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Striking Stability of a Substituted Silicon(II) Bis(trimethylsilyl)amide and the Facile Si−Me Bond Cleavage without a Transition Metal Catalyst

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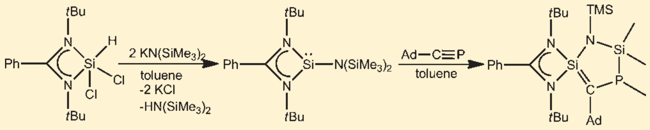
S *Supporting Information*



ABSTRACT: Silicon(II) bis(trimethylsilyl)amide (LSiN($SiMe_3$)$_2$, L= PhC(N*t*Bu)$_2$) (**2**) has been synthesized by the reaction of $LSiHCl_2$ with KN($SiMe_3$)$_2$ in 1:2 molar ratio in high yield where 1 equiv of the latter functions as a dehydrochlorinating agent. **2** exhibits a high stability up to 154 °C and can be handled in open air for a short period of time without any appreciable decomposition. An amazing five-membered cyclic silene (**3**) results from the cleavage of one Si−Me bond of **2** with an adamantyl phosphaalkyne. **3** is the first example of a heavy cyclopentene derivative which consists of four different elements, C, N, Si, and P. Both compounds are characterized by multinuclear NMR spectroscopy, EI-mass spectrometry, and single crystal X-ray diffraction studies.

INTRODUCTION

Synthesis of silylene and exploring its chemistry is at the cutting edge of chemical research not only because it can provide answers to basic questions related to its chemical bonding, structure, and reactivity, but also due to the study of silylene that has the potential of providing useful insights and directions for growing fields such as silicon-based polymers,[1a] photolithiography,[1b] and silicon surface science.[1c,d] Since the successful isolation of the first N-heterocyclic silylene (NHSi) in 1994 by West et al.[2a] several other silylenes have been reported by different groups.[2b−i] Parallel to these results, a few numbers of higher coordinate Si(II) compounds have been isolated by different groups.[3] Nevertheless, despite intensive recent research the progress of studying the chemistry of silylenes is relatively slow which is largely attributed to the very limited synthetic approaches. The most common route to access compounds with low valent silicon atom is the reduction of the parent halogen compounds with strong reducing agents such as sodium or potassium metal or potassium graphite (KC_8). However, the yield of the reduced products is usually very small, sometimes merely 5%,[4] which certainly impedes further investigation. Recently, we demonstrated that Si(II) compounds can be synthesized almost in quantitative yield using N-heterocyclic carbene (NHC) as a dehydrochlorinating agent.[5a] The technique was extended by Cui et al. to access several four- and five-membered NHSis reported beforehand.[5b] We further diversified this dehydrochlorination method by replacing NHC with commercially available LiN($SiMe_3$)$_2$ and reproduced our previously reported silicon(II) chloride, LSiCl (L = PhC(N*t*Bu)$_2$) (which was isolated in 10% yield before)[3c] in 90% yield.[5c] The increase in yield was the breakthrough to carry out systematic reactivity studies with homo-[5c] and heteroalkyne,[6] ketone,[7] diketone,[8] isocyanate,[9] carbodiimide,[9] imine,[10] diimine,[9] COT,[9] diazobenzene,[11] borane,[12] and metal carbonyls.[13] In view of the plethora of reactivities shown by LSiCl, it is highly desirable to develop new methods for the preparation of heteroatom substituted silylenes in good yield. The synthesis of silylene with nitrogen substitution is a nontrivial task. In 1998, Kira and his coworkers showed that bis(diisopropylamino) silylene, which was generated photochemically, is stable at room temperature but only in solution.[14a] In 2003, West et al. reported that bis(bis(trimethylsilyl)amino)silylene is stable only at low temperature and undergoes rapid decomposition above 0 °C.[14b] Therefore, the chemistry of amino silylenes is still unknown and needs further attention. To develop the chemistry of amino silylenes, it is essential to find a more convenient and high yield protocol, rather than the prototypical photochemical generation or alkali metal reduction technique. In a prior publication,[15a] we reported that the reaction of KN($SiMe_3$)$_2$ with Cp*$SiHCl_2$ (Cp* = Me_5C_5) afforded a disilene of composition *E*-[(Me_3Si)N](η^1-Cp*)Si=Si(η^1-Cp*)[N($SiMe_3$)] in 68% yield which was previously reported by Jutzi et al. in less than 10% yield.[15b] We presume that the formation of different products with different metal amides is due to the difference in the size of the metal cations, which increases down the group with the result that the basicity of the amide increases. Hence, we treated $LSiHCl_2$ (**1**) with KN($SiMe_3$)$_2$ in 1:2 molar ratio and obtained LSiN($SiMe_3$)$_2$ (**2**), a silicon(II) bis(trimethylsilyl)amide in good yield. The increase in yield is the requirement to accomplish new reactivity patterns of this unique compound.

