Organometallics **1994,** *13,* 3990−3994

Silicon Compounds with Strong Intramolecular Steric Interactions. 55.[1] Reactions of Sterically Encumbered Silylenes with Pyridine-2-carbaldimines: Cycloadditions versus CH Insertions[†]

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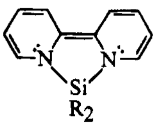
Received May 16, 1994[⊗]

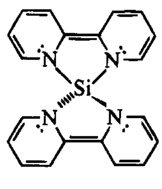
N-Mesitylpyridine-2-carbaldimine reacts with photochemically generated dimesitylsilylene by insertion into the C−H bond of the acyclic >C=N− group to provide the (pyridin-2-yl)-1-silaethane derivative **3**, which is isolated together with the (pyridine-2-carbaldimine-*N,N′*)silicon species **4** as the formal [4 + 1] cycloaddition product. Treatment of *N*-(2,6-diisopropylphenyl)pyridine-2-carbaldimine (**5**) with the sterically more encumbered bis(2,4,6-triisopropylphenyl)silylene gives the C−H insertion product 2-((2,6-diisopropylphenyl)imino)-1,1-bis(2,4,6-triisopropylphenyl)-2-(pyridin-2-yl)-1-silaethane (**7**) almost exclusively. Upon heating, the insertion products **3** and **7** rearrange to the corresponding substituted (pyridine-2-carbaldimine-*N,N′*)silicon compounds **4** and **8**. The structures of the isomeric compounds **7** and **8** have been determined by X-ray crystallography. The molecular structure of **8** shows not only that the heteroaromatic ring of **5** has been converted into a system of conjugated double bonds but also that **8** is considerably more strained than the insertion product **7**.

Introduction

Reactions of silylenes with 2,2′-bipyridyl (bpy) give rise to the violet (bipyridyl-*N,N′*)silicon species **A**, in which the heteroaromatic rings of bpy have been transformed into a system of conjugated double bonds.[2]



A



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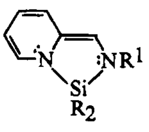

C

This conversion is supported by the NMR data, the dark colors of the products with absorptions at longest wavelength around 560 nm, and the extreme sensitivity of the compounds to air. Attempts to obtain compounds of type **A** in crystalline form suitable for X-ray crystallographic analysis have as yet been unsuccessful because of the high tendency for the formation of twins. Although an X-ray analysis of the related bis(2,2′-bipyridyl)silicon compound **B** has been reported,[3] it has not yet been clarified how this compound could be formed upon sublimation of the insufficiently characterized Si(bpy)$_3$.[4]

Thus, we selected the adducts **C** from silylenes and pyridine-2-carbaldimines as model compounds for the (2,2′-bipyridyl)silicon species **A**; the heteroaromatic rings of compounds **C** have also been transformed into a system of conjugated double bonds. In a short communication, we have reported recently on the X-ray analysis of such a ring system and on the always occurring competitive silylene insertion reaction into the C−H bond of the acyclic −CH=NR group.[5] An insertion product of this type was isolated for the first time in low yield from the reaction of dimesitylsilylene with the pyridine-2-carbaldimine **5**.[6] However, it was not pos-

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[†] Dedicated to Professor Hubert Schmidbaur on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

[1] Part 54: Weidenbruch, M.; Hockemeyer, J.; Peters, K.; von Schnering, H. G. *Z. Anorg. Allg. Chem.* **1994**, *620*, 1163.

[2] (a) Mikulski, C. M.; MacDiarmid, A. G. Unpublished results. Cited in: MacDiarmid, A. G. *Intra-Sci. Chem. Rep.* **1973**, *7*, 83. (b) Weidenbruch, M.; Schäfer, A.; Marsmann, H. *J. Organomet. Chem.* **1988**, *354*, C12. (c) Weidenbruch, M.; Lesch, A.; Marsmann, H. *J. Organomet. Chem.* **1990**, *385*, C47.

[3] Morancho, R.; Pouvreau, P.; Constant, G.; Joud, J.; Galy, J. *J. Organomet. Chem.* **1979**, *166*, 329.

[4] Herzog, S.; Krebs, F. *Naturwissenschaften* **1963**, *50*, 300.

[5] Weidenbruch, M.; Piel, H.; Peters, K.; von Schnering, H. G. *Organometallics* **1993**, *12*, 2881.

[6] Weidenbruch, M.; Piel, H.; Lesch, A.; Peters, K.; von Schnering, H. G. *J. Organomet. Chem.* **1993**, *454*, 35.

