UV-Visible and NMR Spectroscopic Studies of Disilanylene 1,2-Dianions. Questions of Charge Delocalization of Silyl Anions [#]

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The reaction of 1,2-dichloro-1,2-diisopropyl-1,2-disilaacenaphthene with an excess of alkali metal resulted in the formation of the corresponding dialkali metal, 1,2-disila-1,2-acenaphthenediide, as the disilanylene 1,2-dianion. UV-vis and NMR spectroscopic analyses strongly support the delocalization of the silyl anion.

There has been remarkable interest in recent years in the reactivity, structure, and bonding of alkali metal compounds, particularly the organolithium compounds.[1)] Vicinal dimetalo-organic compounds, such as 1,2-dilithioethane, have been reported to react in an abnormal manner, and to have interesting structures.[2)] For this reason, and because of intrinsic interest in compounds of this type, we decided to investigate the corresponding disilanylene 1,2-dianion derivatives.[3)]

Although one of the best methods to form 1,2-dilithioethanes is the reduction of a carbon–carbon double bond, there has so far been no report concerning the reduction of a silicon–silicon double bond to afford a 1,2-dilithiodisilane. Weidenbruch and co-workers reported on the ESR spectra assigned to the disilene anion radicals.[4)] West et al. carried out a one-electron reduction of isolable disilenes by means of cyclic voltametry.[5)] However, the direct dilithiation of 1,2-dihalodisilane without the formation of disilene has not yet been achieved. One of the best precursors for generating 1,2-dilithiodisilane is 1,2-dichloro-1,2-diisopropyl-1,2-disilaacenaphthene (**1**). In particular, the advantage of **1** is that two silicon atoms in **1** are fixed at the distance of a silicon–silicon single bond,[6)] and, hence, a possible silicon–silicon double-bond formation can be avoided.

On the other hand, the question of whether there is Si–C pπ–pπ-electron delocalization in the phenylsilyl anions has been studied by UV, ^{1}H, ^{13}C, ^{29}Si, and ^{7}Li NMR spectroscopies.[7)] These studies conclude that the charge distribution in the phenyl ring is mainly controlled by the π-polarizing effect of the negative silicon atoms, while the corresponding carbanion analogue has been shown to contain considerable π-electron delocalization.

We previously reported on the synthesis and characterization of the dilithium 1,2-disila-1,2-acenaphthenediide (**2a**).[8)] Boudjouk et al. reported on 1,1′-disilafulvalene dianion[9)] and Belzner and co-workers also reported on the synthesis and structure of the 1,2-dilithiodisilane.[10)] As a part of our continuing studies on the generation and structure of disilanylene dianions, in this paper we report on UV-visible and NMR studies of the disilanylene 1,2-dianion (**2**), derived from the dimetallation of 1,2-dichloro-1,2-disilaacenaphthene (**1**).

Results and Discussion

Synthesis of Disilanylene 1,2-Dianions. 1,2-Dichloro-1,2-diisopropyl-1,2-disilaacenaphthene (**1a**) (0.100 g, 0.296 mmol) and an excess of potassium (0.100 g, 2.56 mmol) in THF were sonicated for 30 min at 0 °C under an argon atmosphere to afford a dark-green solution. After removing the unreacted potassium, the addition of an excess of CH_3I to this solution afforded 1,2-dimethyl-1,2-diisopropyl-1,2-disilaacenaphthene (**3**)[6a,11)] in 64% yield. The sonication of **1a** (0.100 g, 0.296 mmol) and an excess of sodium (0.100 g, 4.35 mmol) in THF for 3 h at 0 °C under an argon atmosphere gave a dark-green solution. Although treating of this solution with CH_3I afforded the formation of **3** in 28% yield, in a reaction with Me_3SiCl, 1,2-bid(trimethylsilyl)-1,2-diisopropyl-1,2-disilaacenaphthene (**4**) was formed in 58% yield (Scheme 1).