RESULT AND DISCUSSION

Treatment of **1** with 2 equiv of KN($SiMe_3$)$_2$ in toluene for 12 h afforded a new monomeric N-substituted Si(II) compound in

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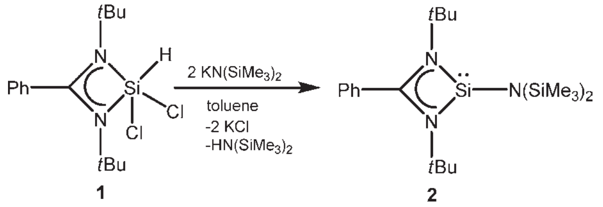
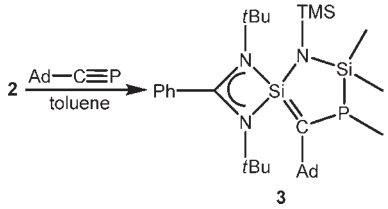
Scheme 1. Synthesis of 2



Scheme 2. Synthesis of 3



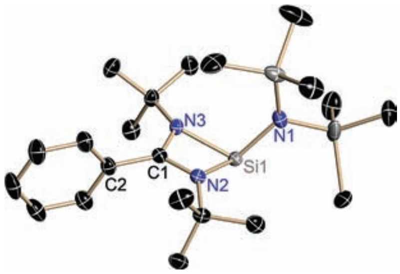


Figure 1. Molecular structure of **2** with the anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms and the disorder of the $N(SiMe_3)_2$ group are not shown for clarity. Selected bond lengths (Å) and angles (deg): N(1)−Si(1) 1.769(7), N(2)−Si(1) 1.8780(10), N(3)−Si(1) 1.8776(10); N(1)−Si(1)−N(2) 108.3(4), N(1)−Si(1)−N(3) 112.2(4), N(3)−Si(1)−N(2) 69.09(4).

almost 78% yield (Scheme 1). Compound **2** is the second example of a system stable at room temperature that contains a Si(II)−N bond. **2** is isolated as a colorless crystalline solid with good solubility in diethyl ether, toluene, and THF. **2** exhibits a high stability up to 154 °C and can be handled in open air for a short period of time without any appreciable decomposition. This remarkable stability is presumably due to the presence of two helmet-like trimethylsilyl groups which shield the Si(II) center.

The ^{1}H NMR spectrum of **2** displays two sets of resonances (δ = 0.44 and 0.63 ppm) for the two $SiMe_3$ groups. A sharp resonance is exhibited at δ = 1.23 ppm for 18 *t*Bu protons, which are shifted downfield relative to those in LSiCl (δ = 1.08 ppm).[3c] The ^{29}Si NMR spectrum of **2** displays three resonances (δ = −8.07, 2.81, and 3.71 ppm). The first corresponds to the Si(II) center while the other two are assigned to the two $SiMe_3$ groups. There is an upfield shift of the Si(II) atom in the ^{29}Si NMR spectrum when compared to that of LSiCl (δ = 14.6 ppm).[3c] This is apparently due to the donation of a lone pair of electrons from the nitrogen atoms to the vacant p orbital of the Si(II) atom so that the deshielding of the Si atom is reduced. In the EI-mass spectrum, the molecular ion is observed as the most abundant peak with highest relative intensity at m/z 419.