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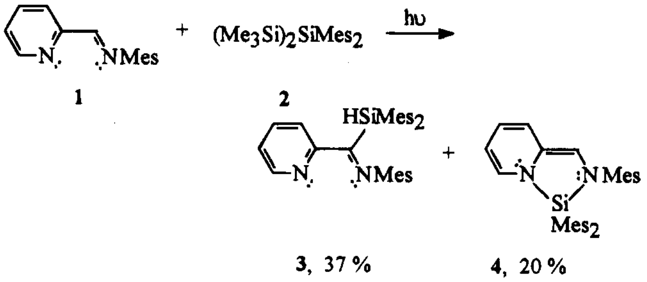
sible to obtain evidence for the coformation of the [4 + 1] adduct.

In order to obtain more information about these unusual reactions of silylenes, we have allowed the pyridine-2-carbaldimines **1** and **5** to react with dimesitylsilylene and the sterically more encumbered bis(2,4,6-triisopropylphenyl)silylene. We now report on the product spectra obtained in each case and on the thermal isomerizations of the silylene insertion products.

Results and Discussion

A. Reaction of Dimesitylsilylene with *N*-Mesitylpyridine-2-carbaldimine (1). A solution of **1** and 2,2-dimesitylhexamethyltrisilane (**2**)[7] was irradiated until **2** could no longer be detected. The resultant red solution was subjected to fractional crystallization, and a red solid was isolated first. According to its spectroscopic data as well as an X-ray analysis,[5] this was identified as the formal [4 + 1] cycloadduct **4**. The product **3** of the silylene insertion reaction into the C—H bond of the acyclic —CH=CN— group was obtained as a yellow, crystalline second fraction.



1 2 3, 37 % 4, 20 %

Mes = 2,4,6-$Me_3C_6H_2$

The simultaneous formation of the isomeric compounds **3** and **4** was suggestive of a common intermediate which can furnish either the insertion product **3** or the formal [4 + 1] cycloaddition product **4**. For the purpose of obtaining more information about this putative intermediate, we then increased the spatial requirements of both the *N*-bonded substituent and the two aryl groups of the silylene.

B. Reaction of Bis(2,4,6-triisopropylphenyl)-silylene with *N*-(2,6-Diisopropylphenyl)pyridine-2-carbaldimine (5). As a silylene with bulky groups, bis(2,4,6-triisopropylphenyl)silylene, first mentioned by Ando et al.[8] and accessible by photolysis of the trisilane **6**, seemed attractive. Recently, West and co-workers[9] described the preparation of **6** in good yield from silicon tetrafluoride and (2,4,6-triisopropylphenyl)lithium with subsequent coupling of the diaryldifluorosilane with chlorotrimethylsilane and lithium. Since silicon tetrachloride is much easier to handle than the tetrafluoride, we performed a similar sequence of reactions starting from the chloride and also obtained **6** in good to very good yield (see Experimental Section).

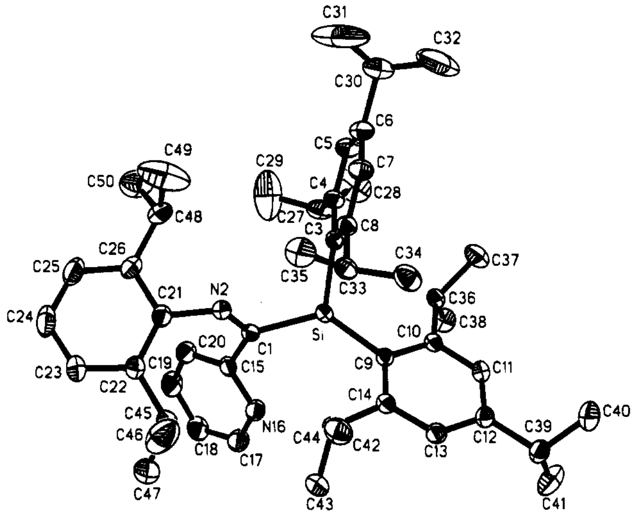
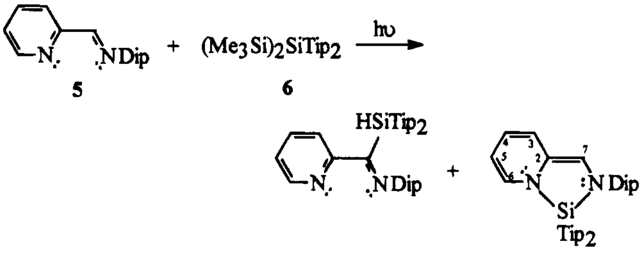


Figure 1. ORTEP drawing and labeling scheme for **7** (hydrogen atoms omitted). Ellipsoids are drawn at 30% probability.



