Formation of Silicon Centered Spirocyclic Compounds: Reaction of N-Heterocyclic Stable Silylene with Benzoylpyridine, Diisopropyl Azodicarboxylate, and 1,2-Diphenylhydrazine

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S *Supporting Information*

ABSTRACT: Three silicon centered spirocyclic compounds **1**−**3**, possessing silicon fused six- and five-membered rings have been prepared by the reaction of NHSi (**L**) [**L** = CH{(C=CH$_2$)-(CMe)(2,6-iPr$_2$C$_6$H$_3$N)$_2$}Si] with benzoylpyridine, diisopropyl azodicarboxylate, and 1,2-diphenylhydrazine, respectively, in a 1:1 ratio. The three spirocyclic compounds (**1**− **3**) were obtained by three different pathways. The reaction of **L** with benzoylpyridine leads to the activation of the pyridine ring, and dearomatization occurred. Treatment of diisopropyl azodicarboxylate with **L** favors a [1 + 4]- rather than a [1 + 2]-cycloaddition product, and the azo compound was converted to hydrazone derivative. Finally the reaction of 1,2-diphenylhydrazine and **L** results in the elimination of hydrogen by activating one of the C−H bonds present in the phenyl ring. All three complexes **1**−**3** were characterized by single crystal X-ray structural analysis, NMR spectroscopy, EI-MS spectrometry, and elemental analysis. In addition the optimized structures of probable products and possible intermediates were investigated using density functional theory (DFT) calculations.
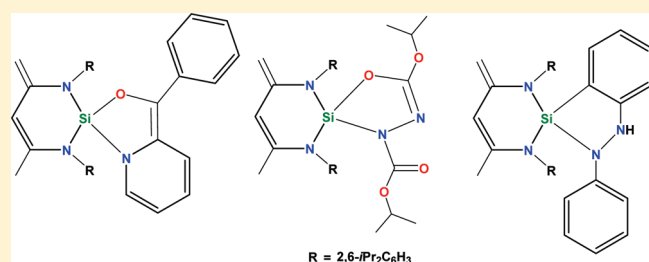
INTRODUCTION

Silylenes are divalent silicon compounds and are extremely reactive species, which are considered to be the silicon analogues of carbenes.[1] In 1994, the first stable N-heterocyclic silylene (NHSi) was reported by Denk et al.;[2] after that many stable N-heterocyclic silylenes (NHSis)[1b−d,3] and a stable N-heterocyclic carbene (NHC) stabilized dichlorosilylene have been reported.[4] The reactivity of NHSis is quite comparable with that of the N-heterocyclic carbenes (NHCs), where the latter led to rapid research activities and to many applications in chemistry.[5,6] However, the reactivity patterns of transition metal complexes of NHCs are relatively different from those of the NHSis.[6m] In general, silylenes have two non bonding electrons like the highest occupied molecular orbital (HOMO) which possesses nucleophilic character and an empty p-orbital as the lowest unoccupied molecular orbital (LUMO) which causes the electrophilic character. So they exhibit both nucleophilic and electrophilic reactive sites at the same silicon atom, quantified by charge density determination.[4] Silylenes are considered to possess an ambiphilic character, behave as Lewis acids as well as Lewis bases.[7] Hence there is intense research activity carried out in the chemistry of NHSis. (Insertion: C−H,[8] N−H,[9] O−H,[10] S−H,[9a] P−P,[11] N−Si,[12] C-X (Cl, Br, I),[13] Si−Cl,[13] P−H,[14] As−H,[14] addition,[9c,15] metal complexes,[16] Lewis acids[17]). Utilizing the stable NHSi (**L**)

[**L** = CH{(C=CH$_2$)(CMe)(2,6-iPr$_2$C$_6$H$_3$N)$_2$}Si],[3c] we reported N−H bond activation of ammonia,[9b] hydrazines,[9c] and C−H as well as C−F bond activation of fluoroarenes.[18] To explore the reactivity of **L** further, we carried out the reactions of **L** with benzoylpyridine, diisopropyl azodicarboxylate, and 1,2-diphenylhydrazine. The silicon atom which is already part of the six-membered ring system based on **L**, acts as a reaction center to form new five-membered ring compounds with the respective reactant keeping the six-membered ring intact and leading to the spirocyclic compounds (**1**−**3**). In all three compounds, the six- and five-membered rings are fused by the silicon center, and the rings are arranged nearly orthogonal to each other. Interestingly the reaction with benzoylpyridine leads to the activation of the pyridine ring, and dearomatization emerged out of the benzoylpyridine. Recently the pyridine activation-dearomatization reaction has materialized as a cost-effective approach to asymmetric synthesis in organic chemistry.[19] The reaction of **L** with diisopropyl azodicarboxylate favors a [1 + 4]- rather than a [1 + 2]-cycloaddition species. Here the hydrazone derivative is formed from the azo compound. Upon reaction of **L** with 1,2-diphenyl-hydrazine, the H atom present in one of the −NH units, and the

