Reactions of a Silanediyl with Carbon−Oxygen and Carbon−Nitrogen Double Bonds

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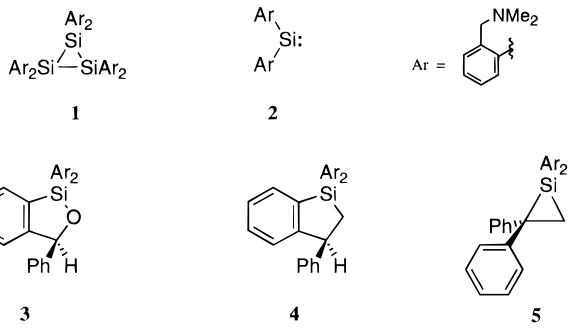
Silanediyl **2** (generated by thermolysis of cyclotrisilane **1**) reacts with benzophenone, tetracyclone, and fluorenone to yield products, which may originate from highly reactive siloxiranes as intermediates. However, using adamantanone as ketone, stable siloxirane **24** is obtained. The interaction of **2** with benzophenone anil or **36** gives heterocyclic compounds **31** and **37**, respectively. The involvement of silaziridines in these reactions, as well as in the reactions of **1** with 1,4-diaza-1,3-butadienes **41a** and **b**, which yield the expected formal [4 + 1] cycloaddition products, remains questionable.

The intense study of the reactions of carbenes with carbonyl compounds contrasts sharply with the quite limited knowledge about the analogous reactions of silanediyls, which is based mainly on the investigations undertaken by Ando et al. In 1977, the first evidence was presented for the formation of a transient siloxirane (siloxacyclopropane) in the reaction of thermally generated dimethylsilanediyl with benzophenone.[1] In 1982, the same group succeeded in isolating and determining the solid state structure of a stable, heavily substituted siloxirane, which was obtained from the reaction of dimesitylsilanediyl with 1,1,3,3-tetramethyl-2-indanone.[2] Subsequent studies showed this strained three-membered ring to be built up via an initial electrophilic attack of the silanediyl to the carbonyl oxygen, thereby forming a silacarbonyl ylide as an intermediate.[3] This reactive intermediate undergoes ring closure to the corresponding siloxirane, thus paralleling the mechanism of the formation of oxiranes in the reaction between carbenes and ketones.[4]

We have reported earlier that cyclotrisilane **1** is in equilibrium with presumably intramolecularly coordinated silanediyl **2** at room temperature and acts toward a variety of substrates as an effective synthetic equivalent of silanediyl **2**.[5] Due to the mild conditions, under which these silanediyl transfer reactions proceed, we were able to synthesize stable strained ring systems such as silacyclopropenes,[6] disilacyclobutenes,[7] and silacyclopropanes.[5] Thus, **1** appeared to be a promising precursor for the synthesis of stable siloxiranes. Herein, we report the results of reactions of **1** with ketones and will describe the transfer of silanediyl **2** to imines and 1,4-diaza-1,3-butadienes.



1 **2** **3** **4** **5**

Results and Discussion

When **1** was stirred for 60 min at 60 °C with 3 equiv of benzophenone, quantitative formation of siloxaindane **3** occurred;[8] that is, silanediyl **2**[5] shows the same chemical behavior as dimethylsilanediyl, which reacts with benzophenone to yield an analogous siloxaindan.[1] Moreover, the outcome of this reaction resembles that of the addition of **2** to styrene, in which silaindan **4** was formed; silacyclopropane **5** was detected and identified as an intermediate of this reaction by means of NMR spectroscopy.[5] Thus, it is tempting to assume that the reaction of **1** with benzophenone proceeds analogously forming a siloxirane **8**, which isomerizes via a vinylcyclopropane−cyclopentene rearrangement and subsequent rearomatization of **9** to yield heteroindan **3** (Scheme 1). However, monitoring the reaction by NMR spectroscopy did not provide any evidence for possible intermediates **8** or **9**; only signals that are attributable to starting material **1** and final product **3** were observed. An alternative mechanistic pathway has to be taken into consideration: Due to the possible intramolecular coordination of silanediyl **2**,[5] it may act as a nucleophile as it is known for tin(II) amides, which undergo nucleophilic attack to acid chlorides.[9,10] Keeping in mind that the 2-((dimethylamino)methyl)phenyl substituent (Ar) shows a pronounced tendency to coordinate to a positively charged

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(1) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1977**, *99*, 6447−6449.
(2) Ando, W.; Hamada, Y.; Sekiguchi, A. *Tetrahedron Lett.* **1982**, *23*, 5323−5326.
(3) Ando, W.; Hagiwara, K.; Sekiguchi, A. *Organometallics* **1987**, *6*, 2270−2271.
(4) Moss, R. A.; Jones, M. Jr. In *Reactive Intermediates*; Jones, M., Jr., Moss, R. A., Eds.; Wiley: New York, 1985; Vol. 3, pp 45−108 and related references cited therein.
(5) Belzner, J.; Ihmels, H.; Kneisel, B. O.; Gould, R. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 305−311.
(6) Belzner, J.; Ihmels, H. *Tetrahedron Lett.* **1993**, *34*, 6541−6544.
(7) Belzner, J.; Ihmels, H.; Kneisel, B. O.; Herbst-Irmer, R. *J. Chem. Soc., Chem. Commun.* **1994**, 1989−1990.
(8) Belzner, J. *J. Organomet. Chem.* **1992**, *430*, C51−C55.