5 6 7, 80 % 8, trace

Dip = 2,6-*i*$Pr_2C_6H_3$; Tip = 2,4,6-*i*$Pr_3C_6H_2$

Photolysis of **6** in the presence of **5** gave rise to a light red solution from which the yellow silylene insertion product **7** was isolated in 80% yield. The absorption at longest wavelength of the remaining mother liquor at approximately 550 nm indicated the presence of traces of the cycloadduct **8**, but its isolation was not possible.

The structure of **7** was substantiated by IR and ^1H and ^{13}C NMR spectroscopy as well as X-ray crystallography (Figure 1, Tables 1 and 2). The Si—C bond length is hardly lengthened in comparison to the normal value of 187 pm, while the C(1)—Si—C(9) angle of the diarylsilylene unit is considerably widened. Because of this large angle widening associated with a propeller-like arrangement of the bulky aryl groups, interactions between the *o*-alkyl substituents are almost completely avoided and a practically strain-free conformation is achieved.

The most striking result from the reaction of **5** with **6** is the unambiguous preference for the C—H insertion product **7** over the formal [4 + 1] cycloaddition product **8**, which could only be detected in trace amounts. Since compound **8** is presumably highly strained and obviously not accessible by this route, we attempted—in analogy to the previously reported[5] thermal isomerization of **3** to **4**—to convert the insertion product **7** into **8**.

C. Thermal Rearrangement of 3 and 7. When it was heated to temperatures above its melting point, **3** underwent slow rearrangement to the isomeric product

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[8] Ando, W.; Fujita, M.; Yoshida, H.; Sekiguchi, A. *J. Am. Chem. Soc.* **1988**, *110*, 3310.

[9] Millevolte, A. J.; Powell, D. R.; Johnson, S. G.; West, R. *Organometallics* **1992**, *11*, 1091.

Table 1. Atomic Parameters ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($pm^2 \times 10^{-1}$) for 7

	x	*y*	*z*	U_{eq}
Si	887(1)	8164(1)	329(1)	39(1)
C(1)	1397(1)	7840(1)	−738(2)	41(1)
N(2)	1798(1)	7328(1)	−421(2)	46(1)
C(3)	756(1)	7376(1)	1289(2)	41(1)
C(4)	183(1)	6967(2)	1045(3)	49(1)
C(5)	93(1)	6449(2)	1861(3)	60(1)
C(6)	530(1)	6308(2)	2902(3)	59(1)
C(7)	1094(1)	6688(2)	3123(3)	57(1)
C(8)	1216(1)	7215(1)	2341(2)	45(1)
C(9)	1062(1)	9010(1)	1266(2)	39(1)
C(10)	559(1)	9250(1)	1783(2)	41(1)
C(11)	639(1)	9861(2)	2489(2)	50(1)
C(12)	1193(1)	10257(2)	2729(2)	47(1)
C(13)	1678(1)	10024(2)	2220(2)	49(1)
C(14)	1627(1)	9413(1)	1500(2)	44(1)
C(15)	1211(1)	8147(2)	−1982(2)	47(1)
N(16)	1201(1)	8859(1)	−2000(2)	59(1)
C(17)	1045(2)	9179(2)	−3074(3)	70(1)
C(18)	872(2)	8814(2)	−4136(3)	73(1)
C(19)	855(2)	8081(2)	−4108(3)	75(1)
C(20)	1034(1)	7741(2)	−3012(3)	59(1)
C(21)	2112(1)	6982(2)	−1249(2)	49(1)
C(22)	2575(1)	7332(2)	−1732(3)	56(1)
C(23)	2852(2)	6943(2)	−2514(3)	75(1)
C(24)	2692(2)	6248(2)	−2801(4)	94(2)
C(25)	2260(2)	5910(2)	−2285(3)	83(2)
C(26)	1964(2)	6258(2)	−1495(3)	60(1)
C(27)	−340(2)	7063(2)	−90(3)	70(1)
C(28)	−989(2)	7072(3)	117(4)	134(3)
C(29)	−301(2)	6524(3)	−992(4)	184(3)
C(30)	401(2)	5751(2)	3776(3)	80(2)
C(31)	828(2)	5166(3)	3927(6)	233(5)
C(32)	376(3)	6070(3)	4943(4)	175(4)
C(33)	1855(1)	7587(2)	2669(2)	49(1)
C(34)	1934(2)	8022(2)	3827(3)	76(1)
C(35)	2401(1)	7064(2)	2749(3)	80(2)
C(36)	−82(1)	8879(2)	1566(2)	46(1)
C(37)	−254(2)	8643(2)	2729(3)	75(1)
C(38)	−600(1)	9338(2)	797(3)	69(1)
C(39)	1260(1)	10934(2)	3480(3)	57(1)
C(40)	1151(2)	10809(2)	4716(3)	95(2)
C(41)	838(2)	11520(2)	2832(3)	98(2)
C(42)	2197(1)	9228(2)	979(3)	50(1)
C(43)	2295(1)	9795(2)	75(3)	64(1)
C(44)	2806(1)	9123(2)	1948(3)	71(1)
C(45)	2799(2)	8084(2)	−1393(3)	65(1)
C(46)	3436(2)	8077(2)	−558(4)	123(2)
C(47)	2808(2)	8541(2)	−2486(4)	121(2)
C(48)	1494(2)	5871(2)	−912(3)	71(1)
C(49)	1814(2)	5460(3)	152(4)	175(3)
C(50)	1042(2)	5393(2)	−1735(4)	115(2)

