Synthesis of the first kinetically stable dibenzosilafulvene

N. N. Zemlyanskii,[a] I. V. Borisova,[a] A. K. Shestakova,[a] Yu. A. Ustynyuk,[b] and E. A. Chernyshev[a]*

[a]*State Scientific Center State Research Institute of Chemistry and Technology of Organoelement Compounds, 38 sh. Entuziastov, 111123 Moscow, Russian Federation. Fax: +7 (095) 273 1213*

[b]*Department of Chemistry, M. V. Lomonosov Moscow State University, 119129 Moscow, Leninskie Gory, Russian Federation. Fax: +7 (095) 932 8846*

The first stable dibenzosilafulvene, 9-{[8-(dimethylaminomethyl)-1-naphthyl]phenylsil-1-ylium}fluoren-9-ide (**7a**), was obtained in one step from 9-fluorenyllithium and chloro[8-(dimethylaminomethyl)-1-naphthyl]phenylsilane as a stable solvate with THF. The structure of the zwitterionic compound **7a** was established by ^{1}H, ^{13}C, and ^{29}Si NMR in solution and in the solid state. The reactions of compound **7a** with crotonaldehyde, ethanol, and triethylethylidenephosphorane are described. The data on the synthesis of alkoxy- and alkylthiochloro-9-fluorenylsilanes and their phosphonium salts are given.

Key words: Si=C double bond, dibenzosilafulvene, N→Si intramolecular coordination, alkoxychloro-9-fluorenyl- and alkylthiochloro-9-fluorenylsilanes, 9-silylfluorenyl anions with phosphonium counterions, NMR spectra.

The kinetic instability of silaolefins is due to two main reasons, namely, the decreased energy of the $2p_\pi$—$3p_\pi$ bonding in the Si=C dyad compared to that of the $2p_\pi$—$2p_\pi$ bonding in the C=C fragment of olefins and the high polarity of the $^{(\delta-)}C{=}Si^{(\delta+)}$ bond, which is due to the considerable difference between the electronegativities of carbon and silicon. The latter factor is even more pronounced for other classes of compounds with Si=X multiple bonds (X = O, S, NR, PR, *etc.*). Therefore, the simplest compounds of this class can be detected and studied only in argon matrices at low temperatures, and the preparation of kinetically stable silaolefins, silanethiones, or silanimines requires that sterically hindered groups be introduced at one or both centers of the Si=X dyad.[1—4]

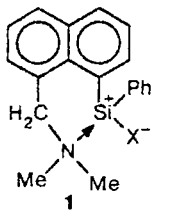
The kinetic stability of compounds containing

$$Si{=}X \leftrightarrow {}^{(\delta+)}Si{-}X^{(\delta-)}$$

multiple bonds can be increased, in principle, by delocalization[5] of the negative charge on the $X^{(\delta-)}$ center and by stabilization of the $^{(\delta+)}Si$ silycenium center, which can be achieved by coordination with nucleophilic groups.

An elegant method for stabilization of compounds with silicon—sulfur, silicon—nitrogen, and silicon—phosphorus multiple bonds has been proposed by Corriu *et al.*,[6] who described the synthesis of a compound of type **1**.

Note that kinetically unstable silaolefin **2** containing no bulky substituents at the silicon atom has also been isolated and structurally characterized as complex **2a**.[7,8] Finally, synthesis of stable silycenium perchlorate **3**

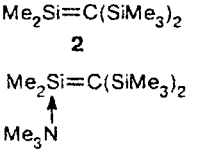


1

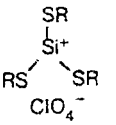
X = S, NBu^t, PPh

$Me_2Si{=}C(SiMe_3)_2$

2



2a



3

R = Pr^i

demonstrates that the positive charge on the sp^2-hybridized Si atom can be partially compensated due to delocalization of the lone electron pairs of the atom that is bound directly to silicon.[9]

Previously we have shown that owing to the efficient delocalization of the negative charge, silafulvenes and dibenzosilafulvenes can be generated in solutions at ambient temperature as kinetically independent species,[10,11] which can be detected as products of their subsequent reactions with nucleophiles, for example, with pyridine or phosphonium ylides.[10—13] It was of interest to carry out reactions of this type with chloro(fluorenyl)silanes containing a heteroatom with a lone electron pair (O or S) attached to the Si atom, a hydride hydrogen atom, or an N→Si intramolecular coordination bond.[6] The general synthetic route included preparation of chloro(9-fluorenyl)silanes **4—6** and their treatment with alkylidenephosphoranes to give dibenzosilafulvenes **7** (Scheme 1), as had been described in our previous studies[10—13] for the reactions of phosphonium ylides with chloro(cyclopentadienyl)- and chloro(fluorenyl)silanes, -germanes, and -stannanes.