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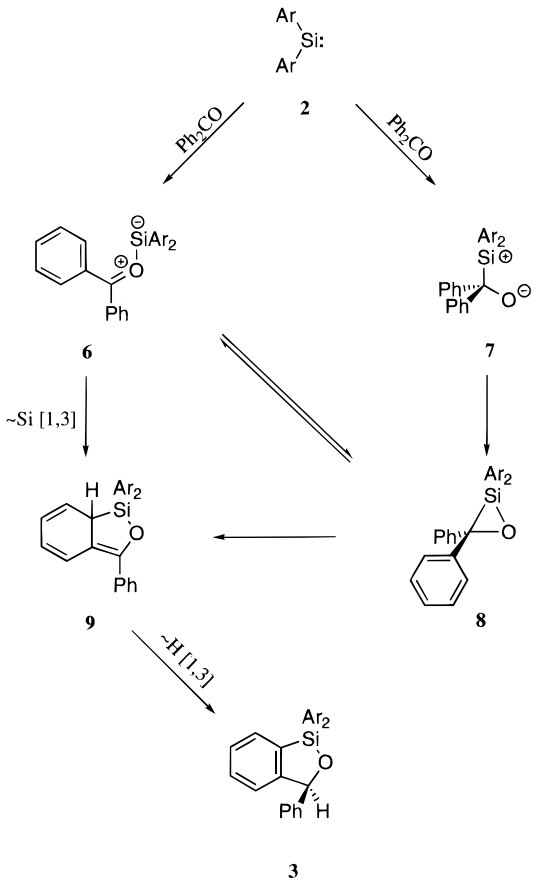
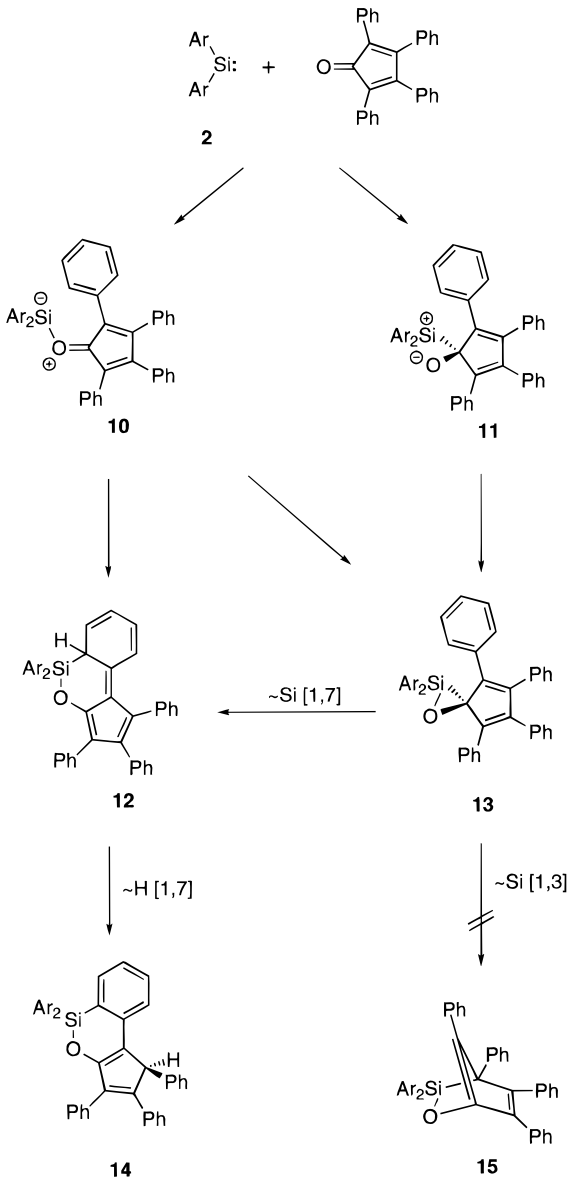
Scheme 1



silicon center,[11] one might speculate that the resulting addition product **7** is stabilized by such a 2-fold intramolecular coordination of its silicon terminus. Formation of a stable Si−O bond and subsequent rearrangement of the resulting siloxirane **8** via **9**, as outlined in Scheme 1, eventually opens the way from **7** to **3**.