The formation of **3** and **4** clearly reveals that the reduction of the dichlorodisilane **1a** with metal to afford dimetal proceeds in a facile manner to the generated 1,2-disila-1,2-acenaphthenediide (**2b** and **2c**). Anions **2b** and **2c** are stable for several hours at 0 °C. A similar reaction of **1a** with an excess of lithium in THF at room temperature gave a dark-blue solution of the 1,2-disila-1,2-acenaphthenediide **2a**.[8)] The half-life period of the disappearance of **2a** in THF is 13.5 h at 30 °C. In order to investigate the substituent effect of the isopropyl groups, a reaction of 1,2-dichloro-1,2-dimethyl-1,2-disilaacenaphthene (**1b**) with excess lithium was carried out. In this reaction, a similar dark-blue solution was also formed, and the trapping reactions using MeI showed the formation of the dilithium 1,2-disilaacenaphthenediide (**2d**). The NMR spectra of this solution showed a quantitative formation of **2d**, the half-life period of the disappearance

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[#] Dedicated to Professor Waldemar Adam upon celebrating his 60th birthday and in honor of his contribution to oxygen chemistry and dialkyldiazene chemistry.

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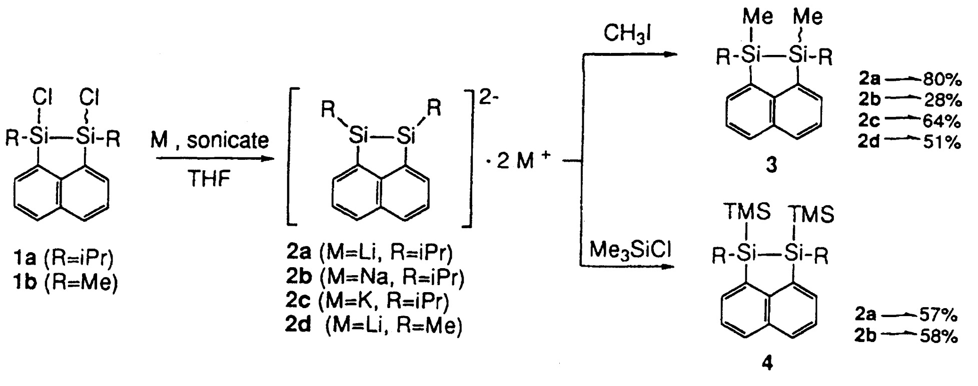

Scheme 1.

in THF is 14 h at 20 °C, somewhat shorter than **2a**. The formation of **2d** reveals that the important factor concerning the formation of the dianions is the disilaacenaphthene skeleton, and not the bulky substituent on the silicon atoms.

UV-Visible Spectral Characterization of 1. Edlund and Buncel have studied phenyl germyl, stannyl and plumbyl anions by optical spectroscopy. These results, together with the previous data for the phenyl silyl anions, provide very strong evidence for the absence of a pπ–pπ-type conjugation in the series PhR_2E^- (E = Si, Ge, Sn, and Pb).[7] Recently, Buncel and co-workers also reported corroborating evidence obtained from a study of silyl anions Ph_2SiH^- and $PhSiH_2{}^-$, and the corresponding carbanions, Ph_2CH^- and $PhCH_2{}^-$.[12]

The UV-visible spectra of the disilanylene dianions **2a**—**2c** in THF are shown in Fig. 1. Table 1 summarizes the optical spectroscopic data for the dianions **2a**—**2c**, and also includes similar data for the phenyl silyl anions and the corresponding carbanions.

Table 1. Absorption Maxima (nm) in THF of **2** and Related Species

		λ_{max} (nm)		
Compound	M=	Li	Na	K
2		610	644	695
5[a)]		582—584	620—623	645—649
Ph_3SiM[b)]		335	346	363
$MePh_2SiM$[b)]		335	344	364
Ph_3CM[c)]		500		486

a) Ref. 14. b) Ref. 18. c) Ref. 17.