Table 2. Selected Bond Lengths (pm) and Angles (deg) for 7

Si—C(1)	191.7(3)	Si—C(3)	189.4(3)
Si—C(9)	189.8(3)	C(1)—N(2)	128.7(3)
C(1)—Si—C(3)	107.7(1)	C(3)—Si—C(9)	111.0(1)
C(1)—Si—C(9)	123.4(1)	Si—C(1)—N(2)	120.3(2)

4, as could be seen from the color change from yellow to red. At 200 °C the rearrangement is complete within 1 h and 4 can be isolated in 70% yield together with small amounts of decomposition products.

$$3 \xrightarrow{\Delta} 4,\ 70\,\% \qquad 7 \xrightarrow{\Delta} 8,\ 10\,\%$$

The analogous rearrangement of 7 proved to be more difficult and did not occur at an appreciable rate below 230 °C. However, this high temperature also caused considerable decomposition of 8. The red, very air-sensitive crystals of pure 8 were obtained in 10% yield by vacuum sublimation from the reaction mixture; this was also accompanied by decomposition reactions.

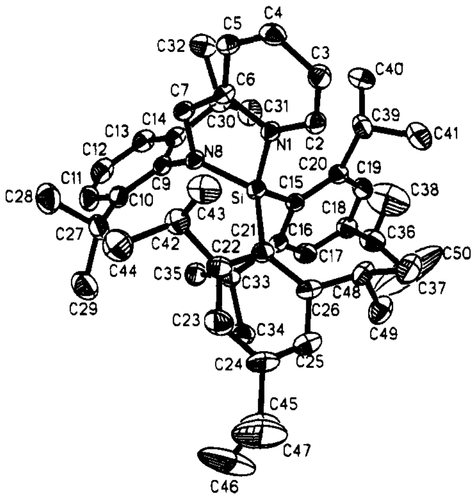

Figure 2. ORTEP drawing and labeling scheme for **8** (hydrogen atoms omitted). Ellipsoids are drawn at 30% probability.

The assumed steric overloading in **8** was immediately confirmed by the ^1H NMR spectrum, in which all isopropyl methyl groups appeared as separate doublets, thus indicating a restriction of free rotation not only about the Si—C bonds but also about the C—C bonds.

The X-ray structure analysis of **8** provided further insights into the steric congestion of the molecule by the three bulky aryl groups (Figure 2, Tables 3 and 4). Although, similar to 7, the Si—C bond lengths are hardly lengthened, the angle between the *ipso* carbon atoms of the aryl rings and the silicon atom has been reduced from 123.4° in 7 to 109.1° in **8** upon addition of the diarylsilylene to the two nitrogen atoms. This is probably the reason for the observed hindered rotation of the isopropyl groups.

Furthermore, the molecular structure of **8** indicated that the heteroaromatic ring of **5** has been transformed into a system of conjugated double bonds by the silylene addition. The average bond lengths of 134 pm for the double bonds and 143 pm for the single bonds are typical for systems of alternating single and double bonds. The angular sums of 359° for N(1) and 358° for N(2) show that both nitrogen atoms have practically planar environments and thus inevitably create the acute N—Si—N angle of 89.7° and the slightly stretched Si—N bond lengths.[10] Spectra of solutions as well as the crystal structure of **8** demonstrate that the practically strain-free compound **7** is favored over the isomer **8**. In harmony with this, the reaction of **5** with **6** furnishes almost exclusively **7**, from which **8** can only be obtained under drastic reaction conditions.