In order to suppress a [1,3] silicon shift in a possibly formed siloxirane, tetracyclone was chosen as another ketone: in this case, a vinylcyclopropane−cyclopentene rearrangement of the resulting siloxirane **13** should not be energetically feasible, because a strained bridgehead olefin **15** would be generated (Scheme 2). The reaction of **1** with 3 equiv of tetracyclone gave rise to the clean formation of a single compound, but the appearance of a singlet at δ 4.90 in the ^{1}H NMR spectrum of the product as well as a methine signal at δ 55.2 in the ^{13}C NMR spectrum was not in accordance with the expected siloxirane structure **13**. The complex NMR and mass spectra did not allow an unambiguous identification of the obtained product; however, X-ray diffraction analysis revealed that compound **14** has been formed.[12] Seemingly, a siloxirane **13**, if formed at all in this reaction, now releases ring strain by undergoing a [1,7] silicon shift to form **12**, which yields **14** after a concluding [1,7] hydrogen shift. Again, the involvement of a siloxirane **13**, which can be built up by an electrophilic attack of **2**

Scheme 2



to the carbonyl oxygen and subsequent ring closure of the resulting sila ylide **10**, or alternatively, via a nucleophilic addition of **2** to the carbonyl function of tetracyclone yielding **11**, is not necessary in order to explain the formation of **14**: Its precursor **12** may be the product of an electrocyclic ring closure of the initially generated sila carbonyl ylide **10** as well.

Fluorenone, too, turned out to be an inappropriate starting ketone for the synthesis of a stable siloxirane from **1**: When **1** was reacted with 3 equiv of fluorenone, a mixture of cyclotrisilane and the 2:1 adduct **16** was obtained. The reaction was driven to completion by addition of another 3 equiv of the ketone. The formation of a 2:1 adduct from a ketone and a silanediyl is not without precedents: Ando has reported that the photolytic generation of dimethylsilanediyl in the presence

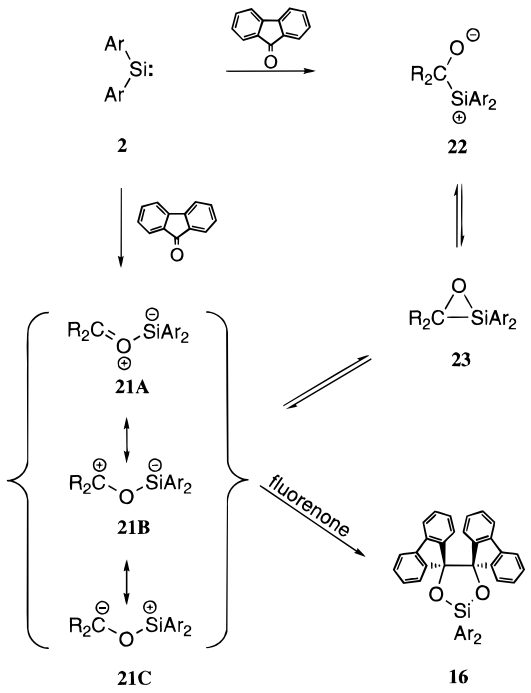
(9) Lappert, M. F.; Misra, M. C.; Onyszchuk, M.; Rowe, R. S.; Power, P. P.; Slade, M. J. *J. Organomet. Chem.* **1987**, *330*, 31−46.

(10) Kinetic investigations show that the reactions of **1** with substituted styrenes and alkynes are favored by electron-withdrawing substituents, i.e., the rate-determining step of the addition of silanediyl **2** to the multiple bond is of nucleophilic character: Belzner, J.; Ihmels, H.; Dehnert, U. Unpublished results.

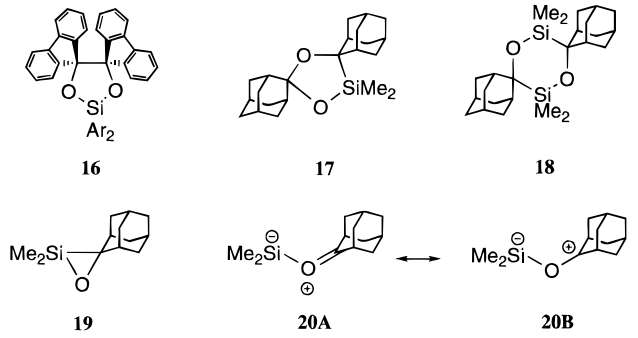
(11) Belzner, J.; Schär, D.; Kneisel, B. O.; Herbst-Irmer, R. *Organometallics* **1995**, *14*, 1840−1843.