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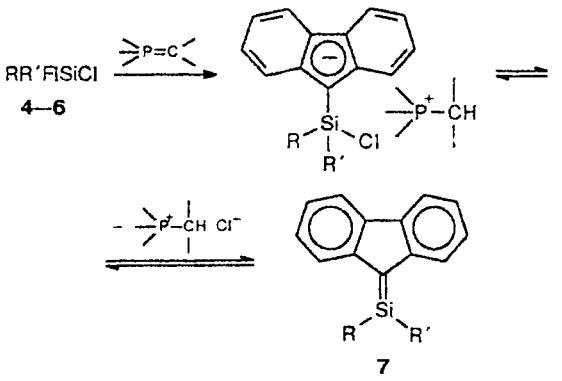
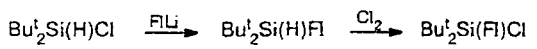
Scheme 1



4: R = Ph, R′ = 8-(dimethylaminomethyl)-1-naphthyl
5a: R = R′ = Pr^{i}O
6a: R = R′ = Bu^{n}S
Fl = 9-fluorenyl

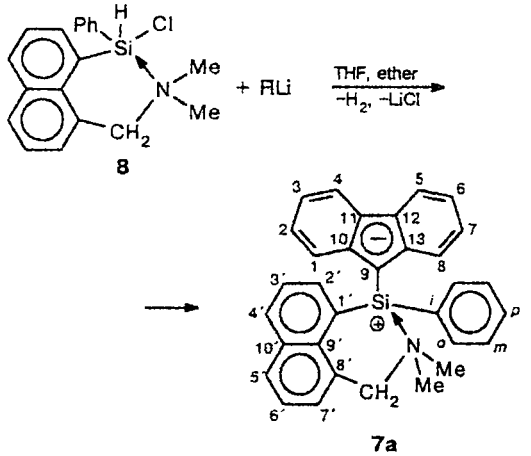
It was found that dichloro[8-(dimethylaminomethyl)-1-naphthyl]phenylsilane[14] does not react with fluorenyllithium in a mixture of Et_2O with THF, which is apparently due to steric reasons. Therefore, we decided to use the synthetic route proposed by Barton *et al.*[15] for the preparation of sterically hindered chloro(fluorenyl)silanes (Scheme 2).

Scheme 2



We found that the reaction of chlorosilane **8** with fluorenyllithium follows an unusual pathway and directly leads to dibenzosilafulvene **7a**, which was isolated as a stable solvate with THF (Scheme 3).[16]

Scheme 3



Note that the reactions of organolithium compounds with chlorosilanes normally involve Si—Cl bonds rather than Si—H bonds and that attempts to dehydrochlorinate chloro(fluorenyl)silanes by treatment with RLi result only in the formation of lithium salts of dialkylchlorosilylfluorene.[15,17]

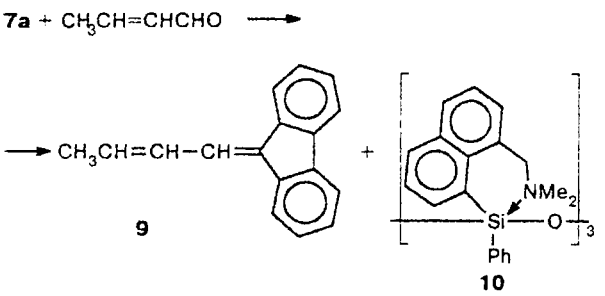
The structure of **7a** was proved unambiguously by its ^1H, ^{13}C, and ^{29}Si NMR spectra. The occurrence of the strong intramolecular N→Si coordination bond is clearly manifested in the ^1H NMR spectrum as nonequivalence of the Me groups at the nitrogen atom and the protons of the CH_2 group, which gives an AX spectrum with a typical value of 14.5 Hz for the geminal spin-spin coupling. The signals of the protons of the CH_3 and CH_2 groups in the spectrum of **7a** are shifted ~0.8—1.3 ppm and 0.4—0.6 ppm downfield, respectively, in relation to their positions in the spectrum of the initial compound **8** in which the N→Si coordination bond is not that strong. In the spectrum of silanethione (**1**, X = S) that we recorded,[10] these shifts of the signals observed in a pyridine-d_5 solution amount to ~ 0.8—1.2 ppm and 0.3—1 ppm, respectively.

