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High Yield Access to Silylene RSiCl (R = PhC(N*t*Bu)$_2$) and Its Reactivity toward Alkyne: Synthesis of Stable Disilacyclobutene

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Abstract: Two new approaches for synthesizing RSiCl, (R = PhC(N*t*Bu)$_2$) are reported by the reaction of RSiHCl$_2$ with bis-trimethyl silyl lithium amide and N-heterocyclic carbene respectively. In the former method silylene is produced in 90% yield. The silylene was treated with biphenyl alkyne to afford the disilacyclobutene system. This is a rare example of two five-coordinate silicon centers arranged adjacent to each other in a four-membered ring. Furthermore, we fluorinated the four-membered ring by trimethyltin fluoride to obtain the fluoro substituted disilacyclobutene.

Introduction

In the past 20 years N-heterocyclic silylenes attracted much attention because of their structure, bonding, and potential applications in transition metal catalysis.[1] A handful of room temperature stable silylene complexes were since then synthesized and structurally characterized.[2] In 2006, we successfully prepared the first heteroleptic chloro silylene stabilized by a benzamidinato ligand with *t*Bu substituents on nitrogen atoms. It was prepared by reduction of LSiCl$_3$ (L = PhC(N*t*Bu)$_2$) with finely divided potassium in 10% yield.[3] The reactivities of bare silylenes are well documented but little is known about the chemistry of substituted silylenes.[4] However, due to the low yield of LSiCl, further investigations were limited. Hence, there is a high quest for an alternative route to silylene under mild conditions with good yield.

Benkeser and his co-workers discussed the formation of the SiCl$_3$ anion when trichlorosilane is treated with amines.[5] We showed that N-heterocyclic carbene could function as a dehydrochlorinating agent and we were able to isolate a Lewis base stabilized dichloro silylene.[6] Subsequently Cui et al. reported the isolation of four- and five-membered silylenes using the same approach.[7] We employed these two techniques further and found out two new routes for the preparation of LSiCl in good yields. No silylenes have been isolated so far by using lithium amide as dehydrochlorinating agent.

Results and Discussion

Previously we used SiCl$_4$ for the preparation of LSiCl$_3$, which we further selectively reduced with finely divided potassium to LSiCl.[3] In the new procedure we reacted HSiCl$_3$ with *tert*-butyl carbodiimide and phenyl lithium to yield LSiHCl$_2$. The compound was characterized by NMR spectroscopy, EI-mass spectrometry, and elemental analysis. A toluene solution of LSiHCl$_2$(**1**) and 1,3-di-*tert*-butylimidazol-2-ylidene under stirring immediately changed the color from colorless to yellow and finally to brown-red with the formation of a white precipitate. The insoluble white precipitate was identified as 1,3-di-*tert*- butylimidazolium chloride and the soluble part as the silylene **2** with 35% yield, which was confirmed by NMR spectroscopy, EI-mass spectrometry, and compared to a previously reported sample (Scheme 1). However **2** is easily accessible in 90% yield from the direct reaction of **1** with LiN(TMS)$_2$ as a base in molar ratio of 1:1. The increase in the yield for **2** with the new method allows investigating its reactivity.

Silicon-containing small ring compounds are of interest because of their versatile role as building blocks in organosilicon chemistry.[8] Therefore we turned our attention toward alkyne to prepare cyclobutene analogues of silicon since alkynes are well-known labile and effective trapping reagents for main group

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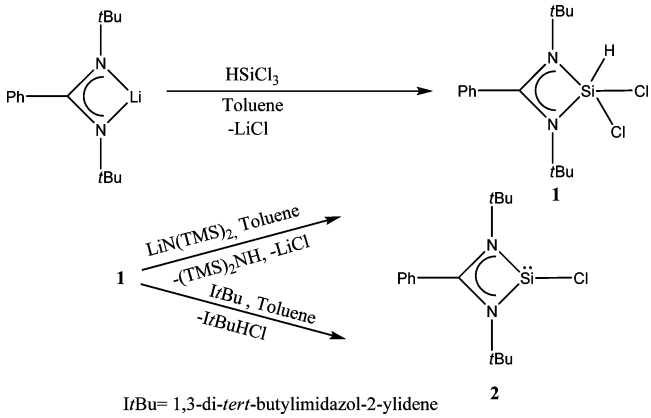
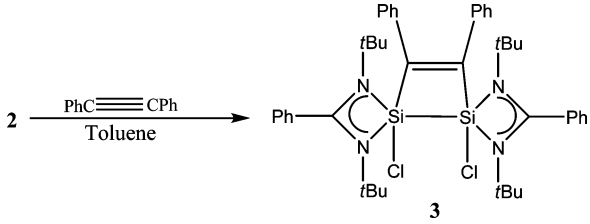
Scheme 1. Preparation of **1** and **2**