Scheme 1. Synthesis of 1, 2, and 3
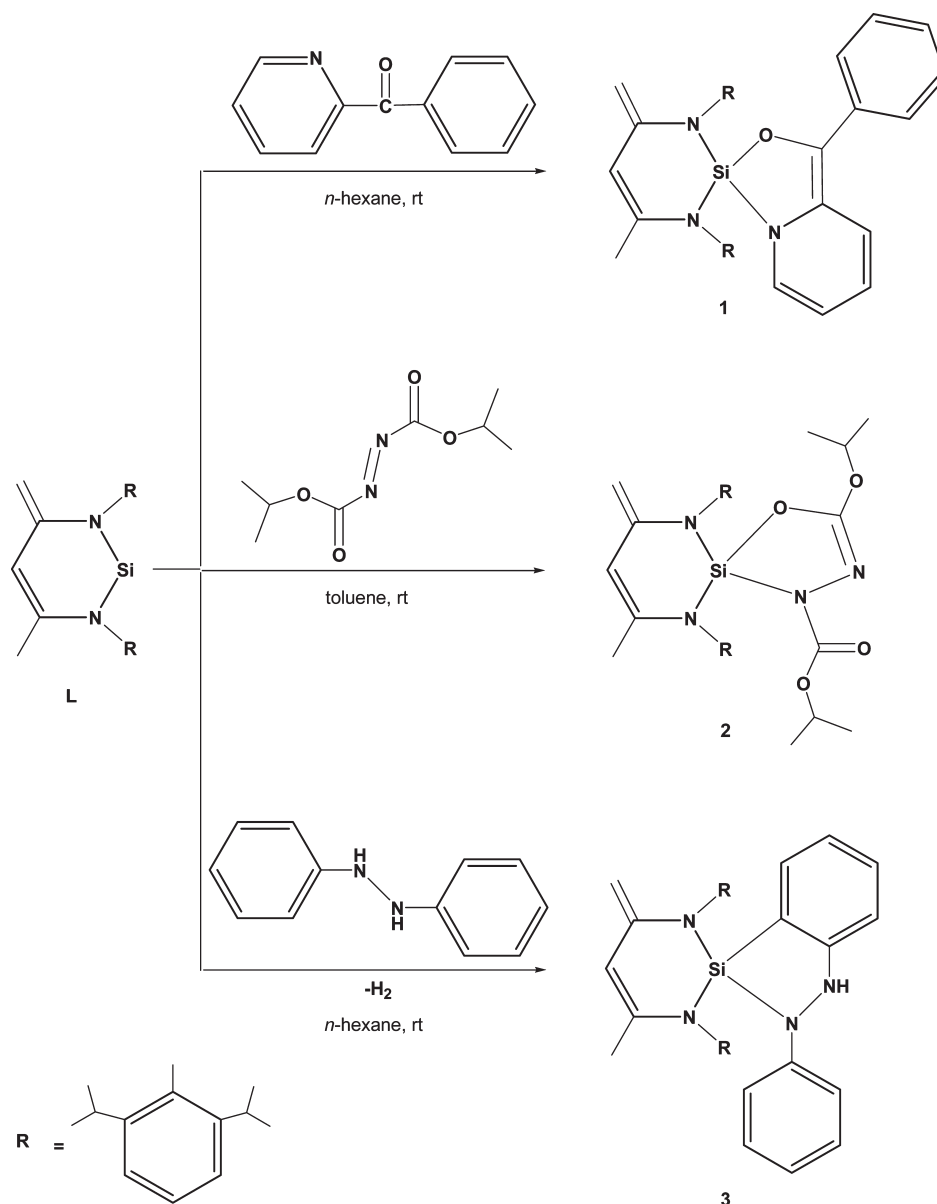
H atom present in the *o*-position of one of the phenyl rings which is attached with the uncleaved NH unit in 1,2-diphenylhydrazine gets activated with the elimination of hydrogen.
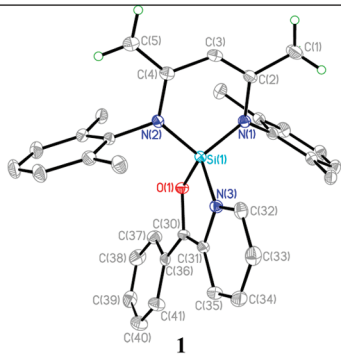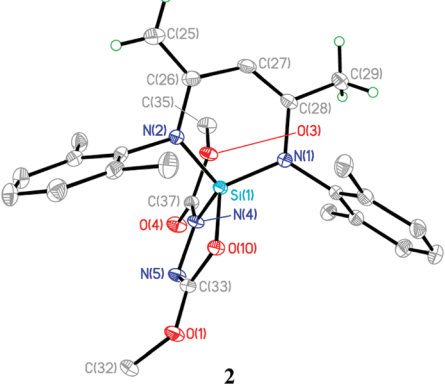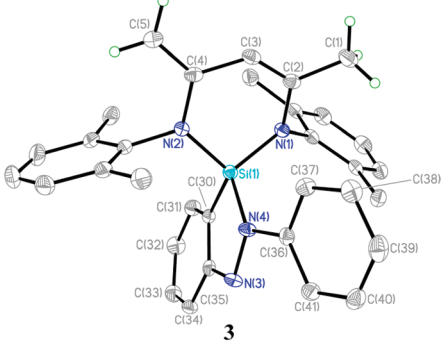
■ RESULTS AND DISCUSSION

Compounds **1**, **2**, and **3** were obtained in good yield upon treatment of **L** with benzoylpyridine, diisopropyl azodicarboxylate, and 1,2-diphenylhydrazine in 1:1 ratio, respectively, as represented in Scheme 1. They were fully characterized by NMR spectroscopy, EI-MS, and elemental analysis. Furthermore, all structures were unequivocally confirmed by single crystal X-ray structural analyses.

