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Note

The thermally stable silylene Si[$(NCH_2Bu^t)_2C_6H_4$-1,2]: reaction with pyridine and quinoline

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Abstract

Two equivalents of the thermally stable silylene Si[$(NCH_2Bu^t)_2C_6H_4$-1,2] (**1**) react with pyridine to yield the 1-aza-2,3-disilacyclobutane derivative (**2**), which is labile and slowly rearranges via a 1,3-H shift to the 2-pyridyldisilane (**3**). A similar reaction of **1** with quinoline gives 1-aza-2,3-disilacyclobutane derivative (**4**), which is stable. The X-ray structures of **2** and **3** are discussed.
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1. Introduction

The chemistry of silylenes, the two-valent and two-coordinate analogues of carbenes, has attracted increasing attention in recent years with the discovery of thermally stable bis(amino)silylenes Si[(NBu^t)CHCH(NBu^t)] [1], Si[$(NBu^t)CH_2CH_2(NBu^t)$] [2] and Si[$(NCH_2Bu^t)_2C_6H_4$-1,2] [3], and the first isolable bis(alkyl)silylene Si[$C(SiMe_3)_2CH_2CH_2C(SiMe_3)_2$] [4]. The bis(amino)silylenes show a great variety of reactions, which were summarised in two review articles [5,6]. Among those reactions are addition reactions to unsaturated organic compounds, which lead in the majority of cases to interesting new silicon containing heterocycles. In a recent article we reported on the reactivity of Si[$(NCH_2Bu^t)_2C_6H_4$-1,2] (**1**) [abbr. as Si(NN)] towards compounds containing CN double bonds [7]. We found that the reactions of **1** with various imines yielded the tetravalent silicon compounds **I**–**VI** (Scheme 1).

We now present data on the reactions of the silylene **1** with compounds in which the CN double bond is constituent of a heteroaromatic compound, specifically with pyridine and quinoline. Interestingly, it was reported that the silylene Si[(NBu^t)CHCH(NBu^t)] was unreactive towards pyridine [1].

2. Results and discussion

Treatment of the silylene **1** with pyridine in a 1:1 ratio or an excess pyridine afforded the crystalline compound **2** (Scheme 2). The latter, however, is not stable in solution and partially (to about 60%) dissociates into its factors. The ^{1}H, ^{13}C and ^{29}Si NMR spectroscopic data of a C_6D_6 or $CD_3C_6D_5$ solution of **2** show signals assigned to pyridine, **1** and **2**. At elevated temperature, a solution of **2** was converted into compound **3**. The reaction of **1** with quinoline yielded compound **4**, which in contrast to **2** did not dissociate in solution and was thermally stable (Scheme 2).

Each of the yellow, crystalline compounds **2**–**4** was characterised by multinuclear NMR spectroscopy, electron impact mass spectrometry (parent ions observed) (not **2**) and microanalysis (not for **2**).

The molecular structures, determined by single-crystal X-ray diffraction, provide additional evidence for the formation of compound **2** and **3**, and are shown in (Figs. 1 and 2); selected bond lengths and angles are listed in (Tables 1 and 2), respectively. In accordance with the addition of two silylene units to the CN double bond of pyridine the planarity of the C_5N ring in