ItBu= 1,3-di-*tert*-butylimidazol-2-ylidene

Scheme 2. Preparation of **3**



carbene analogues.[9] The formation of disilacyclobutene was commonly achieved by the reduction of 1,2-bis(chloroalkylsilyl)-benzene with sodium.[10] But a promising alternative strategy represents the utilization of unsaturated silicon compounds and alkyne to obtain disilacyclobutene system. We already reported the successful preparation of the cyclopropene analogue of aluminum.[11] This prompted us to investigate whether LSiCl is also capable of giving novel strained silicon−carbon cycles.

LSiCl was reacted with biphenyl alkyne in toluene at ambient temperature under stirring overnight (Scheme 2). The solution was concentrated and kept for crystallization. After 4 days colorless crystals of 1,2-disilacyclobutene **3** were obtained suitable for X-ray crystallography. The structure of the compound was confirmed by NMR spectroscopy, EI-mass spectrometry, X-ray crystallography, and elemental analysis. The ^{29}Si NMR showed a resonance at −109.53 ppm. The value is consistent with that of the reported trisilacyclopentane derivative[6] and also with those known for cyclic silicon compounds.[12] In the EI−MS spectrum, only fragments were observed. All ions are in accordance with the proposed formula of **3**.

The molecular structure of **3** is shown in Figure 1.[13] Compound **3** crystallizes in the monoclinic space group $P2_1/c$ (Table 1). The Si−Si bond length of 2.36(4) Å is comparable with those of compounds containing Si−Si single bonds.[14] The distance between the two carbon atoms in the ring (1.36(12) Å) corresponds to a carbon carbon double bond. The Si−C bond distances are (1.92(9) Å and 1.93(9) Å) in the expected range.[15] The most important feature is the four-membered Si_2C_2ring that is almost planar (sum of the internal angles 357.82°). The amidinate ligands and chlorine atoms are disposed above and below the Si_2C_2 ring in such a way that the Si centers exhibit trigonal bipyramidal coordination sites. To the best of our knowledge, two five-coordinate silicon centers arranged adjacent to each other in a four-membered ring have not been reported so far.

To give a mechanistic insight of the reaction we postulate that initially there is an oxidative addition between chloro silylene and biphenyl alkyne resulting in the formation of a strained three-membered ring. Usually such type of cycloaddition or oxidative addition reactions is very common for heavier group 14 elements with unsaturated hydrocarbon.[16] The strained three-membered ring undergoes a facile rearrangement by the insertion of another silylene molecule, thus giving rise to a stable four-membered disilacyclobutene system with formation of a Si−Si bond (Scheme 3). This is an oxidative addition followed by insertion reaction which is novel in the case of a Si(II) system. Although we were not able to trap the silacyclopropene, we were recently successful in characterizing the corresponding alumacyclopropene.[11] Therefore, the formation of silacyclopropene as an intermediate proceeds with very high plausibility.

To obtain the complexation energy of the reaction, the energy of the isolated moieties **2**, **3**, and biphenyl alkyne were calculated. All the calculations were performed on the B3LYP/TZVP[17−19] level of calculation with Turbomole.[20] Individual optimization and energy calculations on each part were performed. Subsequent calculations of frequencies yielded only positive frequencies for all parts. (Calculated energy of **2** −1444.399479989 au, energy of biphenyl alkyne