The molecular structure of **2** is shown in Figure 1 while the important bond lengths and angles are provided in the legend of Figure 1. **2** crystallizes in the triclinic space group $P\bar{1}$.[16] The bis(trimethylsilyl)amino group is involved in disorder with nearly equivalent site occupation factors (s.o.f.) and restrained bond lengths and angles. For this reason, only values for one of each the disordered moieties will be given. The coordination geometry around the Si1 atom is trigonal pyramidal with the sum of the bond angles around Si1 atom of 290°. The geometry is consistent with the presence of a stereochemically active lone pair of electrons at the Si(II) atom.[3c,d] The four-membered Si1−N2−C1−N3 ring is not planar. The Si(II) atom is shifted out of the plane defined by C1−N2−N3 by 0.537(3) Å, thus, arranged to a distorted trigonal pyramid with the three nitrogen atoms in the basal positions. The Sil lone pair marks the apex of the trigonal pyramid. The two Si 1−N(ligand) bond lengths are identical (1.878(1) and 1.878(1) Å), while the Si1−$N(SiMe_3)_2$ bond length is 1.769(7) Å. The latter is 0.045 Å longer than the equivalent distance in the previously reported $LSiNMe_2$ (1.724(2) Å)[3d] but very similar to the theoretically calculated value of $[\{(Me_3Si)_2N\}_2Si]_2$ (1.779 Å).[14b]

The chemistry of heteroatom substituted silylenes is one of the foci of current research and no reactivity of silicon(II) bis(trimethylsilyl)amide has been mentioned so far. It is understandable that the chemistry of **2** will be different from that of LSiCl due to its higher thermal stability and the presence of a strong Si−N bond instead of a labile Si−Cl bond. To compare the reactivity of **2** with that of LSiCl, we treated **2** with PhC≡CPh and AdC≡P. The reactions of LSiCl with PhC≡CPh and AdC≡P afforded 1,2-disilacyclobutadiene[5c] and 1,3-disilacarbaphosphide derivative,[6] respectively. With PhC≡CPh, **2** did not react, but with AdC≡P, it furnished a five-membered cyclic silene.

Silenes are usually prepared by thermal and photochemical rearrangement of suitable acyl silanes, easily accessible from reactions of acid chlorides with silyl anions, by sila-Peterson reaction, and β-elimination of inorganic salts.[17] Apeloig, Kira, and Sekiguchi independently showed that the sila-Peterson reaction is very useful for synthesizing stable silenes.[17b−e] Kira et al. also reported that dialkyl silylene isomerizes to the corresponding silaethene via an apparent 1,2-silyl migration at room temperature.[2e] Recently, some disilenides are independently brought to the fore by Sekiguchi[18a,b] and Scheschkewitz et al.[18c,d,e] Several cyclic silenes were obtained by the reactions of disilenides with acid chlorides.[19] Herein, we present a convenient synthesis of a cyclic silene from a heteroleptic Si(II) compound.

Treatment of an equimolar mixture of AdC≡P and **2** in toluene for 12 h furnished the cyclic product **3**, which was formed in about 65% yield as red crystals (Scheme 2). Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with the asymmetric unit containing two whole molecules.[16] Only one of the nearly identical molecules will be discussed. The molecular structure of **3** with relevant bond lengths and angles is shown in Figure 2. It is the first example of a five-membered cyclic silene formed by four different elements. The sum of the internal bond angles of **3** is 533°. The $CNSi_2P$ ring does not exhibit a slight envelope conformation but is twisted. The P and Si2 atoms are removed from the plane defined by C−Si1−N by more than 0.3 Å, each arranged at opposite sides of the plane. The ring can be considered as a heavy cyclopentene derivative consisting of two Si atoms, and one each of C, N, and P atoms. Both of the silicon atoms display a distorted tetrahedral coordination geometry and

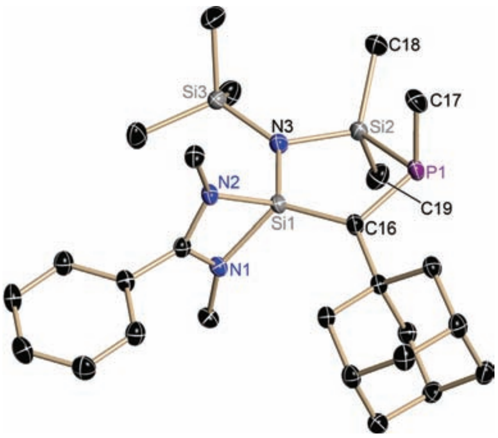
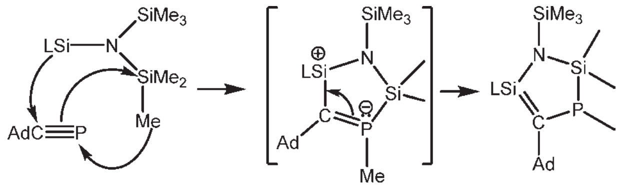


