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Silicon Compounds with Strong Intramolecular Steric Interactions. 52.[1] Unexpected Rearrangement of Silylene Insertion into Cycloaddition Products[†]

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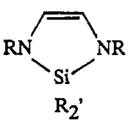
Summary: Photolysis of hexamethyl-2,2-dimesityltrisilane in the presence of N-mesitylpyridine-2-aldimine (**3**) *gives the silylene C–H insertion product* **4a** *together with the [4 + 1] cycloaddition product* **5a**. *Heating of neat* **4a** *as well as of the sterically more encumbered N-2,6-diisopropylphenyl derivative* **4b** *leads to an unexpected rearrangement of the C–H insertion products into the 1,3-diaza-2-silacyclo-4-pentene derivatives* **5a,b**. *The X-ray structure analysis of* **5a** *shows that the heteroaromatic ring of* **3** *has been converted into a system of conjugated double bonds.*

1,4-Diheterodienes, for example 1,4-diazabutadienes or 2,2′-bipyridyl (bpy), react with silylenes containing electron-releasing groups to give the formal [4 + 1] cycloaddition products **1** and **2**. While the formation of **1**[2] presumably takes place in a manner analogous to the well-known trapping reactions with buta-1,3-dienes,[3] the reaction of bpy with silylenes cannot be interpreted so easily. The NMR data and the violet colors, which are reflected in the longest wavelength absorptions of ~560 nm, as well as the extreme air sensitivity are indicative of structure **2**,[4] in which the heteroaromatic rings of bpy have been converted into a system of conjugated double bonds. Nevertheless, a Lewis acid–base adduct[5] resulting from the respective silylene and the nitrogen atoms of the bidentate bpy ligand cannot be completely excluded. Unfortunately, we have been unable to obtain crystals of the ring system **2** suitable for an X-ray structure analysis to date. There is an X-ray structure determination available for the related bis(2,2′-bipyridyl)silane.[6] However, it is not clear how this compound is formed during the sublimation of Si(bpy)$_3$.[7]



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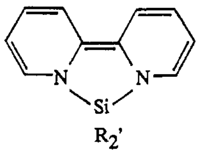

2

In order to obtain more information about the formation and structures of these ring systems, analogous reactions were carried out using pyridine-2-aldimines **3**. As opposed to bpy, these imines contain only one heteroaromatic ring, but they do make possible a wide variation of the substituents on the acyclic nitrogen atom. While in the presence of aliphatic groups only unstable [4 + 1] cycloadducts are obtained in most cases,[8] the photolysis of hexamethyl-2,2-dimesityltrisilane[9] and **3a** in *n*-pentane yielded a red solution from which 20% of red **5a**[10] was isolated, upon cooling to −30 °C. After prolonged cooling at −30 °C, 37% of yellow **4a**[10] was obtained.

Replacement of the mesityl groups by the bulkier *N*-2,6-diisopropylphenyl groups resulted in the formation of both the CH insertion product **4b**[8] (31%) and the cycloadduct **5b**[11] (23%).

[†] Dedicated to Professor Otto J. Scherer on the occasion of his 60th birthday.

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(5) Gillette, G. R.; Noren, G. H.; West, R. *Organometallics* **1989**, *8*, 487 and references cited therein.

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(9) Fink, M. J.; Michalczyk, M. J.; Haller, K. J.; West, R.; Michl, J. *Organometallics* **1984**, *3*, 793.

(10) **4a**: yellow solid; mp 131 °C (beginning rearrangement); ^{1}H NMR (300 MHz, C_6D_6) δ 1.99 (s, 3H, *p*-CH_3), 2.10 (s, 3H, *o*-CH_3), 2.13 (s, 3H, *o*-CH_3), 2.34 (broad, 6H, *o*-CH_3), 2.57 (broad, 12H, *o*-CH_3), 6.29 (s, 1H, SiH), 6.48 (broad, 1H), 6.64 (broad, 1H), 6.70 (s, 4H, Mes H), 6.76 (s, 2H, Mes H), 6.89 (broad, 1H), 8.18 (broad, 1H); ^{13}C NMR (75.44 MHz, C_6D_6) δ 18.45, 20.75, 21.11, 24.45, 121.07, 123.61, 123.94, 124.94, 126.96, 129.16, 129.30, 131.17, 133.31, 136.18, 138.89, 144.77, 149.75, 183.35 (SiCN); IR (KBr) ν 2168 (SiH) cm^{-1}; mass spectrum (EI/70 eV) *m/z* 490 (M^+, 100 %); UV–vis λ (ϵ) 270 (6570), 410 (530) nm. Anal. Calcd for $C_{33}H_{38}N_2Si$: C, 80.77; H, 7.80; N, 5.71. Found: C, 80.49; H, 7.80; N, 5.53. **5a**: red solid; mp 210 °C (sublimes); ^{1}H NMR (300 MHz, C_6D_6) δ 2.03 (s, 6H, *p*-CH_3), 2.08 (s, 6H, *o*-CH_3), 2.09 (s, 3H, *p*-CH_3), 2.39 (s, 12H, o-CH_3), 5.04 (H5, dd, 1H, $^3J_{H4,H5}$ = 6.5 Hz; $^3J_{H5,H6}$ = 6.5 Hz), 5.48 (H7, s, 1H), 5.60 (H4, dd, 1H, $^3J_{H3,H4}$ = 9.5 Hz), 6.05 (H3, d, 1H), 6.11 (H6, d, 1H), 6.64 (s, 2H, Mes H), 6.71 (s, 4H, Mes H); ^{13}C NMR (75.44 MHz, C_6D_6) δ 19.11, 20.97, 24.21, 24.46, 103.96 (C5), 110.32 (C7), 119.32 (C4), 119.76 (C3), 122.25 (C2), 129.44, 129.75, 132.84 (C6), 134.96, 136.64, 138.05, 139.77, 144.23, 144.42; IR (KBr) ν 1605 s, 1588 m (C=C) cm^{-1}; mass spectrum (CI, isobutane) *m/z* 491 (MH^+, 100 %); UV–vis (*n*-hexane) λ 448, 473, 505, 546 nm.