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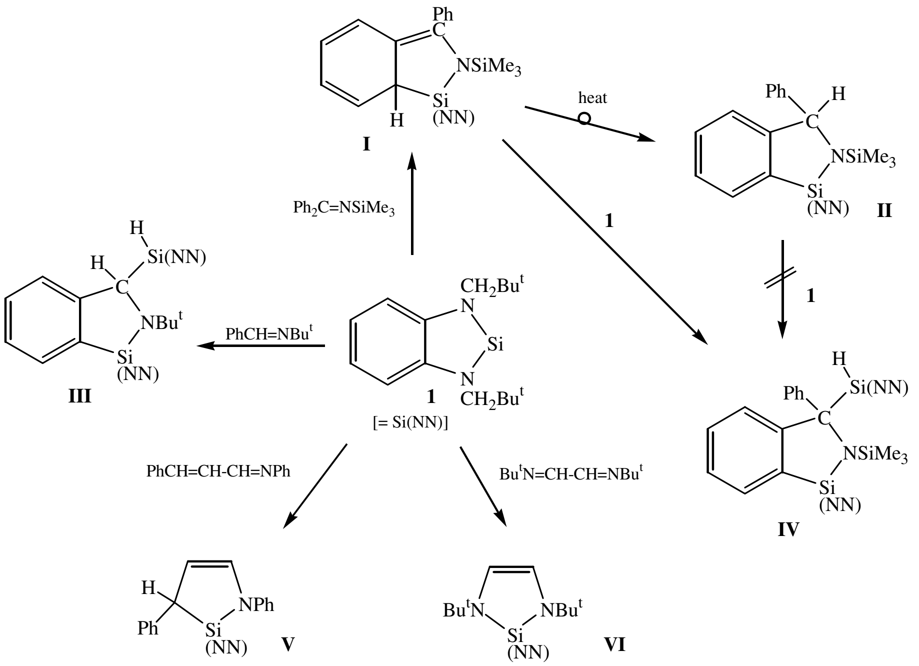
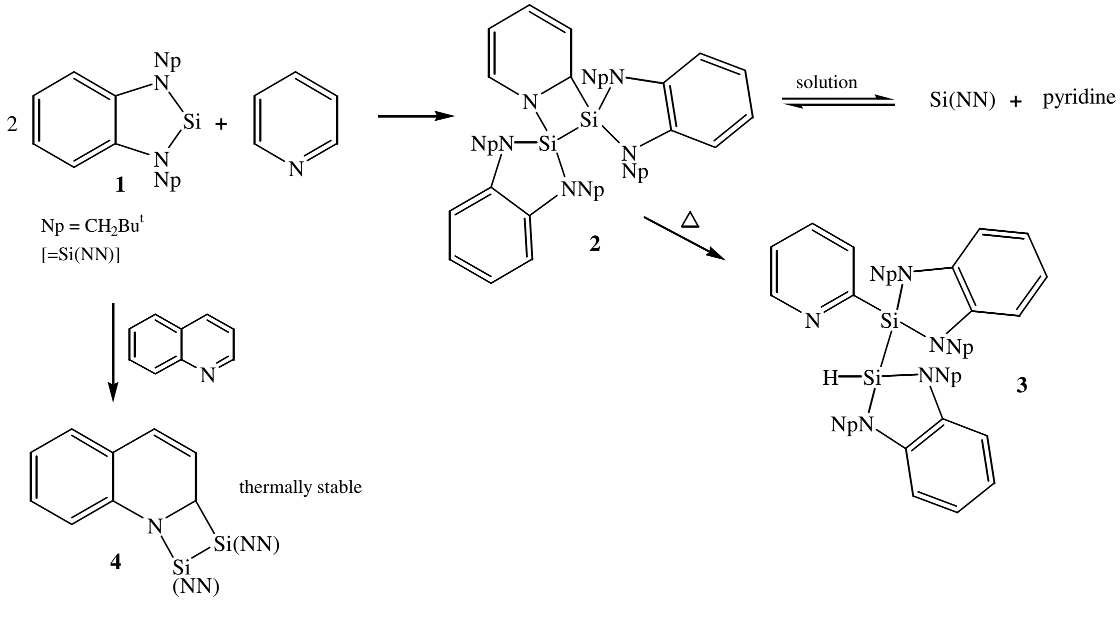


Scheme 1.



Scheme 2.

compound **2** is lost; the atom C(33) is disordered 0.87:0.13 over two positions displaced on either side of the C_4N plane. The N–C bonds in the C_5N ring show further a significantly shorter N(5)–C(37) than N(5)–C(33) bond [1.386(3) and 1.486(3) Å, respectively]; there probably is some π-electron interaction of the neighbouring C–C double bond with the lone pair at the planar N(5) (sum of angles at N 359.95°). The Si(1)–Si(2) bond length of 2.3717(9) Å is similar to that in related four-membered Si–Si–C–O [2.352(3) Å] [8] or Si–Si–C=N [2.385(3) Å] [9] ring structures. The Si(1)–Si(2) bond in compound **3** is much longer [2.4056(8) Å], but shorter than in the disilane $[\{C_6H_4(NCH_2Bu^t)_2\text{-}1,2\}Si(Bu^t)]_2$ [2.465(7) Å] [10]. All other structural parameters of compound **2** and **3** are unexceptional.