The reaction of **L** with an equimolar amount of benzoylpyridine in *n*-hexane at room temperature proceeds rapidly with the formation of burgundy red colored solution of the dearomatized

pyridine product **1**. It is soluble in *n*-hexane, *n*-pentane, toluene, and benzene. Moreover it is stable both in the solid state as well as in solution for a long time without any decomposition under an inert gas atmosphere. The ^{29}Si NMR spectrum of **1** shows a single resonance at $\delta = -53.95$ ppm, which is upfield shifted compared to **L** (δ 88.4 ppm) because in **1** the silicon atom is more shielded. The γ-C*H* proton for compound **1** in the ^{1}H NMR spectrum observed at $\delta = 5.31$ ppm is upfield shifted compared to that of **L** (δ 5.44 ppm). The NCC*H*$_2$ protons in **1** resonate at 3.34 and 3.96 ppm (δ for **L** = 3.32 and 3.91 ppm). The concomitant of the dearomatized pyridine ring has been clearly established in ^{1}H NMR of the upfield shift of hydrogen atoms present in the pyridine ring. The dearomatized pyridine ring shows multiplets in the region of 4.86−4.93(1H), 5.45−5.53(1H), and 6.13−6.21(2H), respectively, in its ^{1}H NMR spectrum. These values indicate the possible dearomatized

Table 1. Molecular Structure[a] and Bond Parameters for the Compounds 1, 2, and 3

Entry	Molecular structure	Bond lengths / Å		Bond angles / °	
1		Si(1) – N(1)	1.7055(11)	N(1) – Si(1) – N(2)	105.59(6)
		Si(1) – N(2)	1.7075(11)	N(3) – Si(1) – O(1)	92.30(5)
		Si(1) – N(3)	1.7468(12)	N(1) – Si(1) – O(1)	114.02(5)
		Si(1) – O(1)	1.6345(10)	N(2) – Si(1) – O(1)	113.85(5)
		C(30) – O(1)	1.4116(15)	N(1) – Si(1) – N(3)	115.91(5)
		C(30) – C(31)	1.3643(19)	N(2) – Si(1) – N(3)	115.24(6)
		C(30) – C(36)	1.4516(19)	Si(1) – N(3) – C(31)	109.47(9)
		C(31) – C(35)	1.4440(19)	N(3) – C(31) – C(30)	112.05(11)
		C(35) – C(34)	1.346(2)	C(31) – C(30) – O(1)	112.43(11)
		C(34) – C(33)	1.438(2)	C(30) – O(1) – Si(1)	113.63(8)
		C(33) – C(32)	1.342(2)		
		C(32) – N(3)	1.3793(18)		
		C(31) – N(3)	1.4288(17)		
		C(1) – C(2)	1.4735(19)		
		C(4) – C(5)	1.3705(19)		
2		Si(1) – N(1)	1.6889(12)	N(1) – Si(1) – N(2)	107.39(6)
		Si(1) – N(2)	1.6994(12)	N(4) – Si(1) – O(10)	89.49(5)
		Si(1) – N(4)	1.7373(12)	N(1) – Si(1) – O(10)	114.23(5)
		Si(1) – O(10)	1.6714(10)	N(2) – Si(1) – O(10)	110.29(5)
		C(33) – O(10)	1.3553(16)	N(1) – Si(1) – N(4)	118.77(6)
		C(33) – N(5)	1.2843(18)	N(2) – Si(1) – N(4)	115.73(6)
		N(5) – N(4)	1.4299(15)	Si(1) – N(4) – N(5)	112.42(8)
		C(25) – C(26)	1.352(2)	N(4) – N(5) – C(33)	105.88(11)
		C(28) – C(29)	1.4849(19)	N(5) – C(33) – O(10)	121.78(12)
				C(33) – O(10) – Si(1)	109.31(8)
3		Si(1) – N(1)	1.7182(14)	N(1) – Si(1) – N(2)	102.80(7)
		Si(1) – N(2)	1.7265(14)	N(4) – Si(1) – C(30)	90.48(7)
		Si(1) – N(4)	1.7600(14)	N(1) – Si(1) – C(30)	118.11(7)
		Si(1) – C(30)	1.8400(16)	N(2) – Si(1) – C(30)	117.28(7)
		C(30) – C(31)	1.402(2)	N(1) – Si(1) – N(4)	114.71(7)
		C(31) – C(32)	1.381(2)	N(2) – Si(1) – N(4)	113.98(7)
		C(32) – C(33)	1.390(3)	Si(1) – N(4) – N(3)	112.77(10)
		C(33) – C(34)	1.379(2)	N(4) – N(3) – C(35)	110.52(13)
		C(34) – C(35)	1.400(2)	N(3) – C(35) – C(30)	117.29(14)
		C(35) – C(30)	1.398(2)	C(35) – C(30) – Si(1)	108.09(11)
		C(35) – N(3)	1.401(2)		
		N(3) – N(4)	1.4425(18)		
		C(1) – C(2)	1.487(2)		
		C(4) – C(5)	1.351(2)		

[a] Hydrogen atoms in their respective molecular structure have been omitted for clarity except on backbone carbon atom.

pyridine ring product which is reported in the literature.[19b] Moreover **1** shows its molecular ion peak in its mass spectrum at m/z 627.4.