The ^{13}C NMR spectrum of dibenzosilafulvene **7a** clearly resembles those of the alkali metal salts of fluorene[18] and silylfluorenyl anions, which have been studied in our previous works[12,19] and are also described below.* The C(9) resonance signal at 70.28 ppm, like these signals for other silylfluorenyl anions, is shifted downfield relative to its position in the spectra of silylfluorenes by more than 30 ppm, whereas the C(3,6) signal is shifted upfield by ~ 12 ppm. The signals of the carbon atoms in the *ortho*- and *para*-positions of the phenyl ring attached to the silicon atom are displaced downfield with respect to those in the spectrum of the initial **8** by 5.5 and 6.0 ppm, respectively. The CH_3 groups are clearly nonequivalent, and their signals are displaced downfield in relation to those in the ^{13}C NMR spectrum of chloride **8**. The ^{29}Si signal at 3.57 ppm occurs in the same region as those for compounds **1**.[10] We also recorded the ^{13}C CP MAS NMR spectrum of solid dibenzosilafulvene **7a** using rotation of the sample at the magic angle and cross-polarization. The positions of the signals in this spectrum proved to be similar to those in the spectrum recorded in solution, which confirms that the structures of dibenzosilafulvene **7a** in the crystalline state and in solution in pyridine-d_5 are identical.

Similarly to silaolefins[1] and the lithium salt of chloro(diisopropyl)silylfluorene,[17] compound **7a** readily reacts with crotonaldehyde but does not react with benzophenone or acetone (Scheme 4).

* The data of the ^1H, ^{13}C, and ^{29}Si NMR spectra reported for the lithium salt of chlorodiisopropylsilylfluorene by Couret *et al.*[17] differ substantially from those reported by Edlung[18] and obtained in our studies;[12,13,19] this is apparently due to the fact that Couret *et al.*[17] recorded the spectra in dichloromethane, which is not inert toward carbanions of the fluorenyl series.

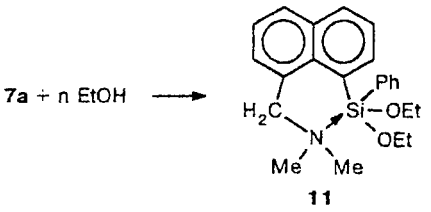
Scheme 4



9 10

Dibenzosilafulvene **7a** eliminates fluorene under the action of alcohols (Scheme 5).

Scheme 5

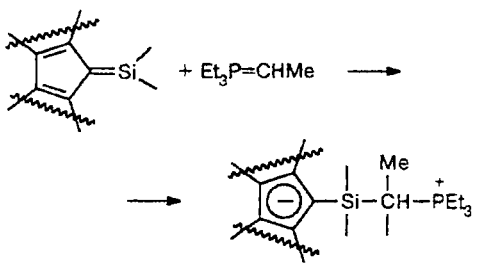


11

Note that protolysis of the C(9)—Si bond under the action of weak electrophilic reagents such as alcohols is not typical of silylated fluorenes. Apparently, the N→Si coordination in dibenzosilafulvene **7a** results in an additional polarization of the C(9)—Si bond and facilitates desilylation.

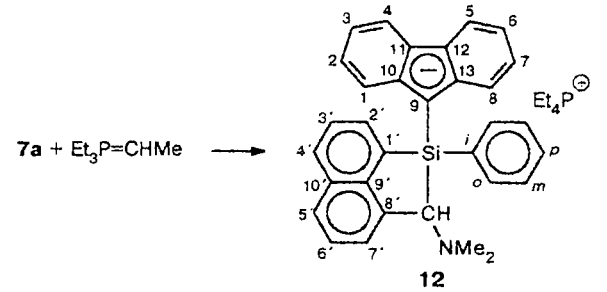
We also studied the interaction of dibenzosilafulvene **7a** with $Et_3P{=}CHMe$. Previously we have shown[12,13,19] that in the case of silafulvenes and dibenzosilafulvenes as well as silanethione (**1**, X = S), this reaction affords betaines (Scheme 6).

Scheme 6



In the case of dibenzosilafulvene **7a**, we did not detect the formation of a stable betaine; instead, the reaction gave silaacenaphthene derivative **12** (Scheme 7).

Scheme 7



12

Silanethione (**1**, X = S) behaves in a similar way under thermodynamically controlled conditions.[20]

The data obtained by spectroscopy and the chemical behavior make it possible to claim that compound **7a**, which can formally be regarded as a derivative of dibenzosilafulvene, has a zwitterionic nature.

Based on the result of the reaction of **7a** with $Et_2P{=}CHMe$ and the published data[13] on the synthesis of perchlorate **3**, we decided to prepare chloro(fluorenyl)di(isopropoxy)silane (**5a**), di(butylthio)(chloro)fluorenylsilane (**6a**), and fluorenyl(diisopropoxy)silane (**13**) and to make them react with $Ph_3P{=}CMe_2$.