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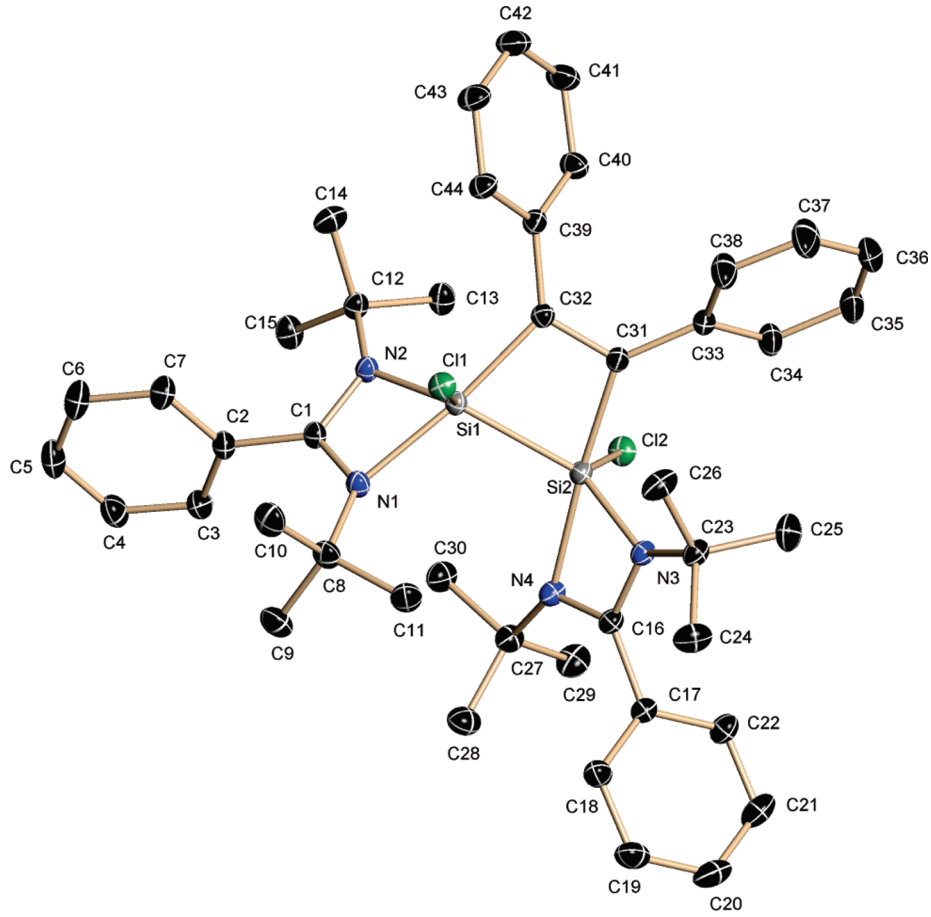

Figure 1. Crystal structure of **3**. Hydrogen atoms are not shown for clarity. Selected bond distances (Å) and bond angles (deg): Si(1)−N(2) 1.8389(8), Si(1)−C(32) 1.9285(9), Si(1)−N(1) 1.9943(8), Si(1)−Cl(1) 2.1688(3), Si(1)−Si(2) 2.3659(4), Si(2)−N(3) 1.8284(8), Si(2)−C(31) 1.9348(9), Si(2)−N(4) 2.0370(9), Si(2)−Cl(2) 2.1551(3), C(31)−C(32) 1.3694(12); N(2)−Si(1)−C(32) 108.30(4), N(2)−Si(1)−N(1) 68.46(3), C(32)−Si(1)−N(1) 173.99(4), N(2)−Si(1)−Cl(1) 117.83(3), C(32)−Si(1)−Cl(1) 90.40(3), N(1)−Si(1)−Cl(1) 86.88(3), N(2)−Si(1)−Si(2) 124.71(3), C(32)−Si(1)−Si(2) 74.76(3), N(1)−Si(1)−Si(2) 111.25(3), Cl(1)−Si(1)−Si(2) 117.322(14), N(3)−Si(2)−C(31) 109.78(4), N(3)−Si(2)−N(4) 67.91(3), C(31)−Si(2)−N(4) 175.62(4), N(3)−Si(2)−Cl(2) 114.46(3), C(31)−Si(2)−Cl(2) 91.59(3), N(4)−Si(2)−Cl(2) 86.18(3), N(3)−Si(2)−Si(1) 126.47(3), C(31)−Si(2)−Si(1) 74.54(3), N(4)−Si(2)−Si(1) 109.83(3), Cl(2)−Si(2)−Si(1) 118.779(14).

Table 1. X-ray Data for Compound **3**

	3
empirical formula	$C_{44}H_{56}Cl_2N_4Si_2$
molecular weight	768.01
color	colorless
CCDC-No.	748995
crystal system	monoclinic
space group	$P2_1/c$
a [Å]	13.1830(4)
b [Å]	13.2275(4)
c [Å]	24.4548(8)
α [deg]	90
β [deg]	94.5010(1)
γ [deg]	90
V [Å^3]	4251.2(2)
Z	4
ρ_{calc} [g m^{-3}]	1.200
μ [mm^{-1}]	0.244
F(000)	1640.0
$wR2$ (all data)	0.1388 (25354)

−539.2917962348 au and of **3** −3428.103152781 au) The overall stabilization energy is −0.0123966 au (−7.77885 kcal/mol). This value, however, is too low due to a basis set superposition error. A counterpoise correction[21] was applied, and therefore 6 additional calculations were necessary. Each of the aforementioned moieties was calculated in its final geometry once with basis set contributions from the other parts of the molecule, where the nuclear charge of these other parts was set to zero, and once for the isolated parts in their final geometry. Subtracting these values leads to the counterpoise energy of ΔEcp −3.69048 kcal/mol. This is an estimate for the artificial energy lowering the whole molecule due to the basis set contributions from **2**, **3**, and biphenyl alkyne. The corrected final complexation energy with counterpoised corrected complexation energy is −4.08839 kcal/mol. In summary, the calculation does not give an answer for the preferred formation of the four-membered ring system.