The dearomatized pyridine ring product **1** was unambiguously established by single crystal X-ray structural analysis. **1** crystallizes in the triclinic space group $P\bar{1}$ and the molecular structure is shown in Entry 1 of Table 1. We propose that the reaction of **L** with benzoylpyridine followed the $[1 + 4]$-cycloaddition reaction as represented in Scheme 2. The silicon atom is in a distorted tetrahedral geometry, made up from three nitrogen atoms and a single oxygen atom. Among the three nitrogen atoms, one originates from the dearomatized pyridine ring of the benzoylpyridine and the two others from the chelating ligand. The silicon atom is shifted out of the plane defined by N1, N2, C3, C4, and C2 significantly by 0.28 Å. The angle included by O1—Si1—N3 is 92.30(5)° and differs from ideal tetrahedral symmetry while the

angle between N1—Si1—N2 is 105.59(6)°. There is a shortening of bonds observed between the Si atom and the nitrogen atoms of the supporting ligand. The average bond distance between Si—N_{av} in **1** is 1.7065(11) Å, whereas in **L** it is 1.7345(10) Å. There is appreciable change in the N—Si—N bite angle at the silicon atom with the backbone ligand. In **1** it is 105.59(6)°, whereas in **L** it is 99.317(54)°. The bond lengths of Si1—N3(py) and Si1—O1 are 1.7468(12) and 1.6345(10) Å, indicating single bond character.[20] The bond distances between adjacent carbon atoms in the dearomatized six-membered pyridine ring (N3, C31, C35, C34, C33, C32) of compound **1** possess both single and double bond character, the bond distances between C31—C35 and C34—C33 are 1.4440(19) and 1.438(2) Å indicating C—C single bonds, and the bond distances between C35—C34 and C33—C32 are 1.346(2) and 1.342(2) Å indicating C═C double bonds. The bond distances of C32—N3 and N3—C31 are

Scheme 2. Proposed Mechanism for the Formation of 1
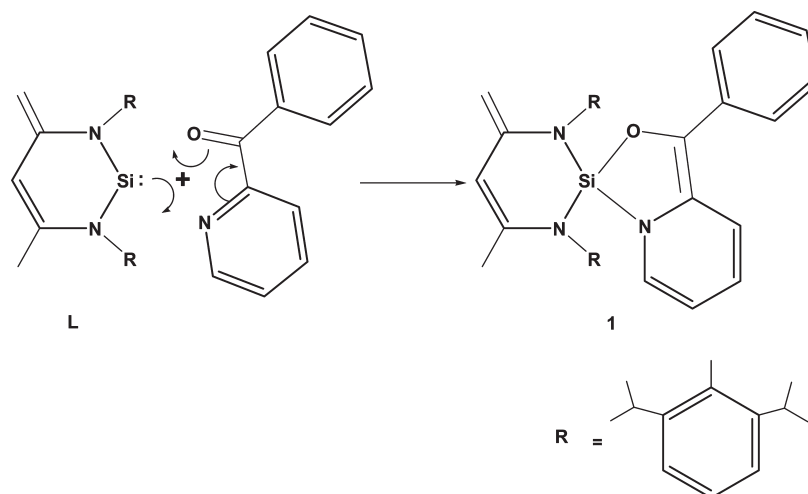
Scheme 3. Proposed Mechanism for the Formation of 2
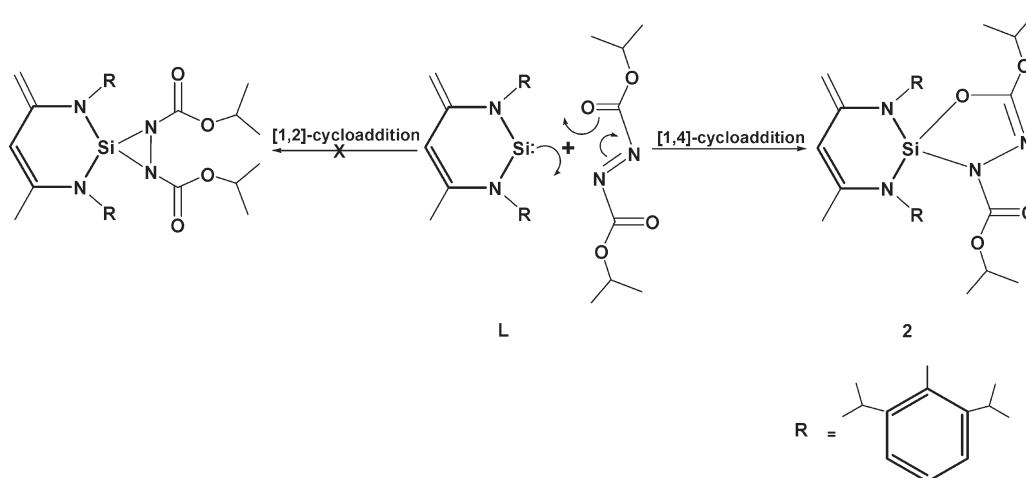
1.3793(18) and 1.4288(17) Å. The distance between C30−C31 is 1.3643(19) Å indicating C═C double bond character.[21] These results substantiate the depicted *Lewis* formula of **1** (Scheme 1).