Silanes **5a** and **6a** were synthesized by the exchange of trichloro(fluorenyl)silane with Et_3SnOPr^i and $Pb(SBu^n)_2$, respectively. In the case of $FlSi(H)Cl_2$, the reaction with Et_3SnOPr^i was accompanied by liberation of metallic tin. Therefore, to replace both chlorine atoms, we used $Me_2Ge(OPr^i)_2$ (Scheme 8).

Scheme 8

$$FlSi(H)Cl_2 + Me_2Ge(OPr^i)_2 \longrightarrow FlSi(OPr^i)_2H + Me_2GeCl_2$$

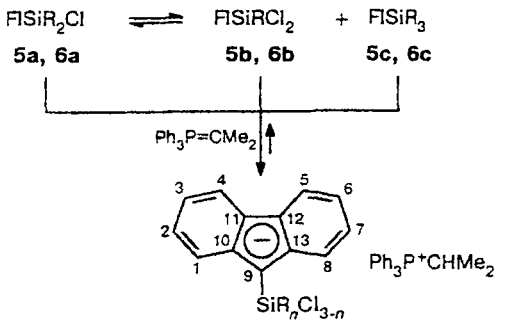
13

The reactions of compounds **5a**, **6a**, and **13** with $Ph_3P{=}CMe_2$ lead to the corresponding carbanions with phosphonium counterions. As shown by NMR spectroscopy, the starting fluorenylsilanes **5a** and **6a** partially disproportionate in solution to give mixtures of compounds **5a—c** and **6a—c**, respectively, whose reactions with $Ph_3P{=}CMe_2$ yield phosphonium salts **14a—c** and **15a—c** (Scheme 9).

All the isolated alkoxysilyl- and alkylthiosilylfluorenes and their salts with phosphonium counterions were characterized by NMR spectroscopy using the criteria that we developed previously[12,13,19] for NMR identification of compounds of this type. Compounds **5c** and **14c** were obtained by an alternative synthetic route.

These results, together with the published data on the deprotonation of chloro(fluorenyl)silanes, make it possible to conclude that elimination of chloride ions is not typical of the $Fl^-R_2SiCl\ M^+$ type salts (R = Alk, Ph, SR, OR; M^+ = Li^+ or Ph_3P^+Alk) in solution. However, the chlorosilyl-substituted fluorenyl anion with

Scheme 9



14a—c: R = OPr^i;
15a—c: R = SBu^n
n = 2 (**a**), 1 (**b**), 3 (**c**)

an N→Si intramolecular coordination bond is converted in solution into the corresponding dibenzosilafulvene.

Experimental

^{1}H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra were measured on a Bruker AM-360 spectrometer for degassed solutions of the samples in pyridine-d_5, THF-d_8, and benzene-d_6 using tetramethylsilane (^{1}H, ^{13}C, and ^{29}Si) and 85% H_3PO_4 in D_2O (^{31}P) as standards. The ^{13}C NMR signals were assigned using ^{13}C-INEPT and ^{13}C-DEPT procedures and also using ^{13}C NMR spectra without spin-spin proton decoupling. The ^{13}C MAS NMR spectra with cross-polarization and a speed of rotation of 2.7—3.4 kHz were measured on a Bruker MSL-300 spectrometer at ~20 °C (using adamantane as the external standard).

Chlorosilanes[14] and phosphonium ylides ("salt-free")[21] used as the starting compounds were prepared by known procedures. All the syntheses were carried out in an atmosphere of dry argon or *in vacuo*.

Trichloro(9-fluorenyl)silane and dichloro(9-fluorenyl)silane were synthesized by the reaction of fluorenyllithium with a two- or threefold excess of $SiCl_4$ or $HSiCl_3$ in benzene at ~20 °C. Trichlorosilane $FlSiCl_3$, yield 61.6%, b.p. 150 °C (0.1 Torr), m.p. 110—111 °C (from heptane). Found (%): C, 52.84; H, 2.57; Cl, 35.81. $C_{13}H_9Cl_3Si$. Calculated (%): C, 52.11; H, 3.03; Cl, 35.49. ^{13}C NMR (THF-d_8), δ: 46.07 (C-9); 121.09 (C-4,5); 126.12 (C-1,8); 127.67 (C-3,6); 128.32 (C-2,7); 139.59 (C-11,12); 142.57 (C-10,13). The reaction also gives Fl_2SiCl_2 as a by-product in ~30% yield, m.p. 173—174 °C (from heptane, *cf.* Ref. 22).