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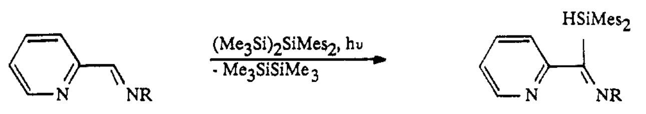
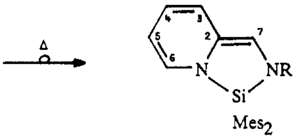


3a, b

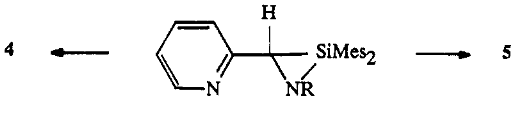
4a, R = Mes
4b, R = 2,6-iPr$_2$C$_6$H$_3$

4a, b



5a, R = Mes
5b, R = 2,6-iPr$_2$C$_6$H$_3$

The simultaneous formation of the isomeric compounds 4 and 5 during photolysis indicates that they probably result from common intermediates. In the first step dimesitylsilylene presumably reacts with the acyclic CN double bond in a [2 + 1] fashion to provide the azasilacyclopropane derivatives 6, which can easily be rearranged to give CH insertion products 4 or the formal [4 + 1] cycloaddition products 5.



6

The reactions of 2,3-dimethylbutadiene with methylphenylsilylene[12] and diphenylsilylene[13] proceed similarly to give an intermediate silacyclopropane which subsequently rearranges to yield two isomeric products as well. Unlike 6, this intermediate does not contain a hydrogen atom in the direct vicinity of the silicon atom and, therefore, the subsequent reaction must proceed via a somewhat different mechanism.

When **4a** is heated to temperatures above its melting point, the color changes from yellow to red, which indicates that a rearrangement is taking place. Under these conditions, the spectral data[10] show that **4a** unexpectedly rearranges to form the isomeric compound **5a**, which is isolated in 70% yield along with decomposition products. It can be assumed that, at elevated temperatures, the equilibrium between 4, 5, and 6 is irreversibly shifted in the direction of the five-membered ring, which is presumably thermodynamically favored. Similarly, upon heating of **4b** to ca. 200 °C the rearranged compound **5b** is isolated in 53% yield.

However, attempts to rearrange **4a** or **4b** into **5a** or **5b** by means of photolysis were unsuccessful. In both cases the starting materials were almost quantitatively recovered.

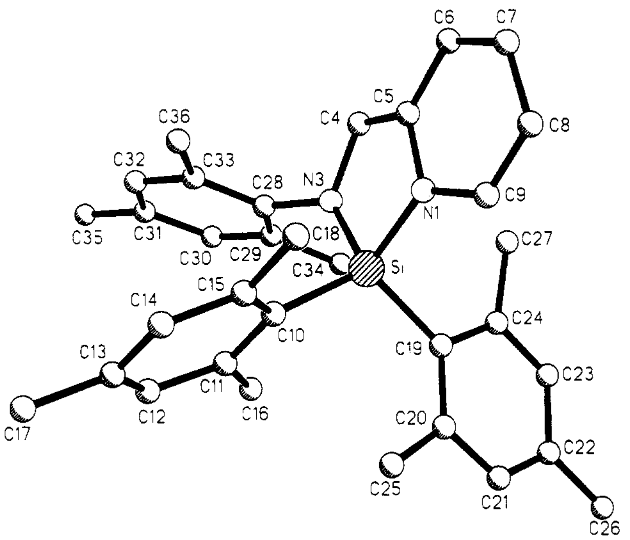


Figure 1. Molecular structure of **5a** in the crystal (hydrogen atoms omitted). Selected bond lengths (Å) and bond angles (deg): Si–N1 = 1.759(4), Si–N3 = 1.762(3), N3–C4 = 1.419(5), C4–C5 = 1.348(6), C5–C6 = 1.433(6), C6–C7 = 1.330(8), C7–C8 = 1.436(9), C8–C9 = 1.344(7), C9–N1 = 1.363(6); C10–Si–C19 = 113.2(2), N1–Si–N3 = 90.0(2).