(12) Details of X-ray structure determination as well as tables of atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates of compounds **14** and **42a** have been deposited with the Cambridge Crystallographic Data Centre. These data may be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

Scheme 3

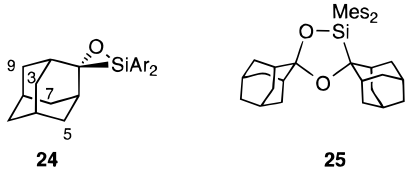


of adamantanone results in the formation of two products, **17** and **18**.[13] Again, a siloxirane **19**, which is in



equilibrium with the ring-opened dipole **20** under the reaction conditions, is assumed to be the crucial intermediate. The orientation of the second adamantanone unit in **17** is governed by the charge distribution of **20**, which is described by the resonance structures **20A** and **20B**. Similar arguments apply to the formation of 1,3-dioxolanes as major products in the reaction of carbenes with aldehydes.[14] Thus, the exclusive formation of **16**, in which the incorporation of the second carbonyl unit is exactly the opposite compared to **17**, may be rationalized best by the involvement of an ylide **21**, in which negative charge density is located at the carbon terminus whereas the silicon center is positively charged. Indeed, it seems reasonable to assume that a Lewis structure **21C** contributes the most to the ground state of **21** because it benefits from a 2-fold stabilization: The negative charge is delocalized into the fluorenyl substituent forming an aromatic 14-electron system; moreover, the positively charged silicon terminus of **21** can be stabilized by the intramolecular coordination of the amino side arms of both aromatic substituents. Again, two mechanistic pathways to **21** have to be considered: **21** can be generated directly by an electrophilic attack of **2** to the carbonyl oxygen of fluorenone. Alternatively, the reaction may be initiated by a nucleophilic attack of **2** to the carbonyl center. Ring closure of **22** to form **23** and subsequent heterolytic cleavage of a Si−C bond eventually results in the generation of **21**; the driving force for this reorganization would be the formation of a strong Si−O bond as well as the aromatic stabilization of the negative charge.[15]

Finally, the reaction of **1** with 3 equiv of adamantanone allowed the synthesis of a stable compound, to which we ascribe the structure of siloxirane **24**. This result is surprising in view of the fact that the reaction of the bulkier dimesitylsilanediyl with the same ketone did not stop at the stage of the corresponding siloxirane, but instead yielded the 2:1 adduct **25**.[16] Especially valuable for elucidating the cyclic structure of **24** are its NMR data: The ^{29}Si NMR signal is observed at δ −77.2 and fits well into the shift range reported for other saturated three-membered silacycles such as cyclotrisilanes or silacyclopropanes.[17] The ^{1}H NMR as well as the ^{13}C NMR spectrum of **24** show, probably due to dynamic processes, very broad signals at room temperature, which sharpen up appreciably at elevated temperatures. The *spiro* carbon atom absorbs at δ 84.6, which is in good accordance with δ 89.9 reported by Ando for a indanone-derived siloxirane.[2] A ^{1}H,^{1}H COSY spectrum of **24** indicates that the geminal protons at C-3 and C-5 are, presumably due to the anisotropic effect of the aryl substituents at silicon, in quite different chemical environments and thus give rise to an AB system, whereas the protons located at C-7 and C-9, respectively, have quite similar chemical shifts.



Despite the chemical similarities between ketones and imines, almost nothing is known about the reactions of silanediyls with the latter compounds. Only in 1993, Weidenbruch reported that photolytically generated dimesitylsilanediyl reacts with pyridine-substituted aldimines **26** to yield a mixture of **27**, which is formally the insertion product of a silanediyl into the C−H bond of **26**, and **28**, the formal [4 + 1] cycloaddition product; both compounds are assumed to result from a rearrangement of an initially formed silaziridine **29**.[18] In order to get more insight into the reactivity of **2** toward imines, **1** was stirred with 3 equiv of perphenylated ketimine **30**, and heteroindan **31** was obtained. The close structural relationship between **8** and **31** suggests that **31** is formed via a similar mechanistic pathway as **8** (cf. Scheme 1). It is worth mentioning that the isomeric compound **32** is not formed; **32** would result from a [1,3] silicon shift of

(13) Ando, W.; Ikeno, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **1978**, *100*, 3613−3615.

(14) See, e.g.: de March, P.; Huisgen, R. *J. Am. Chem. Soc.* **1982**, *104*, 4592−4952.

(15) Another mechanistic pathway from **1** to **16** via radical intermediates cannot be excluded, but seems less probable.

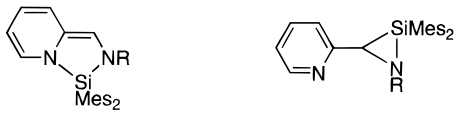
(16) Ando, W.; Hamada, Y.; Sekiguchi, A. *J. Chem. Soc., Chem. Commun.* **1983**, 952−954.

(17) See, e.g.: Williams, E. A. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1989; pp 511−554.

(18) Weidenbruch, M.; Piel, H.; Peters, K.; von Schnering, H. G. *Organometallics* **1993**, *12*, 2881−2882.