The formation of the bi- **2** or tricyclic **4** compounds probably proceeded via a three-membered intermediate **VII**, or its quinoline-based analogue, followed by insertion of **1** into the C–Si or N–Si bond. This sequence of addition of **1** to a multiply bond, followed by

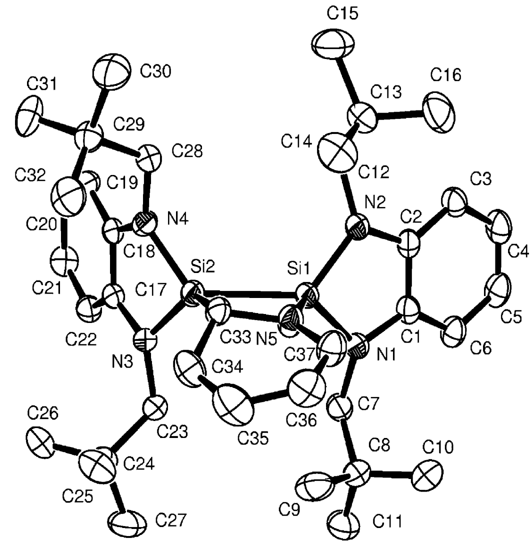


Fig. 1. Molecular structure of compound **2**.

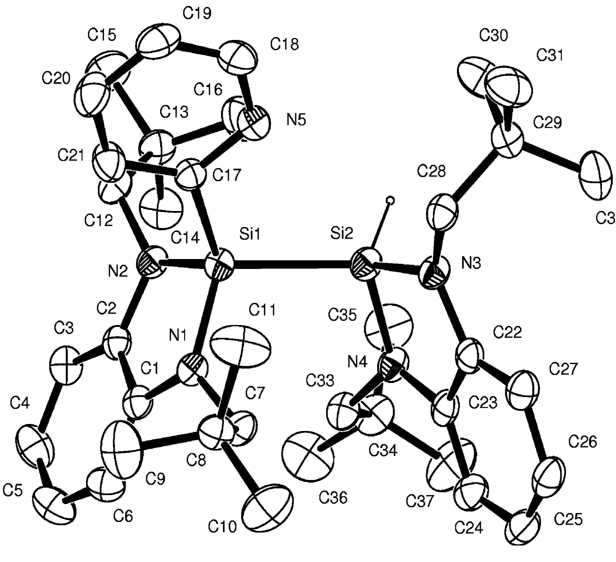


Fig. 2. Molecular structure of compound **3**.

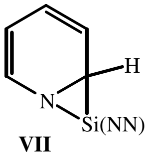
Table 1
Selected bond lengths (Å) and angles (°) for **2** and **3**

	2	**3**
Si(1)–Si(2)	2.3717(9)	2.4056(8)
Si(1)–N(1)	1.734(2)	1.7386(17)
Si(1)–N(2)	1.737(2)	1.7451(17)
Si(2)–N(3)	1.738(2)	1.7455(17)
Si(2)–N(4)	1.729(2)	1.7502(17)
Si(1)–N(5)	1.749(2)	
Si(2)–C(33)	1.940(3)	
N(5)–C(33)	1.486(3)	
N(5)–C(37)	1.386(3)	
Si(1)–C(17)		1.880(2)
N(1)–Si(1)–N(2)	92.63(10)	93.05(8)
N(3)–Si(2)–N(4)	92.01(10)	92.37(8)
N(5)–Si(1)–Si(2)	75.10(7)	
N(5)–C(33)–Si(2)	95.8(2)	
C(33)–Si(2)–Si(1)	76.16(8)	
C(33)–N(5)–Si(1)	111.6(2)	

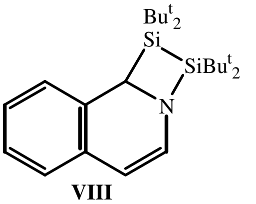
Table 2
Crystal data and refinement for complexes **2** and **3**