The putative intermediate which should arise during the simultaneous formation of **3** and **4** as well as in the thermal isomerization could be an unstable Lewis acid–base adduct of the type **9** formed by interactions between the free electron pair of the imine nitrogen atom and the silylene. Adducts between silylenes with bulky substituents and various amines were recently detected in matrices.[11] In such a case, the rate at which the respective pyridine-2-carbaldimine adduct changes from the preferred *transoid* conformation into the *cisoid*

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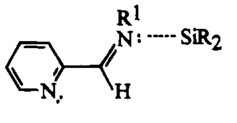
Table 3. Atomic Parameters (×10^4) and Equivalent Isotropic Displacement Coefficients (pm^2 × 10^{-1}) for 8

	x	y	z	U_{eq}
Si	2043(1)	1207(1)	320(1)	44(1)
N(1)	1242(2)	1340(1)	1111(2)	45(1)
C(2)	1154(2)	1766(1)	1928(3)	55(1)
C(3)	564(2)	1785(2)	2592(4)	62(2)
C(4)	−8(2)	1349(2)	2471(4)	63(2)
C(5)	68(2)	926(2)	1727(3)	57(1)
C(6)	704(2)	889(1)	1027(3)	48(1)
C(7)	910(2)	482(2)	308(3)	52(1)
N(8)	1596(1)	583(1)	−234(2)	44(1)
C(9)	1649(2)	236(1)	−1310(3)	50(1)
C(10)	2126(2)	−232(2)	−1156(4)	60(2)
C(11)	2125(3)	−576(2)	−2189(5)	76(2)
C(12)	1674(3)	−463(2)	−3333(5)	79(2)
C(13)	1200(2)	−6(2)	−3474(4)	67(2)
C(14)	1177(2)	356(2)	−2481(3)	55(1)
C(15)	2214(2)	1621(1)	−1094(3)	45(1)
C(16)	2832(2)	1456(1)	−1747(3)	51(1)
C(17)	2992(2)	1770(2)	−2758(3)	62(2)
C(18)	2579(2)	2235(2)	−3167(4)	63(2)
C(19)	1972(2)	2386(2)	−2550(4)	63(2)
C(20)	1773(2)	2097(1)	−1552(3)	53(1)
C(21)	2956(2)	1262(2)	1613(3)	51(1)
C(22)	3150(2)	837(2)	2528(3)	59(1)
C(23)	3897(3)	836(2)	3283(4)	79(2)
C(24)	4447(2)	1249(2)	3237(4)	84(2)
C(25)	4219(2)	1687(2)	2483(4)	76(2)
C(26)	3482(2)	1719(2)	1691(3)	59(1)
C(27)	2585(2)	−404(2)	102(4)	71(2)
C(28)	2172(3)	−887(2)	611(5)	98(2)
C(29)	3451(3)	−552(2)	69(5)	105(2)
C(30)	615(2)	838(2)	−2713(3)	60(1)
C(31)	731(3)	1166(2)	−3875(4)	83(2)
C(32)	−246(2)	658(2)	−2821(4)	86(2)
C(33)	3338(2)	945(1)	−1406(3)	55(1)
C(34)	4200(2)	1077(2)	−849(4)	74(2)
C(35)	3317(2)	569(2)	−2546(4)	70(2)
C(36)	2785(3)	2564(2)	−4256(5)	89(2)
C(37)	3293(5)	2967(4)	−3957(7)	442(10)
C(38)	2107(4)	2775(3)	−5100(6)	194(5)
C(39)	1081(2)	2323(2)	−983(4)	64(2)
C(40)	314(2)	2343(2)	−1945(4)	90(2)
C(41)	1250(3)	2888(2)	−425(5)	103(2)
C(42)	2526(2)	440(2)	2848(4)	66(2)
C(43)	2104(3)	702(2)	3832(4)	86(2)
C(44)	2855(3)	−114(2)	3350(4)	99(2)
C(45)	5265(3)	1216(3)	4052(5)	118(3)
C(46)	5801(3)	912(3)	3527(7)	225(5)
C(47)	5286(3)	1206(3)	5362(6)	180(4)
C(48)	3258(2)	2272(2)	1116(4)	64(2)
C(49)	3811(3)	2491(2)	261(4)	84(2)
C(50)	3187(3)	2682(2)	2140(4)	90(2)

Table 4. Selected Bond Lengths (pm) and Angles (deg) for 8

Si—N(1)	176.6(3)	Si—N(8)	175.9(3)
N(1)—C(2)	138.7(4)	C(2)—C(3)	133.7(6)
C(3)—C(4)	143.6(5)	C(4)—C(5)	132.7(6)
C(5)—C(6)	143.0(5)	C(6)—C(7)	134.5(5)
C(7)—N(8)	142.1(4)	Si—C(15)	189.3(4)
Si—C(21)	191.0(3)		
C(15)—Si—C(21)	109.1(1)	N(1)—Si—N(8)	89.7(1)
Si—N(8)—C(9)	133.7(2)	Si—N(8)—C(7)	110.7(2)
C(7)—N(8)—C(9)	113.5(3)	Si—N(1)—C(2)	128.5(2)
Si—N(1)—C(6)	112.0(2)	C(2)—N(1)—C(6)	118.5(3)

form by rotation about the central C—C single bond would be decisive for the product formation.