Dichlorosilane $FlSi(H)Cl_2$, yield 45.3%, b.p. 133—135 °C (0.1 Torr), m.p. 92—93 °C (from hexane). Found (%): C, 58.83; H, 3.60; Cl, 27.01. $C_{13}H_{10}Cl_2Si$. Calculated (%): C, 58.88; H, 3.80; Cl, 26.74. ^{1}H NMR (C_6D_6), δ: 3.60 (br.s, 1 H, H-9); 5.03 (d, 1 H, SiH, J = 1.5 Hz); 7.10—7.58 (m, 8 H, H_{arom}). ^{13}C NMR (C_6D_6), δ: 42.72 (C-9); 120.60 (C-4,5); 125.16 (C-1,8); 127.13 (C-3,6); 127.31 (C-2,7); 139.62 (C-11,12); 141.68 (C-10,13).

Chloro(9-fluorenyl)diisopropoxysilane (5a) and (9-fluorenyl)triisopropoxysilane (5c) were synthesized by refluxing stoichiometric amounts of $FlSiCl_3$ and Et_3SnOPr^i in benzene for 1 h. The benzene was evaporated under atmospheric pressure, and the residue was distilled *in vacuo*. Chloride **5a**, yield 93.9%, b.p. 147—149 °C (0.1 Torr). Found (%): C, 66.03; H, 6.57; Cl, 9.90. $C_{19}H_{23}ClO_2Si$. Calculated (%): C, 65.78; H, 6.68; Cl, 10.22. ^{1}H NMR (THF-d_8), δ: 0.93, 1.07 (both d, 12 H, Me, J = 6.1 Hz); 4.04 (sept, 2 H, OCH, J = 6.1 Hz); 4.02 (br.s, 1 H, H-9); 7.24—7.84 (m, 8 H, Fl). ^{13}C NMR (THF-d_8), δ: 25.11, 25.42 (both Me), 41.98 (C-9), 68.38 (OCH), 120.90 (C-4,5), 126.25 (C-1,8), 127.12 (2 C, C-3,6 and C-2,7), 142.36 (C-11,12), 142.76 (C-10,13). ^{29}Si NMR (THF-d_8), δ: −43.08.

Triisopropoxide **5c**, yield 78.4%, b.p. 152—157 °C (0.1 Torr), n_D^{20} 1.5280. Found (%): C, 70.97; H, 8.03. $C_{22}H_{30}O_3Si$. Calculated (%): C, 71.31; H, 8.16. ^{1}H NMR (THF-d_8), δ: 1.18 (d, 18 H, Me, J = 6.1 Hz); 4.02 (sept, 3 H, OCH, J = 6.1 Hz); 4.24 (br.s, 1 H, H-9); 7.24—7.88 (m, 8 H, Fl). ^{13}C NMR (THF-d_8), δ: 25.86 (Me), 39.98 (C-9), 66.57 (OCH), 120.90 (C-4,5), 126.13 (C-1,8), 126.39 (C-3,6), 126.71 (C-2,7), 142.15 (C-11,12), 144.85 (C-10,13). ^{29}Si NMR (THF-d_8), δ: −59.82.

According to the NMR spectra, chloride **5a** partially disproportionates to give dichloride **5b** and triisopropoxide **5c**.

Dichloride **5b**. ^{1}H NMR (THF-d_8), δ: 1.05 (d, 6 H, Me, J = 6.1 Hz); 3.85 (br.s, 1 H, H-9); 4.33 (sept, 1 H, OCH, J = 6.1 Hz), 7.24—7.84 (m, 8 H, Fl). ^{13}C NMR (THF-d_8), δ: 25.06 (Me), 43.70 (C-9), 70.36 (OCH), 120.34 (C-4,5), 126.19 (C-1,8), 127.42 (C-3,6), 127.76 (C-2,7), 141.12 (C-11,12), 142.56 (C-10,13). ^{29}Si NMR (THF-d_8), δ: −20.81.

9-Fluorenyl(diisopropoxy)silane (13) was prepared in a similar way from equimolar amounts of $FlSi(H)Cl_2$ and $Me_2Ge(OPr^i)_2$. Yield ~100%, m.p. 57—58 °C (from hexane). Found (%): C, 73.24; H, 7.65. $C_{19}H_{24}O_2Si$. Calculated (%): C, 73.03; H, 7.74. ^{1}H NMR (C_6D_6), δ: 1.06, 1.10 (both d, 12 H, Me, J = 6.1 Hz); 3.94 (br.s, 1 H, H-9); 3.95 (sept, 2 H, OCH, J = 6.1 Hz); 4.82 (d, 1 H, SiH, J = 0.7 Hz); 7.34—7.94 (m, 8 H, Fl). ^{13}C NMR (C_6D_6), δ: 25.17, 25.32 (both Me), 41.19 (C-9), 66.84 (OCH), 120.17 (C-4,5), 125.32 (C-1,8), 126.14 (C-3,6), 126.52 (C-2,7), 141.64 (C-11,12), 143.43 (C-10,13).