Similar to **1**, compound **2** also contains a newly formed five-membered ring after the reaction of diisopropyl azodicarboxylate with **L**. We presume that the reaction also proceeds via [1 + 4]-cycloaddition like that in **1** rather than a [1 + 2]-cycloaddition as represented in the Scheme 3. Unlike **1**, compound **2** is insoluble in *n*-hexane and *n*-pentane but soluble in benzene and toluene. It is stable in both the solid and the solution state under an inert atmosphere. Like **1**, the ^{29}Si NMR spectrum of compound **2** shows upfield resonance δ at −53.94. In the ^{1}H NMR spectrum the γ-C*H* proton for compound **2** is observed at δ = 5.27 ppm which is upfield shifted compared to that of **L**. The NCC*H*$_2$ protons resonate at δ 3.34 and δ 3.89 ppm. Compound **2** shows its molecular ion peak in its EI-MS at *m/z* 646.3.

Compound **2** crystallizes in the orthorhombic space group *Pca*2$_1$. The molecular structure for compound **2** is shown in

Entry 2 of Table 1. Here the azo compound (−N═N−C−) has been converted to the hydrazone derivative (−N−N═C−). In **2**, the silicon atom is coordinated in a distorted tetrahedral geometry comprising three nitrogen atoms (two from the supporting ligand and one from the hydrazone moiety) and one oxygen atom. The angle defined by O10−Si1−N4 (89.49(5)°) is slightly shorter than the corresponding angle in compound **1** while N1−Si1−N2 includes an angle of 107.39(6)°. As in **1**, there is Si−N bond shortening observed toward the supporting ligand. The silicon atom is shifted out of the plane defined by the N$_2$C$_3$-plane of the six-membered SiN$_2$C$_3$ ring by 0.35 Å. The N−N [N(4)−N(5) 1.4299(15) Å] and C−O [C(33)−O(10) 1.3553(16) Å] bond distances present in the newly formed five-membered ring of **2** are quite comparable to those values as reported in the literature.[22] The distance between C(33)−N(5) is 1.2843(18) Å indicating C═N double bond character.

The reaction of **L** with an equimolar amount of 1,2-diphenyl-hydrazine in *n*-hexane at room temperature leads to **3** in almost

Scheme 4. Proposed Mechanism for the Formation of 3
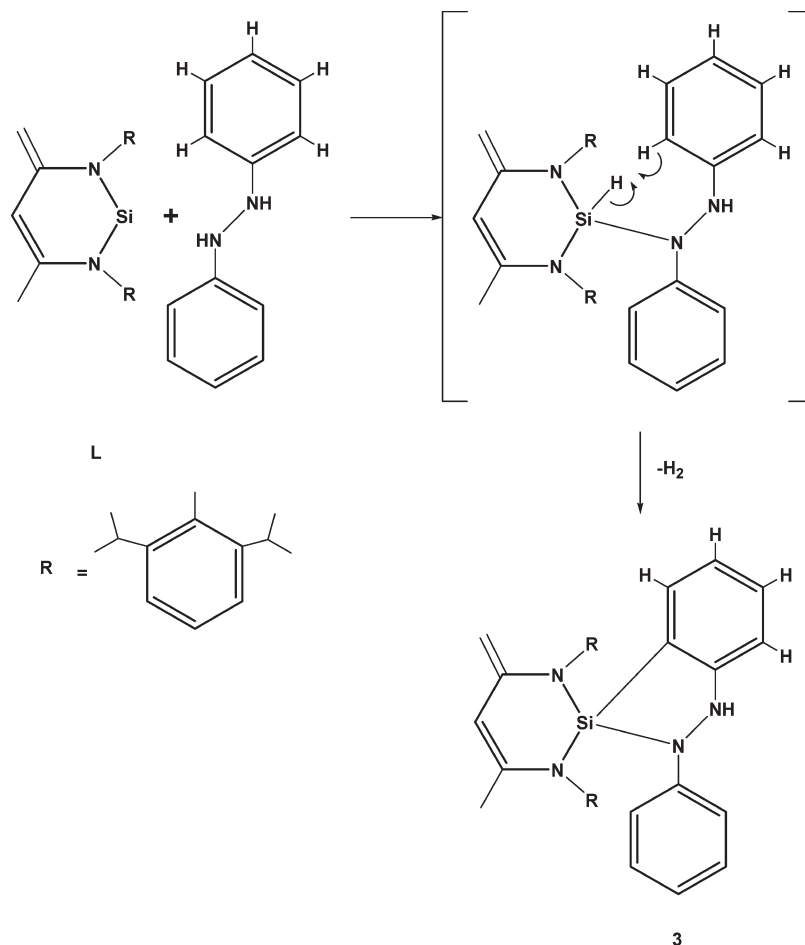
quantitative yield with elimination of hydrogen. We assume that initially one of the N−H bonds present in 1,2-diphenylhydrazine gets activated and then the C−H bond present in *o*-position of one of the phenyl rings which is attached with the uncleaved NH unit in 1,2-diphenylhydrazine gets activated with elimination of hydrogen as represented in Scheme 4. Like **1**, compound **3** is soluble in *n*-hexane, *n*-pentane, benzene, and toluene. In addition it is stable in both the solid and the solution state under an inert atmosphere. The ^{29}Si NMR spectrum of compound **3** shows a resonance at $\delta = -39.35$ ppm, which is upfield shifted similar to those of **1** and **2**. In the ^{1}H NMR spectrum the γ-C*H* proton for compound **3** resonates at $\delta = 5.40$ ppm, which is upfield shifted compared to that of **L**. The N−H proton shows a broad singlet at 4.68 ppm and the NCC*H*$_2$ protons exhibit sharp singlets at 3.33 and 4.02 ppm. The molecular ion peak of compound **3** is observed at m/z 626.4.