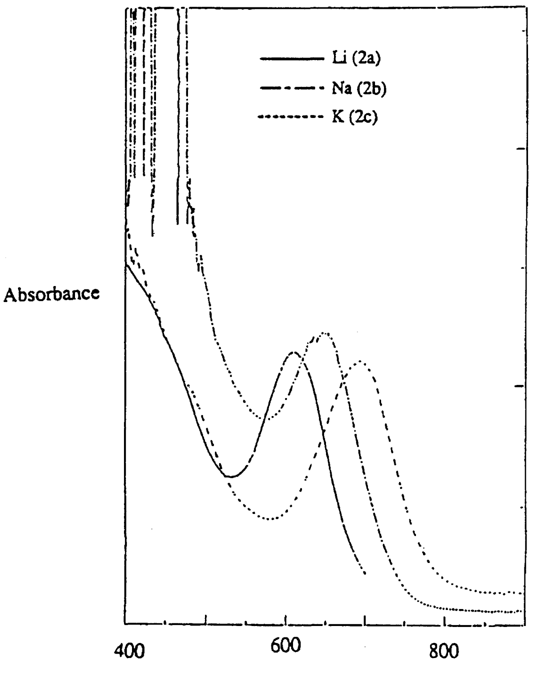

Fig. 1. Visible absorption spectra of 1,2-disila-1,2-acenaphthlenediide **2**.

The contrast between the λ_{max} values for the carbanion Ph_3C^- and the silyl anion Ph_3Si^- is striking. This is due to the difference in the type of electronic transition involved, via $\pi \rightarrow \pi^*$ for Ph_3C^- and $n \rightarrow \pi^*$ for Ph_3Si^- (i.e. from an unconjugated pπ pair on Si to a π^* molecular orbital of the phenyl group(s)). The 9,10-disilaanthracene dianions,[13] which were recently reported in our laboratory, also showed bothochromic shifts compared to the carbon systems. On the other hands, the λ_{max} values for the dianions **2a**—**2c** are shifted to longer wavelength compared to the phenyl silyl anions and the carbon–dianion systems.[14] There are two possible reasons for this shift: a) an increase in the HOMO energy level due to an electronic repulsion of the adjacent negative charges on the silicon atoms; b) an increase in the degree of conjugation between the pπ pair on Si and the naphthyl ring due to the structural orientation of the two silyl anions and the naphthyl ring in the same plane.

In a previous study[15] of the solvent and cation dependence of the electronic absorption spectra of the phenyl methyl anions, it was found that λ_{max} varied with the type of ion pair present via, a contact ion pair (CIP) or a solvent-separated ion pair (SSIP).[16,17] In diethyl ether, although both Ph_3CLi (λ_{max} = 446 nm) and Ph_3CK[17] (λ_{max} = 467 nm) were found to exist predominantly as CIP, in THF the λ_{max} values (Table 1) were taken as indicative of 95% SSIP formation for Ph_3CLi, and 65% SSIP formation for Ph_3CK. Similarly, for the silyl anions it was concluded by Evans et al. that although in THF Ph_3SiK exists as CIP, for Ph_3SiLi there is some degree of SSIP formation.[18] In a more solvating medium, DME, at −80 °C, the λ_{max} values of 376, 380, and 374 nm for Ph_3SiLi, Ph_3SiK, and Ph_3SiCs were taken as indicating that the SSIP absorbs at 377±3 nm.[18] Thus, an examination of the results given in Table 1 for the disilanylene 1,2-dianion **2a**—**2c** reveal a bathochromic shift upon going from Li to K. Also, Warhurst-type plots of ν against $1/(r_c+2)$, where r_c is the radius of the cation, are nicely linear (Fig. 2). These are taken as evidence that **2a**—**2c** exist as CIP in THF.

NMR Studies of Disilanylene 1,2-Dianions. In order to shed light on the structure of **2**, detailed NMR measurements of **2a** and **2d** were carried out.[19] The chemical shifts of the aromatic protons in **2a** and **2d**, compared with those of the corresponding 1,2-dichlorodisilanes (**1**),[20] are shifted upfield by around 0.85—1.59 ppm (Table 2). The upfield shifts of the ^{13}C NMR signals for the C-3–C-8 atoms are also shown in Table 3. The most important factor affecting the upfield chemical shifts of the proton and carbon in **2a**, **2d**, **8**, and **9** is the presence of a negative charge on the silicon atom (Chart 1).[21] The ^{29}Si NMR chemical shifts for **2a** and **2d** were observed at −1.24 and −20.22 ppm, respectively.

Table 2. ^1H NMR Chemical Shifts for **2** and Related Species

Compound	H-3,8	H-4,7	H-5,6	Compound	H-2	H-3	H-4
1a[a,b)]	7.92	7.58	8.01	**6**[c)]	7.74	7.48	7.48
1b[a,b)]	7.98	7.63	8.04				
2a[c)]	7.07	6.46	6.46	**8**[c)]	7.40	6.96	6.85
2d[c)]	6.90	6.45	6.45	**9**[d)]	7.41	6.98	6.84

a) *Trans*-form. b) In THF-d_8, internal Me_4Si as standard. c) In THF-d_8, external Me_4Si as standard. d) Ref. 21.