Dibutylthio(chloro)-9-fluorenylsilane (6a). Equimolar amounts of $Pb(SBu^n)_2$ and $FlSiCl_3$ were stirred in benzene for 1 h, the precipitate was filtered off, and the solvent was removed at 20 °C (0.1 Torr) to give 98.5% of chloride **6a** as a thick slightly yellowish oil. Found (%): C, 62.13; H, 6.54. $C_{21}H_{27}ClS_2Si$. Calculated (%): C, 61.96; H, 6.68. ^{1}H NMR (C_6D_6), δ: 0.68 (t, 3 H, CH_3, J = 7.3 Hz); 0.99—1.09 (m, 2 H, CH_2); 1.16—1.27 (m, 2 H, CH_2); 2.30 (t, 2 H, CH_2, J = 7.3 Hz); 4.08 (s, 1 H, H-9); 7.22—7.89 (m, 8 H, Fl). ^{13}C NMR (C_6D_6), δ: 13.39 (CH_3); 21.56 (CH_2); 28.50 (CH_2); 33.74 (CH_2); 45.96 (C-9); 120.51 (C-4,5); 125.96 (C-1,8); 127.01 (C-3,6); 127.51 (C-2,7); 140.39 (C-11,12); 142.02 (C-10,13).

9-{[8-(Dimethylaminomethyl)-1-naphthyl]phenylsil-1-yl-ium}fluoren-9-ide (7a). At −20 °C, a solution of FlLi (3.61 g, 21 mmol) in 80 mL of THF was added dropwise over a period of 30 min to a stirred suspension of chlorosilane **8** (6.81 g, 20.92 mmol) in a mixture of 170 mL of THF and 140 mL of ether. Until ~90% of the solution of FlLi was added, the reaction had occurred almost instantaneously, which had been indicated by rapid discoloration of the solution of fluorenyllithium and dissolution of the suspended chlorosilane. After that, several drops of a solution of FlLi were added, and the mixture acquired an intense cherry color. The resulting mixture was refluxed with stirring for 20 min. The next day a small amount of a yellow solid precipitated from the cherry-colored solution. The mixture was refluxed with stirring for 3 h, and the precipitate was filtered off, washed with THF, and dried in a vacuum of 10^{-3} Torr to give 2.2 g (22.3%) of

complex **7a** · THF as a bright-yellow powder, m.p. 233—234 °C (decomp. in a sealed capillary). Found (%): C, 81.78; H, 6.42; N, 2.67. $C_{36}H_{35}NOSi$. Calculated (%): C, 82.24; H, 6.71; N, 2.66. The substance was poorly soluble in Et_2O, THF, CH_3CN, benzene, and hexane and moderately soluble in pyridine in which it slowly decomposes during storage. ^1H NMR (C_5D_5N), δ: 2.81, 2.88 (both s, 3 H, Me_2N); 4.05, 5.03 (both d, AX spectrum, 2 H, CH_2N, J = 14.5 Hz); 6.02—8.25 (m, 18 H, H_{arom}); 8.48—8.55 (m, 1 H, H-2′). ^{13}C NMR (C_5D_5N), δ: 45.82, 48.63 (both Me_2N), 63.55 (CH_2N), 70.28 (C-9), 114.90 (C-3,6); 119.71 (C-1,8); 122.70 (C-4,5), 126.22, 127.07, 128.14, 130.59, 131.57, 131.98 (C-2′, C-3′, C-4′, C-5′, C-6′, C-7′); 128.55 (*m*-C); 137.62 (*p*-C); 138.56 (*o*-C); 129.31, 129.33, 131.03, 133.62, 134.55, 146.39 (2 C) (C_{ipso}, C-1′, C-8′, C-9′, C-10′, C-10,13, C-11,12). ^{29}Si NMR (C_5D_5N), δ: 3.57.

The reaction of compound 7a with crotonaldehyde. A mixture of compound **7a** (0.41 g, 0.91 mmol) with a twofold excess of crotonaldehyde in 20 mL of THF was kept for 2 days at ~20 °C, and then refluxed for 30 min. The precipitate was filtered off, washed with THF, and dried *in vacuo* to give 0.2 g (72%) of the trimer of [8-(dimethylaminomethyl)-1-naphthyl]phenylsilanone (**10**) as a white amorphous powder. Found (%): C, 73.88; H, 6.41; N, 4.61. $C_{57}H_{57}N_3O_3Si_3$. Calculated (%): C, 74.71; H, 6.27; N, 4.59. Volatile substances were removed from the filtrate *in vacuo* to give a yellow oil, whose ^1H and ^{13}C NMR spectra corresponded to the published data[17] for fulvene **9**.