Compound **3** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of compound **3** is shown in Entry 3 of Table 1. In **3**, the silicon atom exhibits a distorted tetrahedral geometry, made up of three nitrogen atoms (one is derived from the nitrogen atom from the hydrazine part and the other two from the supporting ligand) and one carbon atom from the phenyl ring. Like in **1** and **2**, the SiN$_2$C$_3$ six-membered ring in **3** is dislocated from the plane defined by N$_2$C$_3$ significantly (0.41 Å). The angle N4−Si1−C30 is 90.48(7)°, while the observed angle of N1−Si1−N2 is 102.80(7)° which is the smallest among the
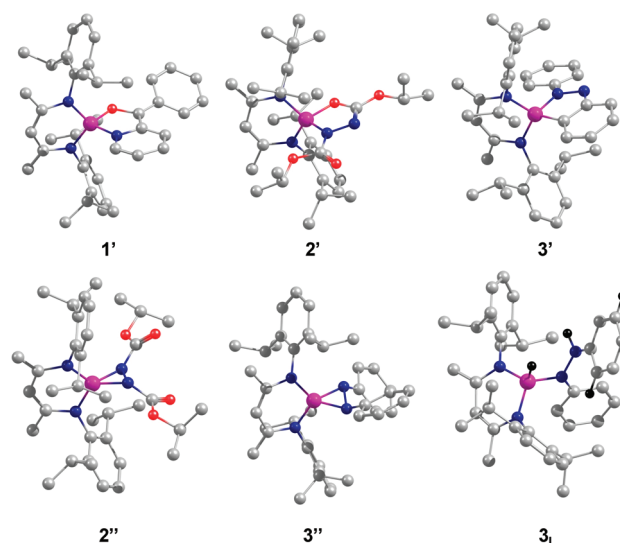

Figure 1. BP86/SVP optimized structures of the complexes with hydrogens removed for clarity. Color code: N blue, O red, Si cyan, C gray, H black.

three compounds. The bond lengths of Si1−N4 and Si1−C30 are 1.7600(14) and 1.8400(16) Å, indicating single bond character.[20] The bond distances of the phenyl ring (between

Table 2. Crystal and Structure Refinement Parameters for Compounds 1, 2, and 3

parameters	1	2	3
empirical formula	$C_{41} H_{49} N_3 O Si$	$C_{37} H_{54} N_4 O_4 Si$	$C_{41} H_{50} N_4 Si$
formula weight	627.92	646.93	626.94
temperature/K	100 (2)	99 (2)	80 (2)
wavelength/Å	0.71073	0.71073	0.71073
crystal system	triclinic	orthorhombic	triclinic
space group	$P\bar{1}$	$Pca2_1$	$P\bar{1}$
unit cell dimensions	a = 11.2420 (7) Å	a = 16.6931 (14) Å	a = 10.9890 (17) Å
	b = 11.5555 (7) Å	b = 12.1192 (10) Å	b = 12.566 (2) Å
	c = 14.8291 (9) Å	c = 17.9703 (15) Å	c = 12.909 (2) Å
	α = 78.5770 (10)°	α = 90°	α = 92.357(3)°
	β = 74.8600 (10)°	β = 90°	β = 93.727(3)°
	γ = 71.9120 (10)°	γ = 90°	γ = 90.731(4)°
volume, Z	1753.22 (19) Å^3, 2	3635.5 (5) Å^3, 4	1777.1 (5) Å^3, 2
density (calculated)	1.189 mg/m^3	1.182 mg/m^3	1.172 mg/m^3
absorption coefficient	0.103 mm^{-1}	0.108 mm^{-1}	0.100 mm^{-1}
F (000)	676	1400	676
Crystal size	0.12 × 0.08 × 0.06 mm^2	0.15 × 0.12 × 0.09 mm^2	0.20 × 0.12 × 0.06 mm^2
θ range for data collection	1.43 to 27.18°	1.68 to 27.13°	1.58 to 25.35°
limiting indices	$-14 \le h \le 14$	$-21 \le h \le 21$	$-13 \le h \le 12$
	$-14 \le k \le 14$	$-15 \le k \le 15$	$-10 \le k \le 15$
	$-19 \le l \le 19$	$-23 \le l \le 23$	$-15 \le l \le 15$
reflections collected	43551	66985	29684
independent reflections	7717 (R_{int} = 0.0312)	8037 (R_{int} = 0.0382)	6480 (R_{int} = 0.0487)
completeness to θ	98.9% (θ = 27.18)	99.9% (θ = 27.13)	99.6% (θ = 25.35)
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	7717/0/424	8037/1/428	6480/23/427
goodness-of-fit on F^2	1.021	1.057	1.030
final R indices [$I > 2\sigma(I)$]	R1 = 0.0399, wR2 = 0.0924	R1 = 0.0293, wR2 = 0.0719	R1 = 0.0405, wR2 = 0.0895
R indices (all data)	R1 = 0.0503, wR2 = 0.0977	R1 = 0.0322, wR2 = 0.0737	R1 = 0.0584, wR2 = 0.0979
largest diff. peak and hole	0.300 and −0.347 e Å^{-3}	0.219 and −0.236 e Å^{-3}	0.255 and −0.323 e Å^{-3}