Figure 2. Molecular structure of **3** with the anisotropic displacement parameters depicted at the 50% probability level. Hydrogen atoms and N*t*Bu methyl groups are not shown for clarity. Only one of the two nearly identical molecules of the asymmetric unit is shown and discussed. Selected bond lengths (Å) and angles (deg): Si1−N3 1.7292(13), Si1−C16 1.7536(13), N3−Si2 1.7801(12), C16−P1 1.8071(13), P1−Si2 2.2155(9); N3−Si1−C16 112.34(6), C16−P1−C17 107.87(7), C16−P1−Si2 94.30(5), C17−P1−Si2 100.74(6), N3−Si2−C18 111.52(7), C18−Si2−C19 109.20(8), N3−Si2−P1 104.10(4), C18−Si2−P1 108.36(6), C16−Si1−N1 120.83(6), Si(1)−C(16)−P(1) 114.06(7), Si(1)−N(3)−Si(2) 108.05(6).

the two Si−N bond lengths are of 1.729(1) and 1.780(1) Å, respectively. The Si 1−C 16 bond length (1.754(1) Å) is even shorter than in Brook's first disilene,[20] $(TMS)_2Si{=}C(OTMS)$-2-Ad (1.764 Å) and only slightly longer than in Scheschkewitz's 1,2-disilacyclobut-2-ene (1.7459(15) Å),[19a] suggesting a Si−C double bond in **3**.[21] The small increase in the Si−C bond length compared to that of Scheschkewitz's cyclic disilene is due to the formation of a five-membered ring instead of a four-membered ring which resulted in ring strain reduction. This may be attributed to the presence of π-donating N atom to Si1 which reduces the polarity of the Si═C double bond significantly, thereby increasing the bond length. The sum of the bond angles around C16 is 360°. This implies that the carbon atom contributing to the Si−C double bond in **3** adopts an essentially planar environment which is in sharp contrast to the strongly pyramidalized Si atom of the Si−C doubly bonded compounds.[19] The planar arrangement may be due to the presence of electronegative substituents like N and P at Si and C, respectively. The presence of electronegative substituents reduces the gap between π and σ^*, thereby enabling stronger mixing of these two orbitals. The geometry of the P atom can best be described as distorted trigonal pyramidal with the sum of the bond angles of 303°. The Si−P and C−P bond lengths are 2.2155(9) and 1.807(1) Å, respectively, which matches with common values for single bonds.[22] N3 adopts a trigonal planar coordination geometry with the sum of bond angles of 360°.

The most intriguing feature of the reaction is the cleavage of one of the Si−C bonds of $SiMe_3$ unit followed by a methyl group migration to the phosphorus atom. Usually, the cleavage of the $C(sp^3)$−Si bonds requires extremely vigorous conditions,[23] but there are very few exceptions using a transition metal catalyst. For example, a Pd catalyzed oxidative methylation of alkenes using trimethylsilyl group as a methyl source has been reported.[24] Following this, the catalytic cleavage of $C(sp^3)$−Si bond in trialkylsilyl groups has also been described using $[RhCl(cod)]_2$[25] but, to our knowledge, there is no example of $C(sp^3)$−Si bond cleavage of trimethylsilyl group without catalytic support of a transition metal at room temperature.

Scheme 3. Tentative Mechanism for the formation of 3



Although the mechanism of the reaction remains vague, we propose that it is a concerted one (Scheme 3). The P atom attacks the Si(IV) center of one of the $SiMe_3$ groups and the lone pair of electrons on Si(II) center attacks the electron deficient carbon of phosphaalkyne. Consequently, there is an oxidative addition under the migration of one Me group from Si(IV) center to the adjacent P atom and simultaneous formation of a Si═C bond.

The spectroscopic data are in agreement with the structures of **3** deduced from single crystal X-ray diffraction studies. In the EI-MS spectrum of **3**, the molecular ion was observed at m/z 597.4 although with low intensity. However, the most abundant peak was observed at m/z 582.3 which corresponds to [**3**-Me]. The ^{31}P NMR spectrum of **3** shows a singlet with ^{29}Si satellites ($\delta = -116.7$ ppm). The ^{29}Si NMR spectrum of **3** displays three resonances for three chemically different Si atoms. The most low-field resonance at $\delta = 14$ ppm corresponds to the silene Si (Si1). A resonance at $\delta = -0.2$ ppm corresponds to $SiMe_3$ group. Another resonance at $\delta = -21.8$ ppm corresponds to Si2 which is attached to P with a unusually low Si−P coupling constant ($^1J(^{29}Si-^{31}P) = 14.79$ Hz).[26]

In summary, we have demonstrated a very convenient synthesis of N-substituted heteroleptic silylene and its reaction with adamantyl phosphaalkyne which leads to the facile formation of stable cyclic silene. Especially interesting is the facile Si−Me bond cleavage at room temperature without any transition metal catalyst which was not observed before. Therefore, this reaction raises a broad variety of possibilities, which are currently being explored in our laboratory.