Interestingly, the ^{29}Si resonance for **8** and **9** is observed at −3.37 and −20.5 ppm, respectively (Table 4).[21] These ^{29}Si NMR chemical shifts are probably due to the difference in the substituents, i.e., methyl or isopropyl. At 173 K, well-resolved quartets with $^1J_{^{29}Si^7Li} = 43.5$ Hz (**2a**) and 41.2 Hz (**2d**) were observed. These observations indicate that **2a** and **2d** have at least a partial covalency at low temperature.

In the ^7Li NMR spectra of **2a** and **2d**, a single peak at 5.79 and 3.00 ppm, respectively, was detected at 183 K in THF-d_8.

Using the *para*-carbon shifts to probe the electron den-

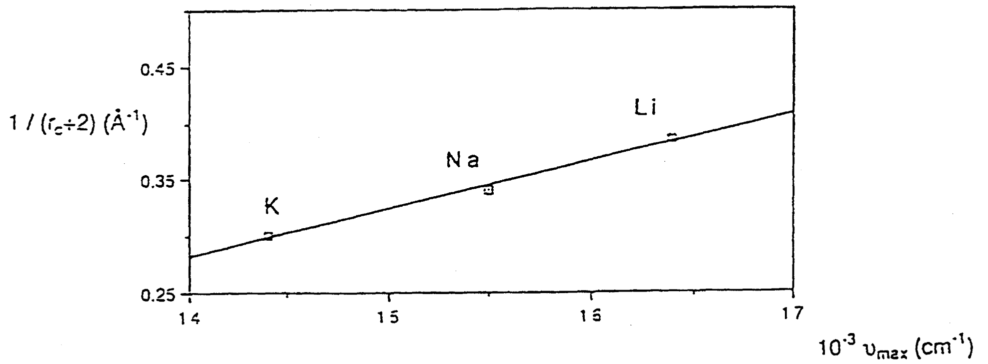

Fig. 2. Warhurst-type plots of 1,2-disila-1,2-acenaphthlenediide **2**.

Table 3. ^{13}C NMR Chemical Shifts for **2** and Related Species

Compound	C-3,8	C-4,7	C-5,6	C-2a,8a	C-5a	C-8b	Compound	C-1	C-2	C-3	C-4
1a[a,b)]	136.86	126.81	132.02	136.23	133.91	146.42	**6**[c)]	133.42	135.18	128.65	131.02
1b[a,b)]	133.44	127.02	131.96	137.70	133.72	145.08	**7**[d)]	134.4	134.0	128.1	130.5
2a[c)]	126.91	117.21	123.88	172.94	136.05	148.90	**8**[c)]	157.16	136.47	126.18	123.78
2d[c)]	125.75	116.59	124.19	176.25	136.00	148.89	**9**[d)]	160.1	135.4	126.7	123.9

a) *Trans*-form. b) In THF-d_8, internal Me_4Si as standard. c) In THF-d_8, external Me_4Si as standard. d) Ref. 21.

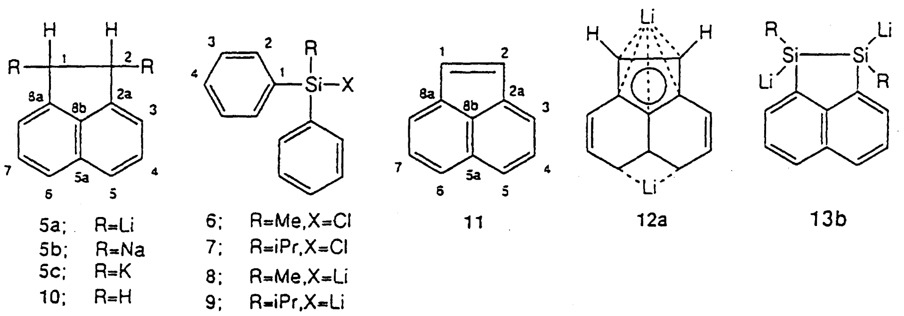

Chart 1. Compounds **5**—**13**.