adjacent carbon atoms C30 to C35) are in the order of 1.38 to 1.40 Å, indicating complete delocalization of π-electron density within the ring, retaining its aromatic character. The distance between N3—N4 is 1.4425(18) Å, indicating N—N bond length which is quite comparable to the N—N bond distances of other hydrazine or hydrazone derivatives which are reported in literature.[22]

In all three reactions, new five-membered rings have been formed ($SiNC_2O$ in **1**, SiN_2CO in **2**, and SiN_2C_2 in **3**). The five-membered rings are nearly orthogonal to the SiN_2C_3 six-membered ring of **L**. The dihedral angles between the planes of six- and five-membered rings are 89.18(3), 88.79(4), and 88.11(4)° in compounds **1**, **2**, and **3**, respectively.

The density functional theory (DFT) optimized structures of the three spirocyclic compounds (**1′**, **2′**, and **3′**) are shown in Figure 1. The gas-phase optimized structures show a close resemblance with the X-ray crystal structure data (see Table 1). The exclusive formation of [1 + 4]-cycloaddition product **2** rather than the [1 + 2]-cycloaddition complex **2″** can be primarily explained from the inherent ring strain present in the latter. This is supported by the fact that **2″** is energetically less stable (ΔE_e = 38.3 kcal/mol) compared to **2′**. A similar but relatively less pronounced effect is visible in **3**, where the [1 + 2]-cycloaddition product **3″** is less stable (ΔE_e = 29.4 kcal/mol) with respect to its isomer **3′** (Figure 1). The reaction of **L** with 1,2-diphenylhydrazine initially

activates one of the N—H bonds to furnish the intermediate **3$_I$** (Scheme 4 and Figure 1). Closer inspection of the DFT optimized **3$_I$** reveals that the *o*-hydrogen of one of the phenyl rings is nearer to silicon than the amine hydrogen (Si—H (from Ph) = 2.850 Å vs Si—H (from —NH-) = 3.268 Å). Moreover, to form [1 + 2]-cycloaddition product **3″**, the C_{ipso}—N—N—C_{ipso} dihedral angle (−111.3°) is required to be reduced so as to facilitate H$_2$ elimination. This configurational alteration induces a steric crowding between the two *o*-hydrogens of the phenyl rings in diphenylhydrazine fragment, resulting in a strained silicon fused three-membered ring (**3″**, Figure 1). The explanation justifies that though the amine hydrogen is more acidic than the aromatic *o*-hydrogen, the C—H activation is a preferred route to [1 + 4]-cycloaddition.

■ **CONCLUSION**

We have shown three new different routes for the synthesis of silicon centered spirocyclic compounds (a) by dearomatization of a pyridine ring, (b) by [1 + 4]- rather than [1 + 2]-cycloaddition product formation involving conversion of azo compound to hydrazone derivative, and (c) by elimination of hydrogen. For all three products the reaction occurred at the silicon atom, and a new five-membered ring was formed, keeping the SiN_2C_3 six-membered ring intact. The experimental results have been supported by DFT calculations. These different

pathways of reactivity shown by **L** make the chemistry of silylene much more fascinating.

EXPERIMENTAL SECTION

All manipulations were carried out in an inert atmosphere of dinitrogen using standard Schlenk techniques and in a dinitrogen filled glovebox. Solvents were purified by MBRAUN solvent purification system MB SPS-800. All chemicals were purchased from Aldrich and used without further purification. **L** was prepared as reported in the literature.[3c] ^{1}H, and ^{29}Si NMR spectra were recorded with a Bruker Avance DPX 200, Bruker Avance DRX 300, Bruker Avance DRX 400, or a Bruker Avance DRX 500 spectrometer, using C_6D_6 as solvent. Chemical shifts δ are given relative to SiMe$_4$. EI-MS 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.

Synthesis of 1. *n*-Hexane (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.47 g, 1.06 mmol) and benzoylpyridine (0.19 g, 1.04 mmol), and the solution immediately turned in color to burgundy red; the reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to about 30 mL and stored at 0 °C in a freezer for 12 h to obtain burgundy red colored single crystals. (0.46 g, 70%). Mp 157−158 °C(decomp). Elemental analysis (%) calcd for $C_{41}H_{49}N_3OSi$ (627): C, 78.42; H, 7.87; N, 6.69. Found: C, 78.79; H, 8.00; N, 6.38. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 1.22−1.44 (m, 21H, CH(CH_3)$_2$), 1.49 (s, 3H, NCCH_3), 1.61 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 3.30 (m, 2H, J = 7 Hz, CH(CH$_3$)$_2$), 3.34 (s, 1H, NCCH_2), 3.89 (m, 2H, J = 7 Hz, CH(CH$_3$)$_2$), 3.96 (s, 1H, NCCH_2), 4.86−4.93 (m, 1H, C$_5$NH_4), 5.31 (s, 1H, γ-CH), 5.45−5.53 (m, 1H, C$_5$NH_4), 6.13−6.21 (m, 2H, C$_5$NH_4), 6.85−7.09 (m, 11 H, C$_6$H$_5$, 2× iPr$_2$C$_6$H$_3$) ppm. ^{29}Si{^{1}H} NMR (59.63 MHz, C_6D_6, 25 °C): δ −53.95 ppm. EI-MS: m/z 627.4 (M$^+$).