EXPERIMENTAL SECTION

All manipulations were carried out in an inert gas atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen filled glovebox. The solvents used were purified by a MBRAUN solvent purification system MB SPS-800. Compound **1** was prepared by literature methods.[5c] All chemicals purchased from Aldrich were used without further purification. ^1H, ^{13}C, ^{31}P, and ^{29}Si NMR spectra were recorded in C_6D_6 using a Bruker Avance DPX 200 or a Bruker Avance DRX 500 spectrometer. EI-mass spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting points were measured in a sealed glass tube on a Büchi B-540 melting point apparatus.

Preparation of 2. Toluene (200 mL) was added to a mixture of **1** (3.31 g, 10.00 mmol) and potassium bis(trimethylsilyl)amide (3.99 g, 20.00 mmol) at ambient temperature. Immediately, the solution turned to a red color with the formation of KCl. The resulting suspension was stirred for 12 h. The solvent was then removed *in vacuo*, and the residue

Table 1. Crystallographic Data for the X-ray Structural Analyses of Compounds 2 and 3

	2	3
Empirical formula	$C_{21}H_{41}N_3Si_3$	$C_{32}H_{56}N_3PSi_3$
F. w.	419.84	598.04
Temperature (K)	100(2)	101(2)
CCDC no.	828727	828728
Wavelength (Å)	0.71073	0.56086
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	8.439(2)	12.866(2)
b (Å)	10.943(2)	16.639(2)
c (Å)	14.350(3)	17.090(3)
α (deg)	95.67(2)	90.72(2)
β (deg)	103.27(3)	108.43(3)
γ (deg)	93.68(2)	91.83(2)
Volume (Å^3)	1278.3(5)	3468.2(11)
Z	2	4
Density (calculated) (Mg/m^3)	1.091	1.146
Absorption coefficient (mm^{-1})	0.196	0.113
F(000)	460	1304
Crystal size (mm^3)	0.35 × 0.30 × 0.15	0.18 × 0.10 × 0.08
θ range for data collection (deg)	1.47 to 26.73	1.32 to 22.75
Index ranges	$-10 \le h \le 10$	$-17 \le h \le 17$
	$-13 \le k \le 13$	$-22 \le k \le 22$
	$-18 \le l \le 18$	$-23 \le l \le 23$
Reflections collected	41035	119976
Independent reflections	5420 [*R*(int) = 0.0182]	19013 [*R*(int) = 0.0310]
Completeness to	99.9%	99.8%
Absorption correction	Semiempirical from equivalents	Semiempirical from equivalents
Max. and min transmission	0.970 and 0.934	0.930 and 0.864
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5420/325/332	19013/0/727
Goodness-of-fit on F^2	1.028	1.026
Final *R* indices [$I > 2\sigma(I)$]	*R*1 = 0.0277, *wR*2 = 0.0739	*R*1 = 0.0366, *wR*2 = 0.0937
R indices (all data)	*R*1 = 0.0291, *wR*2 = 0.0750	*R*1 = 0.0471, *wR*2 = 0.0998
Largest diff. peak and hole (e.Å^{-3})	0.365 and −0.246	0.979 and −0.393

was extracted with toluene (100 mL). The filtrate was concentrated to yield colorless crystals of **2** (3.30 g, 78.62%). Mp 154−158 °C. For the elemental analysis, **2** was treated *in vacuo* overnight. Anal. calcd for **2**, $C_{21}H_{41}N_3Si_3$ (419.8): C, 60.08; H, 9.84; N, 10.01; found: C, 59.68; H, 9.55; N, 10.02; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.44 (s, 9H, Si*Me*$_3$), 0.63 (s, 9H, Si*Me*$_3$), 1.23 (s, 18H, *t*Bu), 6.86−6.96 (m, 5H, Ph) ppm; ^{13}C{^{1}H} NMR (75.46 MHz, C_6D_6, 25 °C): δ 5.19 (Si*Me*$_3$), 5.7 (Si*Me*$_3$), 32.1 (C*Me*$_3$), 57.7 (*C*Me$_3$), 127.6, 127.7, 127.9, 128.1, 128.3, 129.2 (Ph), 156.8 (NCN) ppm; ^{29}Si{^{1}H} NMR (59.62 MHz, C_6D_6, 25 °C): δ −8.07 (*Si*N(SiMe$_3$)$_2$), 2.81 (*Si*Me$_3$), 3.71(*Si*Me$_3$) ppm. EI-MS: *m*/*z*: 419 [M$^+$] (100%).