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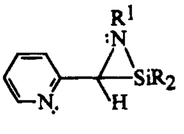

10

An alternative to this is the [2 + 1] cycloaddition of the silylene to the acyclic C—N bond with formation of an intermediate of the type **10**. Depending on the spatial requirements of their substituents, silylenes react with buta-1,3-dienes to furnish unstable[12,13] or stable[14,15] siliranes which can also undergo subsequent reactions. Although both **9** and **10** can be considered as possible intermediates for the concomitant formation of, for example, **3** and **4**, the thermal isomerizations more probably proceed through [2 + 1] adducts of the type **10** because fewer bonds need be cleaved in this process.

Experimental Section

General Procedures. All reactions were carried out in oven-dried glassware under an atmosphere of dry argon. Photolyses were carried out by using a high-pressure mercury immersion lamp (Heraeus TQ 150).

The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM 300 spectrometer using $CDCl_3$ or C_6D_6 as solvent. IR spectra were taken on a Bio-Rad FTS-7 spectrometer. Mass spectra were recorded on a Varian-MAT 212 instrument. UV–vis spectra were recorded on a Shimadzu UV-260 spectrometer. Elemental analyses were performed by Analytische Laboratorien, D-51647 Gummersbach, Germany.

The pyridine-2-carbaldimines **1** and **5** were prepared analogously as described for *N*-(2,6-dimethylphenyl)pyridine-2-carbaldimine,[16] with pyridine-2-carbaldehyde and the corresponding anilines as starting materials. The trisilane **2** was prepared according to the literature procedure.[7]

1,1,1,3,3,3-Hexamethyl-2,2-bis(2,4,6-triisopropylphenyl)trisilane (6). A solution of 1-bromo-2,4,6-triisopropylbenzene (21.8 g, 77 mmol) in diethyl ether (30 mL) was added to a mixture of diethyl ether (30 mL) and finely cut lithium wire (2.15 g, 0.31 mol; 1% sodium content) at 0 °C. The mixture was warmed to room temperature. The reaction was shown to be complete after 15 h by TLC. After filtration of the mixture, the solvent was removed by evaporation. The lithium reagent was suspended in toluene (50 mL), and the mixture was cooled to 0 °C. At this temperature a solution of silicon tetrachloride (5.9 g, 35 mmol) in toluene (20 mL) was added. The mixture was warmed to room temperature and stirred for 10 h. After filtration of the mixture, the solvent was removed by vacuum distillation to yield 15.2 g (86%) of pure dichlorobis(2,4,6-triisopropylphenyl)silane:[17] mp 103–104 °C. ^{1}H NMR (C_6D_6): δ 1.12 (d, 24 H, ^3J = 6.6 Hz), 1.15 (d, 12H,^3J = 6.9 Hz), 2.69 (sept, 2H), 3.97 (sept, 4H), 7.06 (s, 4H). A solution of the dichlorosilane (15.2 g, 30 mmol) in THF (30 mL) was added to mixture of chlorotrimethylsilane (28 g, 0.26 mol) and finely cut lithium wire (3.4 g, 0.49 mol; 1% sodium content) in THF (100 mL) at 0 °C. The mixture was warmed to room temperature and was stirred for 24 h. After this time the reaction was shown to be complete by TLC. Unreacted lithium was filtered off, the solvent was removed, and the residue was redissolved in *n*-pentane. Lithium chloride was removed by filtration over silica gel. Recrystallization from a minimum amount of *n*-pentane yielded 14.8 g (85%) of **6**: mp 203–205 °C. ^{1}H NMR ($CDCl_3$): δ 0.03 (d, 6H, ^3J = 6.4 Hz), 0.27 (s, 18H), 1.12 (d, 6H, ^3J = 6.4 Hz), 1.19 (d, 6H, ^3J = 6.9 Hz), 1.20 (d, 6H, ^3J = 6.9 Hz), 1.32 (d, 6H, ^3J = 6.6 Hz), 1.36 (d, 6H, ^3J

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= 6.6 Hz), 2.81 (sept, 2H), 2.87 (sept, 2H), 3.40 (sept, 2H), 6.80 (d, 2H, ^4J = 1.8 Hz), 7.00 (d, 2H, ^4J = 1.8 Hz).