Table 4. ^{29}Si NMR Chemical Shifts for **2**, Related Species and Other Silyl Anions

Compound	**1a**[a,b]	**1b**[a,b]	**2a**[c]	**2d**[c]	**6**[c]	**7**[d]	**8**[c]	**9**[d]
	8.99	6.20	−1.24	−20.22	13.34	10.0	−3.37	−20.5

a) *Trans*-form. b) In THF-d_8, internal Me$_4$Si as standard. c) In THF-d_8, External Me$_4$Si as standard. d) Ref. 21.

sity in the phenyl ring, Edlund and Buncel reported that the delocalization of charge was reduced by a factor of 9—10 for Ph$_3$SiLi, as compared to the carbanion systems. This reduction results largely due to the possible nonplanarity of the system, which would effectively diminish the pπ–pπ overlap.[7] Meanwhile, Boudjouk and Houg reported on the synthesis and characterization of the 1-silacyclopentadienide anion, in which the incorporation of silicon π-orbitals leads to diffuse and/or delocalize the negative charge into the butadiene moiety.[22] Interestingly, they have also reported that the negative charge in the 9-silafluorenide anion is localized on the silicon, and that annelation essentially eliminates π delocalization.[23]

In the phenyl silyl anions, the major trend upon introducing a negative charge on the silicon atom is that the *ipso*-carbon is strongly deshielded (22—40 ppm) and the *para*-carbon is shielded (6—8 ppm) relative to the neutral compound. The shift changes of the *ortho*- and *meta*-carbons are of a smaller magnitude (1—2 ppm), the *ortho*-carbons being shifted slightly downfield and the *meta*-carbons upfield. In comparison, the analogous ^{13}C NMR chemical shifts of **2a** and **2d**, the *ipso*-carbon is strongly deshielded (36.71, 42.55 ppm) and the *para*-carbon is shielded (8.14, 7.77 ppm) relative to the neutral compound. However the chemical-shift changes of the *ortho*- and *meta*-carbons are much larger than those observed for the phenyl silyl anions and with both the *ortho*- (6.95, 7.69 ppm) and *meta*-carbons (9.60, 10.43 ppm) being shifted upfield. The ^{1}H NMR of **2a** and **2d** reveals that the chemical-shift changes of the naphthyl ring (0.85—1.59 ppm) are also larger than those of the phenylsilyl anions (0.34—0.63 ppm). These observations suggest that the degree of charge delocalization is much larger in **2a** and **2c** compared with phenyl silyl anions.

A comparison of the NMR data of **2a** and **2d** with these carbon analogue **5a**, as summarized in Table 5, reveals a characteristic feature.[14,24] Based on the ^{1}H and ^{13}C NMR chemical shifts, Edlund et al. reported that the structure of the dilithium acenaphthenediide (**12a**) consists of one lithium cation coordinating to the five-membered ring, while the other one is located between the C-5 and C-6 positions. The electronic structure of **5a** is described in terms of a partly localized π-electronic system.[14,25] In contrast to **5a**, the NMR data of **2a** and **2d** and the theoretical calculations at the HF/3-21G* level on these systems support the structure **13b** in which one lithium atom interacts with one silicon atom.[8] The difference between the structures of **2** and **6** can be explained in that the charge delocalization is not sufficient in **2**, and the formation of a silicon–silicon double bond is energitically unfavorable. These conclusions are also supported by our theoretical calculations.[8]

Table 5. ^{13}C NMR Chemical Shifts for **5** and Related Species

Compound	C-1,2	C-3,8	C-4,7	C-5,6	C-2a,8a	C-5a	C-8b
10[a]	129.9	124.7	128.3	127.8	140.7	129.1	129.3
5a[a]	81.0	95.8	128.4	85.3	124.7	148.8	137.1
11[b]	30.1	118.6	127.1	121.9	145.0	131.4	139.1

a) In THF, cyclohexane was used as reference. Ref. 14. b) In CCl$_4$, internal Me$_4$Si as standard. Ref. 22.

