The unusual reaction of [8-(dimethylamino)methyl-1-naphthyl]phenylchlorosilane with fluoren-9-yllithium. Synthesis of kinetically stable dibenzosilafulvene

Irina V. Borisova,[a] **Nikolai N. Zemlyanskii,***[a] **Alla K. Shestakova**[a] **and Yurii A. Ustynyuk**[b]

[a] *State Scientific Centre 'State Research Institute of Chemistry and Technology of Organoelement Compounds', 111123 Moscow, Russian Federation. Fax: +7 095 273 1213*

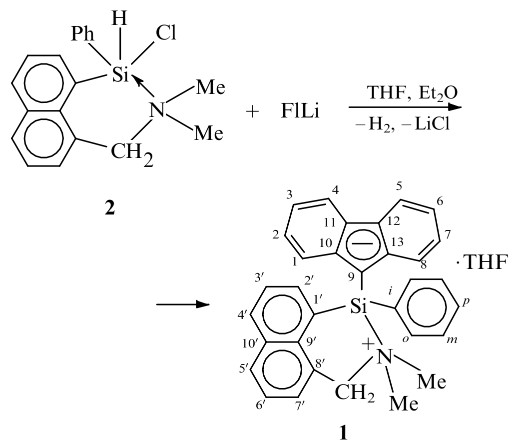
[b] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation. Fax: +7 095 932 8846*

The first stable dibenzosilafulvene, 14-[8′-(dimethylamino)methyl-1′-naphthyl]-14-phenyl-14-silafluorenylide 1, was obtained in one step from fluoren-9-yllithium and [8-(dimethylamino)methyl-1-naphthyl]phenylchlorosilane 2 as a stable solvate with THF; the zwitterionic structure of 1 is established by ^{1}H, ^{13}C and ^{29}Si NMR in solution and solid state and its reactions with crotonaldehyde, ethanol and triethylethylidene-λ^{5}-phosphane are described.

The problem of the synthesis of compounds with multiple p_π-p_π bonds is one of the intriguing tasks in the chemistry of non-transition elements. The syntheses of several kinetically stable silaethylenes[1] and silaallenes[2] have been described, but no silafulvene or dibenzosilafulvene have been isolated in the individual state.

In this work, in continuation of our studies[3–7] of silafulvenes and dibenzosilafulvenes, we report on the synthesis of the first kinetically stable dibenzosilafulvene **1** in which the intramolecular coordination Si←N according to Corriu[8] occurs.

It turned out that the reaction of chlorosilane **2**[9] with fluorenyllithium occurs anomalously. Organolithium compounds usually react with chlorosilane at Si–Cl rather than at Si–H bonds, and only dialkylchlorosilylfluorene lithium salts are formed in attempts to dehydrochlorinate fluorenylchlorosilanes with RLi.[10,11] However, dibenzosilafulvene **1**, isolated as the stable solvate with THF, is the direct product of the reaction presented in Scheme 1.



Scheme 1

Equimolar amounts of the reagents were heated in a diethyl ether–THF (1 : 1) mixture for 3.5 h. The precipitate was filtered off, washed with THF and dried *in vacuo* (10^{-3} Torr). Compound **1** was obtained in a yield of 22.3% as a bright-yellow amorphous powder with mp 233–234 °C (decomp., in a sealed capillary). The compound is poorly soluble in aliphatic and aromatic hydrocarbons, diethyl ether, THF and acetonitrile, and is moderately soluble in pyridine in which it decomposes slowly. The elemental analysis data correspond to the calculated values. The structure of compound **1** was solved unambiguously by ^{1}H, ^{13}C and ^{29}Si NMR spectra.†

Strong intramolecular coordination *via* the Si←N bond is distinctly manifested in the ^{1}H NMR spectrum by the non-equivalence of the CH_3 groups at the nitrogen atom and the protons of the CH_2 group, which give the AX spectrum with a typical value of 14.5 Hz for the geminal coupling constant. It is also noteworthy that the signals of the CH_3 groups and CH_2 protons in the spectrum of compound **1** are shifted to low field by ≈0.8–1.3 and 0.4–0.6 ppm, respectively, compared to their position in the spectrum of the initial compound **2** in which the Si←N coordination is not so strong. These shifts in the spectrum of stable [8-(dimethylamino)methyl-1-naphthyl]phenylsilanethione[8] in a solution of [^{2}H$_5$]pyridine are ≈0.8–1.2 and 0.3–1 ppm, respectively.