Compound **3** is easily converted to the corresponding fluorine derivative **4** using trimethyltin fluoride as a fluorinating agent (Scheme 4). Compound **4** is a colorless solid and soluble in solvents like toluene, ether and THF. **4** was characterized by ^{1}H, ^{19}F, and ^{29}Si NMR spectroscopy. In the ^{19}F NMR spectrum of **4**, a resonance appeared as a sharp singlet at −71.73 ppm with silicon satellite (J_{Si-F} = 254.22 Hz). The values are consistent with those reported in literature.[22]

Experimental Section

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen

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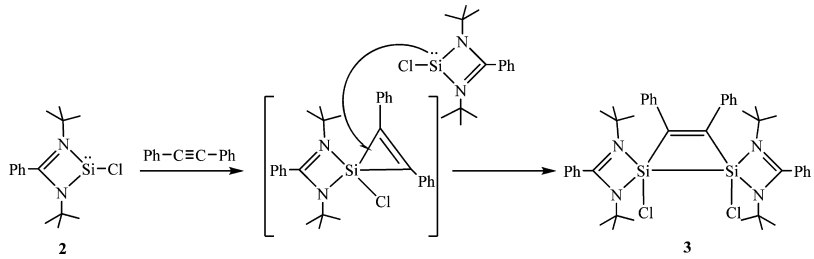
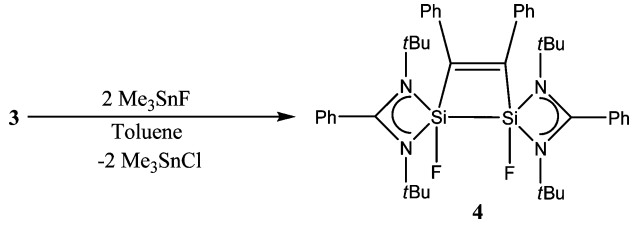
Scheme 3. Suggested Mechanism for the Formation of **3**



Scheme 4. Preparation of **4**



filled glovebox. Solvents used were purified by MBRAUN solvent purification system MB SPS-800. 1,3-Di-*tert*-butylimidazol-2-ylidene[23] and Me_3SnF[24] were prepared by the literature methods. All chemicals purchased from Aldrich were used without further purification. ^1H, ^{13}C, ^{19}F, ^{29}Si NMR spectra were recorded using Bruker Avance DPX 200 or Bruker Avance DRX 500 spectrometers. The NMR spectra were recorded in C_6D_6. The chemical shifts δ are given relative to $SiMe_4$. EI−mass spectra were obtained using a Finnigan MAT 8230 instrument. Elemental analyses were performed by the Institut für Anorganische Chemie, Universität Göttingen. Melting point was measured in a sealed glass tube on a Büchi B-540 melting point apparatus and was uncorrected.

Preparation of 1. PhLi (6.86 mL, 13.72 mmol, 1.8 M in diethyl ether) was added to a solution of *t*BuN═C═N*t*Bu (2.12 g, 13.72 mmol) in diethyl ether (80 mL) at −78 °C. The solution was raised to ambient temperature and stirred for 4 h. To the solution $HSiCl_3$ was added drop by drop (4.25 mL, 17.17 mmol) at −78 °C. The reaction mixture was warmed to room temperature and was stirred for 12 h. The precipitate was filtered off, and after removal of all volatiles the residue was extracted with toluene (20 mL). Storage of the extract at −32 °C in a freezer for 1 day afforded colorless crystals of **1**. Mp 145−150 °C. Elemental analysis (%) calcd for $C_{15}H_{24}Cl_2N_2Si$ (331.36): C, 54.37; H, 7.30; N, 8.45; found: C,54.66; H, 7.63; N,8.06. ^1H NMR (200 MHz, C_6D_6, 25 °C): δ 1.08 ppm (s, 18H, *t*Bu), 6.70 ppm (s, 1H, Si−H), 7.41−7.48 ppm (m, 5H, Ph); $^{13}C\{^1H\}$NMR (125.75 MHz, C_6D_6, 25 °C): δ 31.8 (CMe_3), 54.2 (CMe_3), 128.6, 128.9, 129.1, 129.9, 130.6, 135.6 (Ph), 173.3 ppm (NCN); $^{29}Si\{^1H\}$NMR (99.36 MHz, C_6D_6, 25 °C): δ −96.834 ppm. EI−MS: *m*/*z*(%): 330 [M^+], (100).