To conclude, our UV-visible and NMR spectroscopic studies suggest that the disilanylene dianions **2** have a much larger charge delocalization than those of the phenyl silyl anions, but less compared to the carbanion systems, thus, the charge distribution in the naphthyl ring is mainly controlled by the π-polarizing effect of the negative silicon atoms. The large charge delocalization could be due to the electronic repulsion of the adjacent negative charge on the silicon atoms and/or the orientation of the two silyl anions and the naphthyl ring in the same plane.

Experimental

General Procedure. The melting points were determined using Yanaco micro melting-point apparatus. The ^{1}H, ^{7}Li, ^{13}C, and ^{29}Si NMR spectra were obtained with Brucker AC-400PS (156, 100, and 80 MHz) and AC-300P (117, 75, and 60 MHz) instruments. The ^{7}Li NMR chemical shifts are reported with reference to lithium chloride in MeOH. The mass spectra were obtained on a Shimadzu QP-2000 and QP-5000 spectrometer. The UV-vis spectra were obtained on a Jusco Ubest-50 instrument.

Tetrahydrofuran (THF), benzene and hexane were dried and distilled from sodium diphenylketyl prior to use. THF-d_8 was dried over lithium aluminum hydride, and then transferred into a tube covered with a potassium mirror and distilled before use. All of the reactions involving air- and moisture-sensitive compounds were carried out under a dry argon atmosphere using standard Schlenk techniques.

Gel permeation chromatographic separation was performed on a model LC-908 recycling preparative HPLC (Japan Analytical Industry Co., Ltd.) with a series of Jaigel 1H and 2H columns using toluene as the eluant.

Materials. 1,2-Dichloro-1,2-dimethyl-1,2-disilaacenaphthene (**1b**) was prepared as previously reported.[26]

UV-vis Spectra Measurements. The reaction vessel used in the spectrophotometric studies is shown in Fig. 3. It consists of a cylindrical tube having a capacity of about 30 ml, made of Pyrex brand glass, and equipped with one side arm to which a 10 mm Pyrex UV cell is attached and a second arm consisting a stopcock. This reaction vessel was made to fit into the cell compartment of the Jusco Ubest-50 UV-visible spectrophotometer.

The 40 mg of substrate and excess metal (about 30 mg) were introduced into the reaction vessel. The vessel was then attached

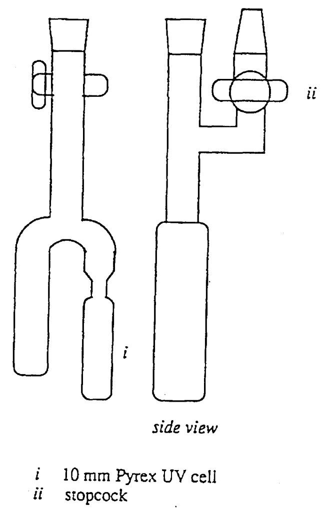

Fig. 3. Reaction vessel for UV-vis spectroscopic studies.

to a vacuum line and evacuated. Then 10 ml of dry and degassed THF was transferred to the vessel under vacuum. The stopcock was closed and the reaction vessel removed from vacuum line. The solution was sonicated for 30 min or 2 h at 0 °C to afford a dark-blue solution. A small amount of this dark-blue solution was transferred to the UV cell, and THF was transferred to the UV cell by cooling the cell to −78 °C, to dilute the solution. The spectra were taken over the range 400—900 nm.

NMR Spectra Measurements. A mixture of the substrate (30 mg) and an excess of lithium (about 30 mg) in 1 ml of THF-d_8 were sonicated for 30 min at 0 °C to afford a dark-blue solution. The reaction vessel was replaced inside the argon glove-box, then, after removing any unreacted lithium, the solution was transferred to the NMR tube, which was sealed before NMR measurements.