2-((2,4,6-Trimethylphenyl)imino)-1,1-bis(2,4,6-trimethylphenyl)-2-(pyridin-2-yl)-1-silaethane (3) and Bis(2,4,6-trimethylphenyl)(*N*-(2,4,6-trimethylphenyl)pyridine-2-carbaldimine-*N*,*N*′)silicon (4). A solution of **1** (0.45 g, 2.0 mmol) and **2** (0.83 g, 2.0 mmol) in *n*-pentane (80 mL) was irradiated for 8 h. After this time the reaction was complete (TLC). The solvent and hexamethyldisilane were removed by vacuum distillation, and the residue was redissolved in a minimum amount of *n*-pentane. Cooling of the red solution to −30 °C provided 0.20 g (20%) of **4**: red solid; mp 210 °C (sublimes). Upon prolonged cooling at −30 °C, 0.36 g (37%) of **3** was obtained: yellow solid; mp 131 °C (rearrangement begins at this point). For spectral data see ref 5.

2-((2,6-Diisopropylphenyl)imino)-1,1-bis(2,4,6-triisopropylphenyl)-2-(pyridin-2-yl)-1-silaethane (7). A solution of **5** (0.53 g, 2.0 mmol) and **6** (1.16 g, 2.0 mmol) in *n*-pentane (100 mL) was irradiated for 5 h. After this time the reaction was complete (TLC). All volatile components were removed by vacuum distillation, and the residue was redissolved in a minimum amount of *n*-pentane. Cooling of the orange solution to −30 °C yielded 1.12 g (80%) of **7**: yellow crystals; mp 182−183 °C. ^{1}H NMR (C_6D_6): δ 0.92 (d, 6H, ^3J = 6.8 Hz), 1.02 (d, 6H, ^3J = 6.8 Hz), 1.19 (d, 12H, ^3J = 6.5 Hz), 1.20 (d, 12H, ^3J = 6.5 Hz), 1.24 (d, 12H, ^3J = 6.9 Hz), 2.81 (sept, 2H), 2.92 (sept, 2H), 3.76 (sept, 4H), 6.30 (dd, 1H, $^3J_{H4,H5}$ = 7.4 Hz, $^3J_{H5,H6}$ = 4.8 Hz), 6.48 (s, 1H, SiH), 6.60 (pseudo t, 1H, $^3J_{H3,H4}$ = 7.4 Hz), 6.80 (d, 1H), 7.05−7.13 (m, 3H), 7.15 (s, 4H), 8.17 (d, 1H). ^{13}C NMR (C_6D_6): δ 23.54, 24.14, 24.18, 24.50, 24.82, 25.02, 28.10, 34.71, 35.20, 121.90, 122.13, 123.63, 123.90, 124.13, 131.29, 134.82, 135.32, 148.66, 149.56, 150.33, 155.30, 155.72, 184.29 (SiCN). IR (KBr): ν 2176 (SiH) cm^{-1}. Mass spectrum (EI, 70 eV): *m/z* 701 (M$^+$, 50%). UV−vis: λ (ϵ) 396 (380) nm. Anal. Calcd for $C_{48}H_{68}N_2Si$: C, 82.22; H, 9.77, N, 4.00. Found: C, 82.08; H, 9.68; N, 3.95.

Preparation of 4 by the Thermal Rearrangement of 3. Neat compound **3** (100 mg) was heated at 200 °C for 1 h. During this time the color changed from yellow to red-brown. The reaction mixture was cooled to room temperature and dissolved in *n*-pentane. Cooling of the red solution to −30 °C afforded 70 mg (70%) of pure **4**. All spectral data were identical with those of an authentic sample.