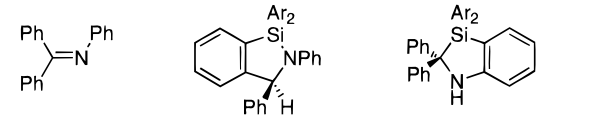
26 **27**

R = Mes, 2,6-*i*PrC$_6$H$_3$

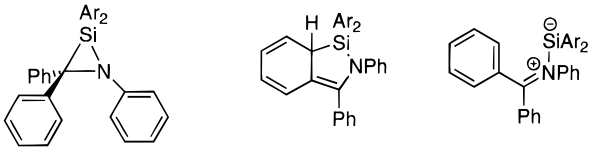


28 **29**

an intermediate silaziridine **33** forming a new bond to the *ortho* carbon of the phenyl substituent, which is located at the nitrogen, and a subsequent [1,3] hydrogen shift. The exclusive formation of **31** may be due to the fact that this [1,3] silicon shift requires the breaking of a Si−N bond in **33**; thus, an alternative [1,3] silicon shift, which proceeds by cleavage of the less stable Si−C bond and finally results via **34** in the formation of **31**, seems to be energetically more favorable. Alternatively, one might speculate that silaziridine **33** is not the precursor of **34**, but rather the initially formed sila ylide **35** undergoes direct ring closure to **34**.

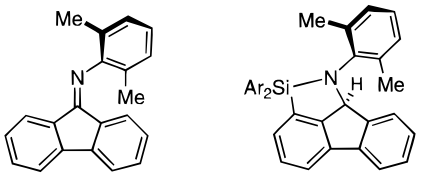


30 **31** **32**

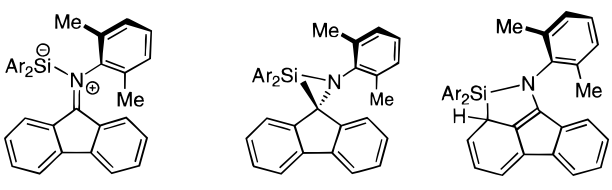


33 **34** **35**

Contrasting the structural similarity between reaction products **8** and **31**, the reaction of **2** with fluorene-derived imine **36** took another course than with fluorenone: Instead of a 2:1 adduct between imine and silanediyl, corresponding to the formation of **16**, the 1:1 adduct **37** was obtained. Presumably, the steric strain imposed to **36** due to the bulky 2,6-dimethylphenyl substituent does not allow the attack of sila ylide **38** to a second molecule of **36**. Thus, **38** or silaziridine **39** undergoes rearrangement to **40**; a concluding [1,3] silicon shift eventually restores the aromatic fluorene system and yields **40**.



36 **37**



38 **39** **40**

When the C−N double bond of the starting imine compound is part of a conjugated system as in 1,4-diaza-1,3-butadienes **41a** and **b**, the corresponding diazasilacyclopentenes **42a**[19] and **b** were obtained quantitatively, as one would expect in view of the fact that di-*tert*-butylsilanediyl underwent the analogous reaction with **41a**.[20] These five-membered rings, which are the formal product of a [4 + 1] cycloaddition reaction between silanediyl and heterodiene, may result from a [1,3] silicon shift of a primarily formed vinylsilaziridine, thus resembling the synthesis of silacylo-3-pentenes by reaction of silanediyls with conjugated dienes, which is known to proceed via intermediate vinylsilacyclopropanes.[21] However, no spectroscopic evidence for the initial formation of vinylsilaziridine in the reaction with azabutadienes could be obtained.

41a: R = *t*Bu
41b: R = *c*C$_6$H$_{11}$

42a: R = *t*Bu
42b: R = *c*C$_6$H$_{11}$

In conclusion, a variety of silicon-containing heterocycles was synthesized by interaction of cyclotrisilane **1** with ketones and imines. The possibility of the transient existence of a siloxirane during the reaction of **1** with benzophenone, tetracyclone, or fluorenone is corroborated by the successful isolation of a siloxirane **24**, whereas the search for a stable silaziridine has still to go on. The question whether the attack of silanediyl **2** to C−O and C−N double bonds is of electrophilic or nucleophilic nature remains a matter, which is currently being adressed by our group.

Experimental Section

General Methods. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 250 MHz (^{1}H), 62.9 MHz (^{13}C), and 59.6 MHz (^{29}Si). Mass spectra were recorded using electron impact (EI, 70 eV) and fast atom bombardment (FAB) mode; HRMS were determined using preselected ion peak matching at $R \sim 10\,000$ to be within ±2 ppm of the exact mass. Melting points are uncorrected. Elemental analyses were performed at Mikroanalytisches Labor der Georg-August-Universität Göttingen.

All manipulations were carried out under an inert argon atmosphere using carefully dried glassware. Solvents used were dried by refluxing over sodium and distilled immediately before use.