Preparation of 3. Toluene (25 mL) was added to the mixture of **2** (0.42 g, 1.00 mmol) and adamantyl phosphaalkyne (0.18 g, 1.00 mmol) at ambient temperature. The mixture was stirred for 12 h. The solvent was removed under vacuum and the residue was treated with 20 mL toluene. Storage of the filtrate at room temperature for 7 days afforded red crystals of **3** (0.39 g, 65.3%). Mp 212−215 °C. Elemental analysis (%) calcd for $C_{32}H_{56}N_3PSi_3$ (597.35): C, 64.27; H, 9.44; N, 7.03; found: C, 64.66; H, 9.43; N, 7.06. ^{1}H NMR (500 MHz, C_6D_6, 25 °C): δ 0.33 (s, 6H, Si*Me*$_2$), 0.46 (s, 9H, Si*Me*$_3$), 0.63 (s, 3H, P-*Me*), 1.16 (br, 18H, *t*Bu), 1.38 (br, 10H, Ad), 6.8−7.1 (m, 5H, *Ph*) ppm; ^{13}C{^{1}H}NMR (75.46 MHz, C_6D_6, 25 °C): δ 2.5 (Si(CH$_3$)$_2$), 5.5 (Si*Me*$_3$), 15.9 (P-CH$_3$, $^1J(^{31}P-^{13}C)$ = 42.79 Hz), 30.7(CCH$_3$), 31.8 (CCH$_3$), 37.7, 38.1, 46.9, 47.1 (adamantyl), 54.8 (CCH$_3$), 55.2 (CCH$_3$), 126.9, 127.4, 128.5, 130.2, 131.9 (Ph), 127.7 (Si-*C*-P, $^1J(^{31}P-^{13}C)$ = 12.78 Hz), 175.2 (NCN) ppm; ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): −116.7 ppm; ^{29}Si{^{1}H}NMR (99.36 MHz, C_6D_6, 25 °C): δ −21.8 (Me$_2$*Si*-P), $^1J(^{29}Si-^{31}P)$ = 14.79 Hz), −0.2 (*Si*Me$_3$), 14 (*Si*=C) ppm. EI-MS: *m*/*z*: 597 [M$^+$] (20%), 582 [M$^+$-Me] (100%).

Crystal Structure Determination. Shock cooled crystals were selected and mounted under nitrogen atmosphere using the X-TEMP.[16] The data for **2** were collected at 100(2) K on an INCOATEC Mo microfocus source[27] with Quazar mirror optics and APEX II detector on a D8 goniometer. An INCOATEC Ag microfocus source was used for data collection of **3** employing an APEX II detector with Ag Kα-radiation enhanced fluorescent layer on a Bruker D8 goniometer. Both diffractometers were equipped with a low-temperature device and used Mo Kα radiation, λ = 0.71073 Å and Ag Kα radiation, λ = 0.56086 Å, respectively. The data of **2** and **3** were integrated with SAINT[28] and an empirical absorption correction (SADABS) was applied.[29] The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-squares methods against F^2 (SHELXL-97).[30] All nonhydrogen-atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to equal to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. In **2**, the $N(SiMe_3)_2$ group is disordered over two positions. It was refined using distance restraints and displacement parameters restraints.

In **3**, relatively high residual density stays in the final structure. It can be modeled with a disorder of Si2 and P1 resembling the two possible twisted conformers of the five-membered ring. Consequentially, the hydrocarbon substituents are involved in the disorder as well. Even though high quality data up to relatively high resolution (d = 0.725 Å) were employed in the refinement, only the two heavy atoms can properly be refined and no residual density peaks could directly be assigned to substituents because of the very low site occupation factors of about 0.04 and 0.02, respectively, for both of the two molecules in the asymmetric unit. Using strong constraints and restraints enabled refinement of a model of the disordered methyl groups. It was decided not to include a model of the disorder in the final refinement. Further details and a model of the disorder can be found in the Supporting Information.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. The crystal data are listed in Table 1. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** CIF files for **2** and **3**. Details about the crystal structure refinement of **3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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