Preparation of 2. Toluene (50 mL) was added to a mixture of **1** (0.31 g, 1.00 mmol) and bis-trimethyl silyl lithium amide (0.17 g, 1.01 mmol) at ambient temperature. Immediately the solution turned to a red color with the formation of LiCl. The resulting mixture was stirred overnight. The solvent was then removed *in vacuo*, and the residue was extracted with toluene (20 mL). The filtrate was concentrated to yield colorless crystals of **2** (0.26 g, 90%).

Alternative Method. Toluene (50 mL) was added to a mixture of **1** (1.00 g, 3.03 mmol) and 1,3-di-*tert*-butylimidazol-2-ylidene (0.6 g, 3.33 mmol) at ambient temperature. The resulting mixture was stirred overnight. The solvent was then removed *in vacuo*, and the residue was extracted with toluene (50 mL). The filtrate was concentrated to yield colorless crystals of **2** (0.32 g, 35%). Mp 159−162 °C. Elemental analysis (%) calcd for $C_{15}H_{23}ClN_2Si$: C, 61.10; H, 7.87; N, 9.51; found: C, 60.95; H, 7.64; N, 9.35; ^1H NMR (200 MHz, C_6D_6, 25 °C): δ 1.08 (s, 18 H, *t*Bu), 6.78−7.05 ppm (m, 5 H, Ph); $^{13}C\{^1H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 31.4 (CMe_3), 53.7 (CMe_3), 126.32, 127.4, 127.9, 128.4, 129.8, 133.0 (Ph), 166.7 ppm (NCN); $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ 14.6; EI−MS: *m*/*z*: 295 [M^+].

Preparation of 3. To the mixture of **2** (0.30 g, 1.02 mmol) and biphenyl alkyne (0.10 g, 0.60 mmol) toluene (20 mL) was added at room temperature. The mixture was stirred overnight. The solid was filtered off and the solution was concentrated and kept at room temperature for 4 days to yield colorless crystals of **3** (0.11 g, 42%). Mp 165−170 °C. Elemental analysis (%) calcd for $C_{44}H_{56}Cl_2N_4Si_2$: C, 68.81; H, 7.35; N, 7.29; found: C, 67.95; H, 7.04; N, 8.35; ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 1.15 (s, 36 H, *t*Bu), 6.78−7.05 (m, 10 H, Ph), 7.28−7.55 ppm (m, 10 H, Ph); $^{13}C\{^1H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 32.83 (CMe_3), 55.23 (CMe_3), 128.5, 128.9, 129.4, 129.9, 130.2, 133.0 (Ph), 156.45 ppm (NCN); $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −109.53 ppm. EI−MS: *m*/*z*: 294 [M^+](100%).

Preparation of 4. To the mixture of **3** (0.5 g, 0.65 mmol) and trimethyltin fluoride (0.24 g, 1.31 mmol) toluene (25 mL) was added and stirred until the solution becomes transparent. After filtration the solution was concentrated and kept at − 32 °C to get pure compound **4** (0.2 g, 41%). Mp 182 − 185 °C. ^1H NMR (300 MHz, C_6D_6, 25 °C): δ 1.23 (s, 36 H, *t*Bu), 7.12−7.28 (m, 10 H, Ph), 7.48−7.75 ppm (m, 10 H, Ph); $^{13}C\{^1H\}$ NMR (125.75 MHz, C_6D_6, 25 °C): δ 32.4 (CMe_3), 53.7 (CMe_3), 127.4, 127.9, 128.4, 129.8, 133.0 (Ph), 166.7 ppm (NCN); ^{19}F (188.31 MHz, $CFCl_3$, C_6D_6, 25 °C): δ −71.73 (J_{Si-F} = 254.22 Hz) ppm: $^{29}Si\{^1H\}$ NMR (99.36 MHz, C_6D_6, 25 °C): δ −117.82, − 115.26 (doublet J_{Si-F} = 254.22 Hz) EI-MS: *m*/*z*: 283 [M^+](100%).

X-Ray Crystallography. Shock cooled crystals were selected and mounted under nitrogen atmosphere using the X-TEMP2. The structure was solved by direct methods (SHELXS) and refined on F^2 using full matrix least-squares methods of SHELXL.

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Supporting Information Available: CIF and theoretical calculation for **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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