Hexakis[2-((dimethylamino)methyl)phenyl]cyclotrisilane (**1**),[8] benzophenone anil (**30**),[22] fluorenone 2′,6′-dimethylanil (**36**),[22] 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene (**41a**),[23] and 1,4-dicyclohexyl-1,4-diaza-1,3-butadiene (**41b**)[23] were prepared according to published procedures.

1,1-Bis[2-((dimethylamino)methyl)phenyl]-3-phenyl-2-oxa-1-silaindan (3). A solution of 123 mg (0.14 mmol) of **1** and 78 mg (0.43 mmol) of benzophenone in 10 mL of toluene was heated for 60 min at 50 °C. The solvent was removed in vacuo, and the residue was crystallized from 10 mL of *n*-hexane at −6 °C to give 109 mg (55%) of **3** as colorless crystals: mp 115−117 °C; ^{1}H NMR (C_6D_6) δ 1.80 (s, 6 H), 1.85

(19) The solid state structure of **42a** (determined by X-ray crystallography) does not differ significantly from that reported by Weidenbruch[20] for another diazasilacyclopentene.

(20) Weidenbruch, M.; Lesch, A.; Peters, K. *J. Organomet. Chem.* **1991**, *407*, 31−40.
(21) See ref 5 and references cited therein.
(22) Reddelien, G. *Chem. Ber.* **1913**, *46*, 2718−2723.
(23) Kliegman, J. M.; Barnes, R. K. *Tetrahedron* **1970**, *26*, 2555−2560.

(s, 6 H), 2.92, 3.61 (2 × d, J = 13 Hz, 2 H), 3.23, 3.24 (2 × d, J = 13 Hz, 2 H), 6.36 (s, 1 H), 6.94−7.33 (m, 14 H), 7.96−8.02 (m, 2 H), 8.09−8.18 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 45.3, 45.4, 64.2, 64.7, 83.2, 124.2, 126.8, 126.8, 126.9, 127.5, 127.7, 128.3, 128.5, 128.9, 129.1, 129.2, 129.9, 133.8, 135.4, 135.7, 137.5, 138.1, 137.8, 144.6, 145.5, 146.3, 153.7; ^{29}Si NMR (C_6D_6) δ −9.20; MS (EI) m/z 478 (3) [M^+], 344 (100) [M^+ − Ar]; HRMS calcd for $C_{31}H_{34}N_2OSi$ 478.2440, found 478.2440.

5,5-Bis[2-((dimethylamino)methyl)phenyl]-1,2,3-triphenyl-1,5-dihydro-4-oxa-5-silacyclopenta[*a*]naphthaline (14). To a solution of 401 mg (0.45 mmol) of **1** in 10 mL of toluene was added 529 mg (1.38 mmol) of tetracyclone. After the solution was stirred for 14 h at rt, toluene was replaced by 8 mL of Et_2O. The resulting slurry was filtered, and the remaining insoluble violet solid was crystallized from THF/Et_2O (1:1) to yield 614 mg (67%) of **14** as pale yellow crystals: mp 168−170 °C; ^{1}H NMR ($CDCl_3$) δ 1.66 (s, 6 H), 1.81 (s, 6 H), 3.26, 3.32 (2 × d, J = 14 Hz, 2 H), 3.39 (d, J = 14 Hz, 2 H), 3.58 (d, J = 14 Hz, 2 H), 4.90 (s, 1 H), 6.88−7.53 (m, 27 H); ^{13}C NMR ($CDCl_3$) δ 44.8, 45.1, 55.2, 63.8, 63.8, 121.3−154.8; ^{29}Si NMR ($CDCl_3$) δ −13.4; MS (EI) m/z 680 (16) [M^+], 635 (7) [M^+ − $HNMe_2$], 546 (100), [M^+ − Ar], 412 (16) [M^+ − 2 Ar], 340 (7) [M^{2+}], 134 (4) [Ar^+], 58 (15) [$CH_2NMe_2^+$]. Anal. Calcd for $C_{47}H_{44}N_2OSi$: C, 82.90; H, 6.51; N, 4.11. Found: C, 82.78; H, 6.58; N, 3.83.

1,1-Bis[2-((dimethylamino)methyl)phenyl]-3,4-bis(fluorenylidene)-2,5-dioxa-1-silacyclopentane (16). A solution of 169 mg (0.19 mmol) of **1** and 205 mg (1.14 mmol) of fluorenone in 20 mL of toluene was stirred for 4 h at 50 °C. After concentration of the solution in vacuo, a yellow solid crystallized at 0 °C, which was washed with 5 mL of *n*-hexane. The solid was dried in vacuo to give 256 mg (68%) of **16** as yellow solid: mp >200 °C; ^{1}H NMR ($CDCl_3$) δ 1.95 (s, 12 H), 3.41 (s, 4 H), 6.72 (dd, J = 7 Hz, 7 Hz, 4 H), 6.92−7.10 (m, 12 H), 7.35−7.39 (m, 2 H), 7.53 (mc, 4 H), 8.63−8.68 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 45.7, 63.8, 93.5, 118.8 (br), 125.2 (br), 126.4, 127.1, 127.6, 130.1, 137.1, 138.0, 140 (very br), 145.4; ^{29}Si NMR ($CDCl_3$) δ −31.5; MS (EI) m/z 656 (1) [M^+], 611 (2) [M^+ − $HNMe_2$], 522 (1) [M^+ − Ar], 476 (78) [M^+ − fluorenone (HRMS)], 180 (100) [fluorenone$^+$], 58 (19) [$CH_2NMe_2^+$]; HRMS calcd for $C_{44}H_{40}N_2O_2Si$ 656.2859, found 656.2859.