The reaction of compound 7a with ethanol. Anhydrous ethanol (0.32 g) was added to a suspension of **7a** (0.79 g, 1.74 mmol) in 15 mL of benzene resulting in an exothermal reaction. The mixture was stirred for 30 min, and the solvents were removed in a vacuum of 1 Torr and then of 10^{-3} Torr to give a yellow oil; according to ^1H and ^{13}C NMR spectra, this was a mixture of fluorene and [8-(dimethylaminomethyl)-1-naphthyl]diethoxy(phenyl)silane (**11**). ^1H NMR (C_6D_6), δ: 1.16, (t, 6 H, $C\underline{H}_3CH_2O$, J = 6.9 Hz); 3.70—3.85 (m, 4 H, two CH_2O groups, J = 6.9 Hz); 4.22 (s, 2 H, CH_2N); 7.16—8.20 (m, 10 H, $H_{arom.}$); 8.86—8.88 (m, 1 H, H-2′). ^{13}C NMR (C_6D_6), δ: 18.36 ($\underline{C}H_3CH_2O$), 42.30 (Me_2N), 58.99 (OCH_2), 63.24 (CH_2N), 124.26, 125.67, 127.12, 127.52, 129.83, 133.20 (C-2′, C-3′, C-4′, C-5′, C-6′, C-7′); 128.04 (*m*-C); 134.55 (*o*-C); 139.52 (*p*-C); 128.50, 135.27, 136.97, 137.47, 137.82 (C_{ipso}, C-1′, C-8′, C-9′, C-10′). The ^{13}C chemical shifts for fluorene coincided with the published data.[18]

The reaction of compound 7a with triethylethylidenephosphorane. The reaction was carried out in an all-sealed evacuated (10^{-3} Torr) setup using the technique of breaking compartment walls.[13] $Et_3P{=}CHMe$ (0.17 g, 1.16 mmol) was added in portions to a suspension of compound **7a** (0.52 g, 1.16 mmol) in 15 mL of THF. A claret-colored solution was formed. The next day the solvent was evaporated *in vacuo* to give a foamed golden-yellow solid. This product was dissolved in pyridine-d_5, transferred into an NMR tube, and sealed off. According to the ^1H, ^{13}C, ^{29}Si, and ^{31}P NMR spectra, this substance was a silaacenaphthene derivative, tetraethylphosphonium 9-(2-dimethylamino-1-phenyl-1,2-dihydro-1-silaacenaphthen-1-yl)fluoren-9-ide (**12**). ^1H NMR (C_5D_5N), δ: 0.50 (dt, 12 H, $(C\underline{H}_3CH_2)_4P^+$, J_{HH} = 7.6 Hz, J_{PH} = 17.9 Hz); 1.02 (dq, 8 H, $(CH_3C\underline{H}_2)_4P^+$, J_{HH} = 7.6 Hz, J_{PH} = 12.8 Hz); 2.53 (s, 6 H, Me_2N); 5.34 (s, 1 H, CH—N); 6.94—8.41 (m, 19 H, H_{arom}). ^{13}C NMR (C_5D_5N), δ: 5.13 (d, $(\underline{C}H_3CH_2)_4P^+$, J = 5.4); 10.48 (d, $(CH_3\underline{C}H_2)_4P^+$, J = 48.7 Hz); 45.16 (s, Me_2N), 61.31 (s, Si—CH—N), 78.86 (C-9), 111.59 (C-3,6); 119.24 and 119.34 (C-1,8 and C-4,5), 121.02 (C-2,7); 125.20, 125.32, 126.73, 127.02, 127.32, 128.53 (C-2′, C-3′, C-4′, C-5′, C-6′, C-7′); 127.39 (*m*-C); 131.73 (*p*-C); 133.01 (C-11,12); 137.10 (*o*-C); 137.59 (C_{ipso}); 141.76, 142.79, 143.55, 145.36 (C-1′, C-8′, C-9′, C-10′); 145.67 (C-10,13). ^{31}P NMR (C_5D_5N), δ: 38.69 ($(CH_3CH_2)_4P^+$). ^{29}Si NMR (C_5D_5N), δ: −12.79.

