m, 15H, C_6H_5), 6.62 (d, 1H, NH), 6.48 (d, 1H, SiH), 1.15 (s, 18H, $C(CH_3)_3$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 172.08, 147.08, 140.00, 134.78, 129.87, 129.67, 129.63, 128.84, 128.69, 128.31, 127.72, 127.01, 54.68, 31.67 ppm. ^{29}Si NMR (99.35 MHz, C_6D_6): δ -99.82 ppm (dd, $J = 299.45$ and $^2J = 10.78$ Hz). EI-MS (70 eV) m/z (%): 453(100%) [$M - 2H - Cl$] $^+$, 489(10%) [$M - H$] $^+$. Anal. Calcd for $C_{28}H_{35}ClN_4Si$: C, 68.47; H, 7.18; N, 11.41. Found: C, 68.47; H, 7.35; N, 11.46.

Synthesis of 3. A solution of 1,3-bis(*tert*-butyl)imidazol-2-ylidene (0.18 g, 1 mmol) in THF (20 mL) was added to a THF solution (30 mL) of **2** (0.49 g, 1 mmol) at $-78^\circ C$. The reaction mixture was allowed to warm gradually to room temperature and stirred overnight. After that all volatiles were removed under vacuum. The residue was dissolved in *n*-hexane (40 mL), and the solution was warmed and filtered over a Celite pad. Single crystals of **3** suitable for X-ray structural analysis were obtained by storing the solution overnight at room temperature. Yield: 0.38 g, 85%. Mp: $299–301^\circ C$. 1H NMR (300 MHz, C_4D_8O): δ 7.44–7.09 (m, 30H, C_6H_5), 4.86 (s, 2H, SiH), 1.06 (s, 36H, $C(CH_3)_3$) ppm. ^{13}C NMR (75.47 MHz, C_4D_8O): δ 169.81, 143.46, 142.30, 137.11, 132.60, 130.50, 130.17, 128.81, 128.25, 128.12, 127.95, 127.50, 126.99, 54.58, 32.01(br) ppm. ^{29}Si NMR (59.63 MHz, C_4D_8O): δ -96.65 ppm (d, $J = 286.18$ Hz). EI-MS (70 eV) m/z (%): 728.4 (100) [$M^+ - N=CPh_2$], 908.5(55) [M^+], 454.2(30) [$M/2$] $^+$. Anal. Calcd for $C_{56}H_{68}N_8Si_2$: C, 73.96; H, 7.54; N, 12.32. Found: C, 73.12; H, 8.07; N, 12.12.

Synthesis of 4. A solution of $PhCH=NPh$ (0.18 g, 1 mmol) in toluene (10 mL) was added to a toluene solution (35 mL) of **1** (0.29 g, 1 mmol) at $-30^\circ C$. The reaction mixture was allowed to warm slowly to room temperature and stirred for an additional 1 h at the same temperature. After that all volatiles were removed under vacuum. The residue was dissolved in *n*-hexane (40 mL), and the solution was warmed and filtered over a Celite pad. The resulting solution was stored overnight at room temperature to afford colorless crystals of **4**. Yield: 0.42 g, 88%. Mp: $117^\circ C$. 1H NMR (C_6D_6 , 500 MHz): δ 7.54–6.62 (m, 15H, C_6H_5), 4.07 (s, 1H, CH), 1.15 (s, 9H, $C(CH_3)_3$), 1.02 (s, 9H, $C(CH_3)_3$) ppm. ^{13}C NMR (125 MHz, C_6D_6): δ 174.16, 159.97, 150.66, 145.71, 131.26, 131.22, 130.15, 129.34, 129.22, 129.11, 128.81, 128.75, 128.24, 126.02, 124.89, 124.22, 121.27, 118.36, 117.79, 54.65, 54.29, 53.28, 31.80, 30.47 ppm. ^{29}Si NMR (C_6D_6 , 59.62 MHz): δ -131.35 ppm. EI-MS (70 eV) m/z (%): 475 (100) [M^+]. Anal. Calcd for $C_{28}H_{34}ClN_3Si$: C, 70.63; H, 7.20; N, 8.83. Found: C, 71.45; H, 7.49; N, 9.08.

X-ray Crystal Structure Determination. Suitable crystals of **2** and **4** were mounted on a glass fiber, and data was collected on

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an IPDS II Stoe image-plate diffractometer (graphite-monochromated Mo K α radiation, $\lambda = 0.71073$ Å) at 133(2) K. The data for **3** were collected from a shock-cooled crystal at 100(2) K on a Bruker SMART 6000 diffractometer equipped with a rotating anode and INCOATEC mirror optics. The structures were solved by direct methods (SHELXS-97)³⁰ and refined by full-matrix least-squares methods against F^2 (SHELXL-97).³⁰ All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically at calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp³-carbon atoms and 1.2 times for all other carbon atoms. Hydrogen atoms bound to nitrogen, silicon and the chiral carbon atoms of **4** were located and refined freely; for the latter only, unlike their location U_{iso} was refined as being dependent on the pivot atoms.

Disordered moieties were refined using bond length restraints, rigid bond restraints, similarity restraints, and ADP restraints. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited

with the Cambridge crystallographic data center. Copies of the data can be obtained free of charge from the Cambridge crystallographic data center via www.ccdc.cam.ac.uk/data_request/cif. **Compound 2:** Space group: $P\bar{1}$; $a = 8.2690(17)$ Å, $b = 9.7193(19)$ Å, $c = 17.875(4)$ Å; $\alpha = 101.04(3)^\circ$, $\beta = 102.46(3)^\circ$, $\gamma = 96.72(3)^\circ$, $R_1 = 0.0647$ for $[I > 2\sigma(I)]$, wR_2 (all data) = 0.1500 (CCDC number for **2**: 778977). **Compound 3:** Space group: $P2_1/n$; $a = 12.7543(3)$ Å, $b = 18.2098(4)$ Å, $c = 13.9106(3)$ Å; $\alpha = 90.0^\circ$, $\beta = 113.1287(7)^\circ$, $\gamma = 90.0^\circ$, $R_1 = 0.0367$ for $[I > 2\sigma(I)]$, wR_2 (all data) = 0.0960 (CCDC number for **3**: 781161). **Compound 4:** Space group: $P\bar{1}$; $a = 11.161(2)$ Å, $b = 15.987(3)$ Å, $c = 16.576(3)$ Å; $\alpha = 89.93(3)^\circ$, $\beta = 83.27(3)^\circ$, $\gamma = 71.19(6)^\circ$, $R_1 = 0.0873$ for $[I > 2\sigma(I)]$, wR_2 (all data) = 0.1633 (CCDC number for **4**: 776751).

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Supporting Information Available: X-ray data for **2**, **3**, and **4** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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