2′,2′-Bis[2-((dimethylamino)methyl)phenyl]-3′-oxa-2′-silaadamantanespirocyclopropane (24). A solution of 255 mg (0.29 mmol) of **1** and 129 mg (0.86 mmol) of adamantanone in 10 mL of toluene was stirred for 12 h at 60 °C. Toluene was removed in vacuo, and 10 mL of Et_2O was added to the residue to give a white slurry. After filtration 179 mg of **24** was obtained as a white solid. Another 123 mg (total 72%) of **24** crystallized from the filtrate: mp 150−152 °C; ^{1}H NMR (323 K, C_6D_6, additional ^{1}H,^{1}H COSY, 333 K) δ 1.67, 2.84 (2 × d, J = 11 Hz, 4 H, 3-H, 5-H), 1.90 (br s, 1 H), 1.91−2.02 (m, 20 H), 3.07, 3.52 (2 × d, J = 13 Hz, 4 H), 7.16−7.21 (m, 6 H), 8.15−8.17 (m, 2 H); ^{13}C NMR (328 K, 75.5 MHz, C_6D_6) δ 28.4, 29.1, 33.7, 38.1, 38.6, 45.8, 64.3, 84.6 (C-1), 126.4, 129.2 , 135.5, 136.5, 144.7, one ar-CH was not detected, probably due to overlap with C_6D_6-signals; ^{29}Si NMR (C_6D_6) δ −77.2; MS (FAB, 3-NBA) m/z (relative intensity) 600 (30) [M^+ + matrix + H], 465 (82) [M^+ + matrix − Ar], 447 (100) [M^+ + H], 402 (25) [M^+ − NMe_2]. Anal. Calcd for $C_{28}H_{38}N_2OSi$: C, 75.29; H, 8.57; N, 6.27. Found: C, 75.13; H, 8.59; N, 6.33.

4,5-Benzo-1,1-bis[2-((dimethylamino)methyl)phenyl]-2,3-diphenyl-2-aza-1-silacyclopent-4-ene (31). A solution of 127 mg (0.14 mmol) of **1** and 108 mg (0.42 mmol) of benzophenone anil was stirred for 12 h at 50 °C. The solvent was removed in vacuo, and the residue was washed with 10 mL of Et_2O to yield 100 mg (43%) of **31** as a white solid: mp 182−184 °C; ^{1}H NMR ($CDCl_3$) δ 1.51 (s, 6 H), 2.14 (s, 6 H), 2.64, 3.06 (2 × d, J = 13 Hz, 2 H), 3.50, 3.79 (2 × d, J = 14 Hz, 2 H), 5.85 (s, 1 H), 6.48 (dd, J = 7, 7 Hz, 1 H), 6.79−6.89 (m, 4 H), 7.00−7.25 (m, 10 H), 7.37−7.43 (m, 3 H), 7.59−7.74 (m, 3 H), 8.00 (d, J = 7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 45.2, 45.4, 63.5, 65.5, 68.9, 118.2 (3 signals), 125.5, 126.1, 126.3, 126.6, 127.0, 127.9, 128.2, 128.5 (2 signals), 128.5 (2 signals), 129.2, 129.8, 130.3, 130.5, 132.4, 132.7, 134.0, 137.7, 138.5, 134.0, 144.2, 145.8, 146.9, 152.0; ^{29}Si NMR (C_6D_6) δ −2.8 (br); MS (EI) m/z 553 (21) [M^+], 419 (52) [M^+ − Ar], 297 (31) [Ar_2-Si^+ + H], 58 (100) [$CH_2NMe_2^+$]; HRMS calcd for $C_{37}H_{39}N_3Si$ 553.2913, found 553.2913. Anal. Calcd for $C_{37}H_{39}N_3Si$: C, 80.24; H, 7.10. Found: C, 80.08; H, 7.20.