Preparation of 1,2-Dichloro-1,2-diisopropyl-1,2-disilaacenaphthene (1a). A solution of 1,8-dilithionaphthalene[27] (10.5 mmol), prepared from 3.00 g of 1,8-dibromonaphthalene (10.5 mmol) and *n*-BuLi (23.4 mmol) in Et_2O, was added dropwise over a period of 90 min to a solution of 1,1,2,2-tetrachloro-1,2-diisopropyldisilane (3.1 g 10.9 mmol) dissolved in 80 ml of Et_2O. The resulting mixture was heated under reflux for 6 h. After the resulting suspension was cooled to ambient temperature, 100 ml of hexane was added. The precipitated salts were filtered off, and the filtrate was concentrated in vacuo. Crystallization from hexane gave 1.49 g (42%) of 1,2-dichloro-1,2-diisopropyl-1,2-disilaacenaphthene (**1a**)[20] (mixture of the *trans*- and *cis*-isomers; *trans* : *cis* = ca.2 : 1); yellow crystals, mp >250 °C. *trans*-form; ^{1}H NMR ($CDCl_3$) $\delta = 1.21$ (d, 6H, $J = 7.36$ Hz), 1.31 (d, 6H, $J = 7.36$ Hz), 1.63 (sept, 2H, $J = 7.36$ Hz), 7.57 (dd, 2H, $J = 6.66, 8.22$ Hz), 7.89 (d, 2H, $J = 6.66$ Hz), 7.96 (d, 2H, $J = 8.22$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = 16.52$ (d), 16.80 (q), 17.35 (q), 125.99 (d), 131.06 (d), 132.79 (s), 132.94 (d), 135.84 (s), 145.54 (s); ^{29}Si NMR ($CDCl_3$) $\delta = 8.82$. *cis*-form; ^{1}H NMR ($CDCl_3$) $\delta = 1.21$ (d, 6H, $J = 6.62$ Hz), 1.31 (d, 6H, $J = 6.62$ Hz), 1.64 (sept, 2H, $J = 6.62$ Hz), 7.57 (dd, 2H, $J = 6.66, 8.22$ Hz), 7.89 (d, 2H, $J = 6.66$ Hz), 7.96 (d, 2H, $J = 8.22$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = 16.41$ (d), 16.74 (q), 17.17 (q), 125.82 (d), 131.10 (d), 132.79 (s), 132.04 (d), 135.54 (s), 145.40 (s); ^{29}Si NMR ($CDCl_3$) $\delta = 7.94$; MS (M^+, relative abundance) 338 (M^+; 35), 295 (M^+ −43; 100). HRMS; Found : *m*/*z* 338.0449. Calcd for $C_{16}H_{20}Si_2Cl_2$: M, 338.0481.

Generation of 1,2-Dilithio-1,2-dialkyl-1,2-disilaacenaphthene (2). A mixture of **1a** (100 mg, 0.3 mmol) and an excess of lithium (100 mg, 14.4 mmol) in 10 ml of THF was sonicated for 30 min at room temperature to afford a dark-blue solution. After removing the unreacted lithium, the solution is directly used in the next step. **2a**; ^{1}H NMR (THF-d_8) $\delta = 1.18$ (d, 6H, $J = 6.0$ Hz), 1.28 (d, 6H, $J = 6.0$ Hz), 1.29—1.32 (m, 2H), 6.43—6.49 (m, 4H), 7.07 (d, 2H, $J = 6.15$ Hz); ^{13}C NMR (THF-d_8) $\delta = 18.81$ (d), 26.26 (q), 26.65 (q), 117.21 (d), 123.88 (d), 126.91 (s), 136.05 (d), 148.90 (s), 172.94 (s); ^{29}Si NMR (THF-d_8) $\delta = -1.24$.

Under similar conditions, 1,2-Disodio- and 1,2-dipotassio-1,2-diisopropyl-1,2-disilaacenaphthene, (**2b**) and (**2c**) were generated with the reaction of **1a** and an excess of sodium or potassium. 1,2-Dilithio-1,2-dimethyl-1,2-disilaacenaphthene (**2d**) was generated from the reaction of **1b** (104 mg, 0.37 mmol), and an excess of lithium (100 mg, 14.4 mmol) in 5 ml of THF was sonicated for 30 min at to 0 °C afford a dark-blue solution. After removing any unreacted lithium, the obtained solution was directly used in the next step. **2d**; ^{1}H NMR (THF-d_8) $\delta = 0.44$ (s, 6H), 6.40—6.50 (m, 4H), 6.90 (d, 2H, $J = 6.45$ Hz); ^{13}C NMR (THF-d_8) $\delta = 2.66$ (q), 116.59 (d), 124.19 (d), 125.75 (s), 136.00 (d), 148.89 (s), 176.24 (s); ^{29}Si NMR (THF-d_8) $\delta = -20.22$.