The reaction of alkoxyfluorenylsilanes 5a and 13 and alkylthiofluorenylsilane 6a with $Ph_3P{=}CMe_2$ (general procedure). The syntheses were carried out in a sealed evacuated (10^{-3} Torr) setup using using the technique of breaking compartment walls.[13] A mixture of compound **5a**, **13**, or **6a** (1 mmol) with $Ph_3P{=}CMe_2$ (1 mmol) in 3 mL of THF-d_8 was kept for 1 h at ~20 °C. The precipitated crystals colored orange-red (**14a**), cherry (**14c**), or bright-yellow (**6a**) were washed twice by decanting THF-d_8. The solvent was removed *in vacuo*, and the residue was dissolved in THF-d_8 or in pyridine-d_5 (for compounds **14c** and **6a**). The solution was transferred to an NMR tube, sealed off, and analyzed by NMR spectroscopy.

Isopropyltriphenylphosphonium 9-(chlorodiisopropoxysilyl)fluoren-9-ide (14a). ^1H NMR (THF-d_8), δ: 1.10, 1.20 (both d, 12 H, Me, J = 6.1 Hz); 4.39 (sept, 2 H, OCH, J = 6.1 Hz); 6.63—8.07 (m, 8 H, Fl). ^{13}C NMR (THF-d_8), δ: 25.61, 25.89 (both Me), 65.52 (OCH), 77.86 (C-9); 111.88 (C-3,6); 118.71 (C-1,8); 119.33 (C-4,5), 120.81 (C-2,7), 127.30 (C-11,12), 144.72 (C-10,13). ^{29}Si NMR (THF-d_8), δ: −37.54.

Isopropyltriphenylphosphonium 9-(dichloroisopropoxysilyl)fluoren-9-ide (14b). ^1H NMR (THF-d_8), δ: 1.30 (d, 6 H, Me, J = 6.1 Hz); 4.60 (sept, 1 H, OCH, J = 6.1 Hz); 6.63—8.07 (m, 8 H, Fl). ^{13}C NMR (THF-d_8), δ: 25.22 (Me), 67.55 (OCH), the signal for C-9 was not detected, because the concentration of the sample was too low; 112.89 (C-3,6); 118.76 (C-1,8); 118.96 (C-4,5), 121.40 (C-2,7), 127.93 (C-11,12), 144.21 (C-10,13). ^{29}Si NMR (THF-d_8), δ: −25.34.

Isopropyltriphenylphosphonium 9-(triisopropoxysilyl)fluoren-9-ide (14c). ^1H NMR (C_5D_5N), δ: 1.36 (d, 18 H, Me, J = 6.1 Hz); 4.67 (sept, 3 H, OCH, J = 6.1 Hz); 7.06—8.69 (m, 8 H, Fl). ^{13}C NMR (C_5D_5N), δ: 26.57 (Me), 64.40 (OCH), 79.55 (C-9); 111.24 (C-3,6); 119.25 (C-1,8); 120.18 (C-4,5), 120.74 (C-2,7), 127.30 (C-11,12), 145.83 (C-10,13). ^{29}Si NMR (C_5D_5N), δ: −48.39.

Isopropyltriphenylphosphonium 9-(diisopropoxysilyl)fluoren-9-ide was prepared from **13** in a similar way. ^1H NMR (THF-d_8), δ: 1.49, 1.51 (both d, 12 H, Me, J = 6.1 Hz); 4.59 (sept, 2 H, OCH, J = 6.1 Hz); 5.80 (s, 1 H, Si—H), 7.00—8.39 (m, 8 H, Fl). ^{13}C NMR (THF-d_8), δ: 25.97, 26.07 (both Me), 64.91 (OCH), 81.10 (C-9); 111.19 (C-3,6); 118.89 (C-1,8); 118.93 (C-4,5), 120.50 (C-2,7), 126.93 (C-11,12), 145.30 (C-10,13). After 1 h at 100 °C, the NMR spectrum did not change.

Isopropyltriphenylphosphonium 9-[di(butylthio)chlorosilyl]fluoren-9-ide (15a). ^1H NMR (C_5D_5N), δ: 0.73 (t, 6 H, CH_3, J = 7.4 Hz); 1.17—1.35 (m, 4 H, CH_2); 1.62—1.70 (m, 4 H, CH_2); 2.99 (t, 4 H, SCH_2, J = 7.3 Hz); 7.14—8.83 (m, 8 H, Fl). ^{13}C NMR (C_5D_5N), δ: 13.70 (CH_3); 22.03 (CH_2); 29.67 (CH_2); 34.25 (CH_2); 78.49 (C-9); 114.31 (C-3,6); 119.53 (2 C, C-1,8 and C-4,5); 122.48 (C-2,7); 129.27 (C-10,13); 144.72 (C-11,12). ^{29}Si NMR (C_5D_5N), δ: 3.74.

The ^1H, ^{13}C, and ^{31}P NMR spectra for the $Ph_3P^+CHMe_2$ cation coincided with those reported previously.[12,19]

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