2,2-Bis[2-((dimethylamino)methyl)phenyl]-1-(2,6-dimethylphenyl)-1-aza-2-sila-1,2-dihydroacefluorenylene (37). A solution of 233 mg (0.26 mmol) of **1** and 221 mg (0.78 mmol) fluorenone 2,6-dimethylanil (**36**) in 20 mL of toluene was stirred for 12 h at 50 °C. Toluene was removed in vacuo, and the residue was crystallized from *n*-hexane to give 349 mg (77%) of **37** as a white solid: mp 164 °C; ^{1}H NMR ($CDCl_3$) δ 1.50 (s, 3 H), 1.63 (s, 12 H), 1.91 (s, 6 H), 2.26 (s, 3 H), 2.03, 3.02 (2 × d, J = 15 Hz, 2 H), 2.59, 3.21 (2 × d, J = 13 Hz, 2 H), 5.90 (s, 1 H), 6.68 (d, J = 8 Hz, 1 H), 6.78 (dd, J = 6, 3 Hz, 1 H), 6.92−7.02 (m, 4 H), 7.21−7.46 (m, 8 H), 7.59 (d, J = 7 Hz, 1 H), 7.67 (d, J = 7 Hz, 2 H), 8.19 (dd, J = 7, 2 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 20.3, 20.5, 44.9, 45.3, 62.2, 64.3, 70.3, 121.1, 121.2, 124.9, 125.2, 125.4, 126.2, 126.4, 126.8, 127.4, 128.2, 128.5, 128.7, 129.0, 129.7, 131.6, 133.7, 134.4, 135.6, 136.7, 136.8, 136.8, 138.0, 140.2, 141.9, 144.4, 145.3, 145.6, 146.6, 148.6, 162.6; ^{29}Si NMR ($CDCl_3$) δ −0.2; MS (EI) m/z 579 (10) [M^+], 534 (100) [M^+ − $HNMe_2$], 489 (71) [M^+ − 2 $HNMe_2$], 476 (52) [M^+ − $HNMe_2$ − CH_2NMe_2]; HRMS calcd for $C_{39}H_{41}N_3Si$ 579.3070, found 579.3069.

1,1-Bis[2-((dimethylamino)methyl)phenyl]-2,5-di-*tert*-butyl-2,5-diaza-1-silacyclopent-2-ene (42a). A solution of 1.497 g (1.68 mmol) of **1** and 850 mg (5.05 mmol) of **41a** in 20 mL of toluene was stirred for 3 h at 60 °C. After removal of toluene in vacuo, ^{1}H NMR spectroscopically pure **42a** remained as a green solid, which was crystallized from toluene to give 1.243 mg (53%) of **42a** as analytically pure green crystals: mp 175 °C; ^{1}H NMR ($CDCl_3$) δ 1.01 (s, 18 H), 2.32 (s, 12 H), 3.82 (s, 4 H), 5.88 (s, 2 H), 7.17 (dd, J = 7, 7 Hz, 2 H), 7.42 (dd, J = 8, 7 Hz, 2 H), 7.83 (d, J = 8, 2 H), 7.88 (d, J = 7 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 30.2, 46.0, 51.8, 62.6, 112.2, 124.0, 127.3, 129.8, 133.5, 137.6, 148.8; ^{29}Si NMR ($CDCl_3$) δ −22.6; MS (EI) m/z 464 (100) [M^+], 407 (2) [M^+ − *t*-Bu], 330 (7) [M^+ − Ar]. Anal. Calcd for $C_{27}H_{44}N_4Si$: C, 72.36; H, 9.54; N, 12.05. Found: C, 72.47; H, 9.64; N, 12.14.

1,1-Bis[2-((dimethylamino)methyl)phenyl]-2,5-dicyclohexyl-2,5-diaza-1-silacyclopent-2-ene (42b). A solution of 68 mg (0.08 mmol) of **1** and 50 mg (0.23 mmol) of **41b** in 0.4 mL of C_6D_6 was heated for 12 h at 50 °C to give ^{1}H NMR spectroscopically pure **42b** as viscous green oil; attempts to crystallize it using a variety of solvents were unsuccessful: ^{1}H NMR (C_6D_6) δ 0.83−1.91 (m, 20 H), 2.03 (s, 12 H), 3.26−3.49 (m, 2 H), 3.51 (s, 4 H), 5.99 (s, 2 H), 7.10−7.27 (m, 4 H), 7.60 (d, J = 7 Hz, 2 H), 7.96 (d, J = 7 Hz, 2 H); ^{13}C NMR (C_6D_6) δ 26.2, 26.7, 34.4, 45.6, 53.3 , 64.2, 112.3 , 126.5, 129.4, 129.8, 136.1, 136.7, 145.7; ^{29}Si NMR (C_6D_6) δ −17.6; MS (EI) m/z 516 (100) [M^+], 382 (10) [M^+ − Ar]; HRMS calcd for $C_{32}H_{48}N_4$-Si 516.3648, found 516.3648.

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Supporting Information Available: Copies of ^{1}H spectra of compounds for which no elemental analysis was obtained, a copy of a ^{1}H,^{1}H COSY spectrum of **24**, and a listing of NMR data with subjective peak assignments (9 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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