Preparation of Bis(2,4,6-triisopropylphenyl)(*N*-(2,6-diisopropylphenyl)pyridine-2-carbaldimine-*N*,*N*′)silicon (8) by Thermal Rearrangement of 7. Neat compound **7** (210 mg, 0.30 mmol) was heated at 230 °C for 1 h. Purification of the crude reaction mixture was accomplished by slow sublimation at 190−200 °C/0.1 mbar, yielding 20 mg (10%) of pure **8**: red crystals; mp 222−224 °C dec. ^{1}H NMR (C_6D_6): δ 0.04 (d, 3H, ^3J = 6.1 Hz), 0.19 (d, 3H, ^3J = 6.8 Hz), 0.50 (d, 3H, ^3J = 6.1 Hz), 0.56 (d, 3H, ^3J = 6.4 Hz), 0.98 (d, 3H, ^3J = 6.8 Hz), 1.13 (d, 3H, ^3J = 7.0 Hz), 1.14 (d, 3H, ^3J = 7.0 Hz), 1.18 (d, 3H, ^3J = 6.6 Hz), 1.19 (d, 3H, ^3J = 7.0 Hz), 1.20 (d, 3H, ^3J = 6.8 Hz), 1.24 (d, 3H, ^3J = 7.0 Hz), 1.34 (d, 3H, ^3J = 6.8 Hz), 1.47 (d, 3H, ^3J = 6.8 Hz), 1.49 (d, 3H, ^3J = 6.8 Hz), 1.58 (d, 3H, ^3J = 6.6 Hz), 1.65 (d, 3H, ^3J = 6.6 Hz), 2.05 (sept, 1H), 2.66 (sept, 1H), 2.76 (sept, 1H), 2.78 (sept, 1H), 3.19 (sept, 1H), 3.75 (sept, 1H), 3.88 (sept, 1H), 4.27 (sept, 1H), 5.16 (ddd, 1H, H5, $^3J_{H4,H5}$ = 7.2 Hz, $^3J_{H5,H6}$ = 7.3 Hz, $^4J_{H3,H5}$ = 1.1 Hz), 5.50 (s, 1H, H7), 5.55 (dd, 1H, H4, $^3J_{H3,H4}$ = 9.7 Hz), 5.96 (d, 1H, H3), 6.66 (d, 1H, H6), 6.75 (d, 1H, ^4J = 1.5 Hz), 6.87−7.16 (m, 3H), 6.99 (d, 1H, ^4J = 1.5 Hz), 7.20 (d, 1H, ^4J = 1.5 Hz), 7.31 (d, 1H, ^4J = 1.5 Hz). ^{13}C NMR (C_6D_6): δ 20.65, 22.27, 22.62, 23.16, 23.73, 23.91, 24.12, 24.36, 24.52, 25.03, 26.07, 27.84, 28.26, 28.48, 29.07, 29.32, 32.80, 34.07, 34.53, 34.60, 35.94, 38.32, 104.56, 113.13, 119.58, 120.01, 120.14, 121.70, 122.05, 123.59, 124.96, 125.15, 127.09, 132.75, 133.38, 134.98, 142.49, 147.60, 149.69, 150.27, 151.48, 151.58, 153.45, 156.28, 158.44. IR (KBr): ν 1536, 1585, 1603 (C=C) cm^{-1}. Mass spectrum (EI, 70 eV): *m/z* 701 (M$^+$, 100%). UV−vis (*n*-hexane): λ 448, 476, 510, 552 nm. Anal. Calcd for $C_{48}H_{68}N_2Si$: C, 82.22; H, 9.77; N, 4.00. Found: C, 80.82; H, 9.55; N, 3.76.

Table 5. Crystallographic Data

	7	**8**
empirical formula	$C_{48}H_{68}N_2Si$	$C_{48}H_{68}N_2Si$
fw	701.17	701.17
a, pm	2162.4(4)	1712.4(3)
b, pm	1868.6(4)	2439.7(4)
c, pm	1141.1(2)	1077.0(3)
β, deg	103.18(1)	99.99(2)
V, pm^3	[4489(1)] × 10^6	[4431(1)] × 10^6
Z	4	4
D(calcd), g cm^{-3}	1.037	1.051
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/a$
cryst size, mm	0.7 × 0.7 × 0.5	0.4 × 0.4 × 0.3
data collection mode	Wyckoff scan	Wyckoff scan
$2\theta_{max}$, deg	55	55
no. of rflns measd	11 136	10 949
no. of unique rflns	9568	9691
no. of rflns, $F > 3\sigma(F)$	6433	5850
linear abs coeff, mm	0.08	0.09
data/param ratio	13.9	12.7
R, R_w	0.070, 0.059	0.081, 0.069

Crystallographic Analysis. Crystal data and numerical details of the structure determinations are given in Table 5. The yellow crystals of **7** were grown from a saturated solution in *n*-pentane by slow cooling to −20 °C. Red crystals of **8** were obtained by rapid sublimation at 230 °C/0.1 mbar. In each case, the crystal was mounted in a thin-walled glass capillary. Data collection was performed on a Siemens R3m/V diffractometer using graphite-monochromated Mo Kα radiation.

The structures were solved by direct phase determination using the Siemens SHELXTL PLUS program system and refined by full-matrix least-squares techniques. Hydrogen atoms were placed in calculated positions, and all other atoms were refined anisotropically.

Acknowledgment. Financial support of our work 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 for H atoms, bond lengths, bond angles, and anisotropic displacement coefficients and figures for **7** and **8** (14 pages). Ordering information is given on any current masthead page.

OM9403683