Synthesis of 2. Toluene (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.37 g, 0.83 mmol) and diisopropyl azodicarboxylate (0.17 g, 0.84 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to 20 mL and stored in a freezer at −32 °C for a week to obtain colorless single crystals. (0.36 g, 67%). Mp 167−170 °C (decomp). Elemental analysis (%) calcd for $C_{37}H_{54}N_4O_4Si$ (646.39): C, 68.69; H, 8.41; N, 8.66. Found: C, 68.21; H, 8.51; N, 7.96. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 0.53 (d, 3H, J = 6 Hz, CH(CH_3)$_2$), 0.60 (d, 3H, J = 6 Hz, CH(CH_3)$_2$), 1.13−1.51 (m, 33H, CH(CH_3)$_2$, NCCH_3), 3.34 (s, 1H, NCCH_2), 3.64 (m, 4H, CH(CH$_3$)$_2$), 3.89 (s, 1H, NCCH_2), 4.42 (m, 1H, J = 6 Hz, CH(CH$_3$)$_2$), 5.09 (m, 1H, J = 6 Hz, CH(CH$_3$)$_2$), 5.27 (s, 1H, γ-CH), 6.97−7.18 (m, 6H, 2 × iPr$_2$C$_6$H$_3$) ppm; ^{29}Si{^{1}H} NMR (79.49 MHz, C_6D_6, 25 °C): δ -53.94 ppm. EI-MS: m/z 646.3 (M$^+$).

Synthesis of 3. *n*-Hexane (60 mL) was added to a 100 mL Schlenk flask containing **L** (0.25 g, 0.56 mmol) and 1, 2-diphenylhydrazine (0.11 g, 0.59 mmol). The reaction mixture was stirred at room temperature for 12 h. The solution was filtered, and the solvent was reduced in vacuo to 20 mL and stored in a freezer at −32 °C for 3 days to obtain colorless single crystals. (0.26 g, 70%). Mp 135−137 °C(decomp). Elemental analysis (%) calcd for $C_{41}H_{50}N_4Si$ (626.95): C, 78.55; H, 8.04; N, 8.94. Found: C, 78.70; H, 8.15; N, 9.52. ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 0.61 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 0.75−0.82 (2d, 6H, CH(CH_3)$_2$), 1.22 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 1.27 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 1.37 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 1.50 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 1.52 (s, 3H, NCCH_3), 1.62 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 3.07 (m, 1H, J = 7 Hz, CH(CH$_3$)$_2$), 3.33 (s, 1H, NCCH_2), 3.47 (m, 1H, J = 7 Hz, CH(CH$_3$)$_2$), 3.92 (m, 1H, J = 7 Hz, CH(CH$_3$)$_2$), 4.02 (s, 1H, NCCH_2), 4.21 (m, 1H, J = 7 Hz, CH(CH$_3$)$_2$), 4.68 (s, 1H, NH), 5.40 (s, 1H, γ-CH), 6.52−7.12 (m, 15 H, C$_6$H$_4$, C$_6$H$_5$, 2 × iPr$_2$C$_6$H$_3$) ppm. ^{29}Si{^{1}H}

NMR (99.36 MHz, C_6D_6, 25 °C): δ −39.35 ppm. EI-MS: m/z 626.4 (M$^+$).

Crystal Structure Determination. Suitable single crystals for X-ray structural analysis of **1**, **2**, and **3** were mounted at low temperature in inert oil under argon atmosphere by applying the X-Temp2 device.[23] The data of **1**, **2**, and **3** (Table 2) were collected on a Bruker D8 three circle diffractometer equipped with a SMART APEX II CCD detector and an INCOATEC Mo microsource with INCOATEC Quazar mirror optics.[24] The data were integrated with SAINT,[25] and an empirical absorption correction with SADABS[26] was applied. The structures were solved by direct methods (SHELXS-97) and refined against all data by full-matrix least-squares methods on F^2 (SHELXL-97).[27] All non-hydrogen-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 1.5U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms.

Computational Details. All calculations are performed in Gaussian03 quantum code.[28] The geometries of all the compounds are optimized with the generalized approximation (GGA) to DFT by using the exchange functional of Becke[29] in addition with the correlation functional of Perdew[30] (BP86). All the atoms are treated with Ahlrich's split valence plus polarization (SVP) basis sets[31] of 6-31G* quality. In all our DFT treatments, the resolution-of-the-identity (RI) approximation (also called "density fitting") for the two electron integrals was employed.[32] The geometries were optimized without any symmetry constraints. All the figures are made in the Chemcraft visualization software.[33]

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** DFT datas for all compounds mentioned in the main text. CIFs for **1** (CCDC-805652), **2** (CCDC-805653), and **3** (CCDC-805654). This material is available free of charge via the Internet at http://pubs.acs.org.

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