	2	**3**
Formula	$C_{37}H_{57}N_5Si_2$	$C_{37}H_{57}N_5Si_2$
Molecular weight	628.06	628.06
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)
a (Å)	9.9192(6)	38.7395(9)
b (Å)	10.8109(4)	10.3366(3)
c (Å)	17.7530(10)	19.4891(5)
α (°)	86.500(3)	90
β (°)	79.710(3)	109.149(2)
γ (°)	80.359(4)	90
U (Å^3)	1845.7(2)	7372.3(3)
Z	2	8
Reflections collected	20,421	28,452
Unique reflections (R_{int})	6453 (0.06)	8728 (0.06)
Reflections with $I > 2\sigma(I)$	4866	6075
Data/restraints/ parameters	6453/0/410	8728/0/402
Goodness-of-fit on F^2	1.057	1.028
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.056$, $wR_2 = 0.129$	$R_1 = 0.058$, $wR_2 = 0.122$
R indices (all data)	$R_1 = 0.081$, $wR_2 = 0.140$	$R_1 = 0.096$, $wR_2 = 0.138$

insertion of **1** into the resulting intermediate, is already well documented [5]. A reaction as its dimer (**1**)$_2$ is ruled out, since **1** is monomeric both in solution and in the solid state [3,11].



VII



VIII

As for the transformation **2** → **3** (but not **4**), the instability of **2** is probably a result of the driving force for the rearomatisation of the pyridine ring via 1,3-H migration; quinoline has less aromatic stabilisation than pyridine. Likewise, the partial dissociation of **2** into its factors in solution is also attributed to the drive for rearomatisation of the pyridine ring [14].

A similar product to **4** has been reported, obtained by reaction of tetra-*tert*-butyldisilene and isoquinoline leading to the 1-aza-2,3-disiletane derivative **VIII** [12]. Transient silylenes are also known to give interesting new products with organic substrates containing a CN multiple bond, as has recently been summarised [7,9].

3. Experimental

All operations and manipulations were carried out under purified argon, by conventional Schlenk techniques. Solvents were dried and degassed before use. The NMR spectra were recorded in benzene-d_6 or toluene-d_8 using Bruker Instruments: Bruker DPX 300 (^1H and ^{13}C) and AMX 500 (^1H and ^{29}Si), and referenced internally to residual solvent resonances or externally (^{29}Si) to $SiMe_4$ (data in δ). Microanalyses were carried out by Medac Ltd. (Brunel University). Electron impact mass spectra were taken from solid samples using a Kratos MS 80 RF instrument. Melting points were taken in sealed capillaries and are uncorrected.

3.1. Preparation of **2**

A solution of **1** (0.32 g, 1.17 mmol) in benzene (10 ml) was slowly added to a solution of pyridine (0.1 ml) in benzene (10 ml). After stirring for 16 h, the solvent was removed in vacuo and the remaining solid was dissolved in *n*-hexane. Cooling at −25 °C afforded 0.28 g (76.5 % yield) of yellow crystals of **2**; m.p. 101–103 °C. ^1H NMR ($CD_3C_6D_5$, 500 MHz, 298 K): δ 0.86, 0.97, 0.98 and 1.0 (4 s, 36 H, CH_3), 2.99–3.67 (m, 8 H, CH_2), 3.79 (br s, 1 H, SiCH), 5.22–5.25 (m, 2 H, 2× CH), 5.79 (sept, 1 H, CH), 6.47 (br d, 1 H, CH), 6.61–6.77 (m, 8 H, phenyl). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.46 MHz, 293 K): δ 29.3, 29.6 and 29.9 (CMe_3), 34.1, 34.4, 34.7 and 34.9 (CMe_3), 53.2 and 56.1 (br, CH_2), 50.4 (SiCH), 109.5, 109.8, 111.0, 117.7, 118.0, 118.5, 124.9, 135.8, 140.1 and 140.5 (phenyl). $^{29}Si\{^1H\}$ NMR ($CD_3C_6D_5$, 99.33 MHz, 293 K): δ 0.8 and 33.1 (br). The solution of **2** also showed signals of the parent silylene **1** and pyridine.