A slow sublimation of **5a** produced very air-sensitive single crystals whose X-ray structure analysis[14] not only establishes the structure of the bicyclic compounds **5** but also indirectly the structure of the bpy adducts **2** (Figure 1).

As expected, silylene addition to **3** does not form a Lewis acid–base adduct; rather, the heteroaromatic ring of **3a** is converted into a system of conjugated double bonds with loss of two π electrons. The average bond lengths of d = 1.345 Å for the double bonds and d = 1.435 Å for the single bonds are typical for a system of alternating double and single bonds. Within the five-membered ring both nitrogen atoms have a nearly planar environment (sum of angles 359.6° for N1 and 355.8° for N3), thereby enforcing a narrow N–Si–N angle of 90° and slightly elongated Si–N distances.[2,15] This structure determination also provides clues as to the cause of the dark colors of the ring systems **2** and **5** as well as the cause of the black color of Si(bpy)$_2$.[6] Obviously, these colors result from one (**5**) or two (**2**) o-quinonoid rings in connection with the sila substitution.

Acknowledgment. Financial support from the Volkswagen-Stiftung, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supplementary Material Available: Tables of crystal data, atomic coordinates and isotropic displacement coefficients, bond lengths, bond angles, and anisotropic displacement coefficients and figures for **5a** (10 pages). Ordering information is given on any current masthead page.

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[11] **5b**: red solid; mp 218–221 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 0.66 (d, 6H, iPr CH$_3$, $^3J_{H,H}$ = 6.7 Hz), 1.23 (d, 6H, iPr-CH$_3$, $^3J_{H,H}$ = 6.7 Hz), 2.00 (s, 6H, p-CH$_3$), 2.27 (broad, 12H, o-CH$_3$), 3.22 (broad, 2H, iPr CH), 4.99 (H5, ddd, 1H, $^3J_{H5,H4}$ = 7.2 Hz, $^3J_{H5,H6}$ = 5.7 Hz, $^4J_{H5,H3}$ = 1.2 Hz), 5.54 (H4, ddd, 1H, $^3J_{H4,H3}$ = 9.6 Hz, $^4J_{H4,H6}$ = 0.9 Hz), 5.65 (H7, s, 1H), 5.98 (H3, dd, 1H), 6.05 (H6, dd, 1H), 6.62 (s, 4H, Mes H), 6.93–7.14 (m, 3H); ^{13}C NMR (75.44 MHz, C_6D_6) δ 20.93, 22.05, 24.35, 27.12, 28.74, 104.20 (C5), 112.62 (C7), 119.50 (C4), 123.61 (C3), 125.18, 126.09, 126.81, 129.86, 132.74 (C6), 139.81, 141.41, 144.44, 148.57; IR (KBr) ν 1603 s, 1591 m (C=C) cm^{-1}; mass spectrum (EI/70 eV) m/z 532 (M$^+$, 100 %); UV-vis (n-hexane) λ (ε) 448 (1300), 473 (1290), 502 (910), 543 (330) nm. Anal. Calcd for $C_{36}H_{44}N_2Si$: C, 81,15; H, 8.32; N, 5.26. Found: C, 80.77; H, 8.25; N, 5.14.

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[14] Crystallographic data for **5a**: $C_{33}H_{38}N_2Si$, mol wt 490.76, orthorhombic, space group $Pbca$, a = 17.468(4) Å, b = 19.514(4) Å, c = 16.625(4) Å, V = 5667(2) Å^3, Z = 8, d_{calcd} = 1.150 g cm^{-3}, $\lambda_{Mo\ K\alpha}$ = 0.710 73 Å, μ = 0.11 mm^{-1}. The data (7168 reflections, 6516 unique) were collected at 23 °C on a Siemens R3m/V diffractometer using the Wyckoff scan mode (θ_{max} = 27.5°), and an empirical absorption correction was applied. The structure was solved by direct phase determination and refined by full-matrix least squares using 3672 reflections with $F > 3\sigma(F)$ to R = 0.080, R_w = 0.067, and GOF = 2.31. All non-hydrogen atoms were refined anisotropically. All calculations were performed on a MicroVAX II computer using Siemens SHELXTL PLUS.

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