Reaction of 1,2-Dilithio-1,2-diisopropyl-1,2-disilaacenaphthene (2a) with Methyl Iodide. To the dianion solution, prepared as described above, was added 1.0 ml of methyl iodide, dropwise, over a period of 30 min at −78 °C. After completing the addition, the resulting mixture was further stirred at the same temperature for 30 min; the bath was then gradually warmed to ambient temperature. The reaction mixture was hydrolyzed and extracted with ether. The organic layers were combined, dried with $MgSO_4$, filtered and concentrated in vacuo. The crude product was chromatographed by HPLC to afford 71 mg (80%) of **3**[20] (mixture of the *trans*- and *cis*-isomers; *trans* : *cis* = ca.3 : 2).; colorless oil, *trans*-form; ^{1}H NMR ($CDCl_3$) $\delta = 0.33$ (s, 6H), 1.13 (d, 6H, $J = 7.2$ Hz), 1.18 (d, 6H, $J = 7.2$ Hz), 1.32—1.34 (m, 2H), 7.47 (dd, 2H, $J = 8.2, 6.5$ Hz), 7.74 (d, 2H, $J = 6.5$ Hz), 7.82 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = -6.78$ (q), 13.36 (d), 18.75 (q), 19.38 (q), 125.43 (d), 128.97 (d), 132.06 (d), 132.76 (s), 142.40 (s), 146.54 (s); ^{29}Si NMR ($CDCl_3$) $\delta = -14.30$. *cis*-form; ^{1}H NMR ($CDCl_3$) $\delta = 0.45$ (s, 6H), 0.99 (d, 6H, $J = 6.6$ Hz), 1.09 (d, 6H, $J = 6.6$ Hz), 1.32—1.34 (m, 2H), 7.47 (dd, 2H, $J = 8.2, 6.5$ Hz), 7.74 (d, 2H, $J = 6.5$ Hz), 7.82 (d, 2H, $J = 8.2$ Hz); ^{13}C NMR ($CDCl_3$) $\delta = -7.02$ (q), 13.81 (d), 18.36 (q), 18.92 (q), 125.34 (d), 128.94 (d), 131.83 (d), 132.69 (s), 142.32 (s), 146.66 (s); ^{29}Si NMR ($CDCl_3$) $\delta = -14.62$; MS (M^+; relative abundance) 298 (M^+; 28), 255 (M^+ −43; 39), 213 (M^+ −85; 100). HRMS; Found : *m*/*z* 298.1609. Calcd for $C_{18}H_{26}Si_2$: M, 298.1573.

Reaction of 1,2-Dilithio-1,2-diisopropyl-1,2-disilaacenaphthene (2a) with Chlorotrimetylsilane. To the dianion solution, prepared as described above, was added 1.0 ml of chlorotrimethylsilane dissolved in 3 ml of THF, dropwise, over a period of 30 min at −78 °C. After completing the addition, the resulting mixture was further stirred at the same temperature for 30 min; the bath was then gradually warmed to ambient temperature. The reaction mixture was hydrolyzed and extracted with ether. The organic layers were combined, dried with $MgSO_4$, filtered and concentrated in vacuo. The crude product was chromatographed by HPLC to afford 71 mg (57%) of **4**; yellow oil, ^{1}H NMR (C_6D_6) $\delta = 0.16$ (s, 18H), 1.23 (d, 6H, $J = 7.33$ Hz), 1.34 (d, 6H, $J = 7.33$ Hz), 1.59—1.64 (m, 2H), 7.31 (dd, 2H, $J = 6.63, 8.01$ Hz), 7.63 (d, 2H, $J = 8.01$ Hz), 7.76 (d, 2H, $J = 6.63$ Hz); ^{13}C NMR (C_6D_6) $\delta = 0.49$ (q), 13.55 (d), 21.14 (q), 21.89 (q), 125.68 (d), 128.93 (d), 133.84 (d), 133.78 (s), 142.44 (s), 147.23 (s); ^{29}Si NMR (C_6D_6) $\delta = -28.25, -14.53$; MS (M^+; relative abundance) 414 (M^+; 30), 371 (M^+ −43; 45), 329 (M^+ −85; 70), 255 (M^+ −159; 75), 207 (M^+ −207; 55), 73 (M^+ −341;

100).

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