3.2. Preparation of **3**

Compound **2** (0.23 g, 0.367 mmol) was dissolved in benzene (10 ml) and heated at 70 °C for 2 days. The solvent was removed in vacuo and the remaining solid was recrystallised from *n*-hexane/benzene to afford 0.16 g (69.6% yield) of yellow crystals of **3**; m.p. 143–145 °C. ^1H NMR (C_6D_6, 300 MHz, 293 K): δ 0.72 (s, 18 H, CH_3), 1.04 (s, 18 H, CH_3), 2.88, 2.93, 2.97 and 3.02 (AB-type, 4 H, CH_2), 3.09, 3.14, 3.2 and 3.25 (AB-type, 4 H, CH_2), 6.6–6.94 (m, 8 H, phenyl) 7.14–7.18 (m, 3 H, pyridyl), 8.58 (dt, 1 H, NCH) and 7.12 (s, 1 H, SiH, $^1J_{HSi}$ 230.9 Hz, $^2J_{HSi}$ 39.84 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.46 MHz, 293 K): δ 28.5 and 28.8 (CMe_3), 33.5 and 35.4 (CMe_3), 54.3 and 57.5 (CH_2), 109.2, 109.8, 117.4, 118.3, 142.1 and 142.9 (phenyl), 124.7, 131.1, 134.7 and 149.4 (pyridyl). $^{29}Si\{^1H\}$ NMR (C_6D_6, 99.33 MHz, 293 K): δ −7.0 ($^1J_{SiH}$ 229.2 Hz), −7.3 ($^2J_{SiH}$ 40.9 Hz). MS *m*/*z* (%) = 627 (43) [M^+]. Anal. Calc. for $C_{37}H_{57}N_5Si_2$ (628.05): C, 70.76; H, 9.15; N, 11.15. Found: C, 70.1; H, 8.98; N, 11.32%.

3.3. Preparation of **4**

Quinoline (0.112 ml, 0.95 mmol) was added to a solution of **1** (0.26 g, 0.95 mmol) in benzene (20 ml) and stirred over night at ambient temperature. The solvent was removed in vacuo and the remaining solid was dissolved in *n*-hexane, filtered and cooled to −25 °C to afford 0.28 g (87.5 % yield) of yellow crystals of **4**; m.p. 165–167 °C. ^1H NMR ($CD_3C_6D_5$, 500 MHz, 228 K): δ 0.81, 0.86 (2 s, 18 H, CH_3), 1.03 (s, 18 H, CH_3), 2.84, 2.87, 3.03, 3.06, 3.11, 3.14, 3.17, 3.22, 3.25, 3.34 and 3.37 (AB-type overlapped, 8 H, CH_2), 4.48 (s, 1 H, SiCH), 5.95 (d, 1 H, CH) and 6.11 (d, 1 H, CH), 6.52–7.08 (m, 14 H, phenyl). $^{13}C\{^1H\}$ NMR ($CD_3C_6D_5$, 75.46 MHz, 293 K): δ 28.7, 29.0, 29.4 and 30.1 (CMe_3), 34.0, 34.5, 34.7 and 35.0 (CMe_3), 51.4 (SiCH), 53.1, 55.1, 56.7 and 57.1 (CH_2), 109.6, 110.1, 110.6, 111.0, 117.7, 118.0, 118.2, 119.7, 121.8, 125.1, 126.2, 126.4, 127.0, 127.5, 128.3, 139.9, 140.8, 141.1 and 144.3. $^{29}Si\{^1H\}$ NMR ($CD_3C_6D_5$, 99.33 MHz, 298 K): δ −1.7 and 33.5. MS *m*/*z* (%) = 677 (10) [M^+]. Anal. Calc. for $C_{41}H_{59}N_5Si_2$ (678.11): C, 72.6; H, 8.77; N, 10.33. Found: C, 71.9; H, 8.43; N, 10.59%.

3.4. X-ray structure determinations for the complexes **2** and **3**

Data for the crystal structure determinations were collected on a Kappa CCD diffractometer at 173(2) K using monochromated Mo-Kα radiation (λ 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL 97 [13], with all non-H atoms anisotropic; for **3** the H atom on Si(2) was freely refined. Crystal data and refinement details are listed in Table 2 .

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data centre, CCDC No. 223698 for compound **2**, CCDC No. 223699 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

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[14] A reviewer pointed out that the transformation **2** → **3** might be base catalysed. This cannot be ruled out due to partial dissociation of **2** into the silylene and pyridine.