The ^{13}C NMR spectrum of compound **1** shows a distinct similarity with the spectra of fluorene alkali salts[12] and silylfluorenyl anions studied previously.[6,13] The resonance signal of C-9 at 70.28 ppm, as with those of other silylfluorenyl anions, is shifted to low field by more than 30 ppm relative to its position in the spectra of silylfluorenes, while the signal of C-3,6 is shifted to the high field by ≈12 ppm. Compared to the spectrum of the initial compound **2**, the signals of *ortho*- and *para*-carbons of the phenyl ring at the silicon atom are shifted to low field by 5.5 and 6.0 ppm, respectively. The non-equivalence of the CH_3 groups and the shifts of the CH_3 signals to low field compared to the spectra of compound **2** are distinctly manifested. The ^{29}Si signal at 3.57 ppm lies in the same region as the signals of

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† ^{1}H, ^{13}C, ^{13}C-INEPT, ^{13}C-DEPT, ^{29}Si and ^{31}P NMR spectra were recorded on a Bruker-AM360 spectrometer with Me_4Si as an internal standard (85% H_3PO_4 for ^{31}P NMR was used as an external standard), δ(ppm), C_5D_5N. ^{13}C MAS-NMR spectra (2.7–3.4 kHz rotation speed) with cross-polarisation were recorded on a Bruker MSL-300 spectrometer at room temperature (adamantane as an external standard).

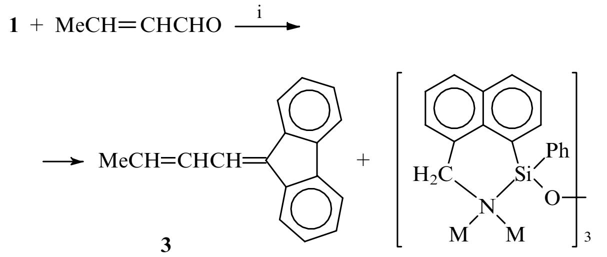
1: ^{1}H NMR (δ, ppm; J_{HH}, Hz): 2.81, 2.88 (2s, 3H, Me_2N); 4.05, 5.03 (2d, AX-spectrum, $J = 14.5$, 2 Hz, CH_2N); 6.02–8.25 (m, 18H, H-arom.); 8.48–8.55 (m, 1H, H-2′). ^{13}C NMR (δ, ppm.): 45.82, 48.63 (Me_2-diastereotop.), 63.55 (CH_2N), 70.28 (C-9), 114.90 (C3,6); 119.71 (C-1,8); 122.70 (C-4,5), 123.73 (C-2,7); 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 (C-*m*); 137.62 (C-*p*); 138.56 (C-*o*); 129.31, 129.33, 131.03, 133.62, 134.55, 146.39 (double intensity) (C-*i*, C-1′, C-8′, C-9′, C-10′, C-10,13, C-11,12). ^{29}Si NMR (δ, ppm): 3.57.

5: ^{1}H NMR (δ, ppm; J_{HH}, J_{PH}, Hz): 0.495 [dt, 12H, $J = 7.6$, 17.9 Hz, $(CH_3CH_2)_4P^+$]; 1.02 [dq, 8H, $J = 7.6$, 12.8 Hz, $(CH_3CH_2)_4P^+$]; 2.53 (s, 6H, Me_2N); 5.34 (s, 1H, CHN); 6.94–8.41 (m, 19H, H-arom.). ^{13}C NMR (δ, ppm; J_{PC}, Hz): 5.13 [d, $J = 5.4$, $(CH_3CH_2)_4P^+$]; 10.48 [d, $J = 48.7$ $(CH_3CH_2)_4P^+$]; 45.16 (s, Me_2N), 61.31 (s, SiCHN), 78.86 (s, C-9), 111.59 (s, C-3,6); 119.24 and 119.34 (2s, C-1,8 and C-4,5), 121.02 (s, C-2,7); 125.20, 125.32, 126.73, 127.02, 127.32, 128.53 (6s, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′); 127.39 (s, C-*m*); 131.73 (s, C-*p*); 133.01 (s, C-11,12); 137.10 (s, C-*o*); 137.59 (s, C-*i*); 141.76, 142.79, 143.55, 145.36 (4s, C-1′, C-8′, C-9′, C-10′); 145.67 (s, C-10,13). ^{31}P NMR (δ, ppm): 38.69 [$(CH_3CH_2)_4P^+$]. ^{29}Si NMR (δ, ppm): −12.79.

[8-(dimethylamino)methyl-1-naphthyl]phenylsilanethione.[8] The ^{13}C CP MAS-NMR spectrum of compound **1** was also measured. The positions of the signals in them are similar to those in the spectrum in solution, which confirms the identity of the structure of compound **1** in the crystalline state and in a solution of [$^2H_5$]pyridine.

Similarly to silaolefins[1] and the diisopropylchlorosilylfluorene lithium salt,[11] compound **1** readily reacts with crotonaldehyde (Scheme 2).

Compound **1** eliminates fluorene under the action of alcohols (Scheme 3).



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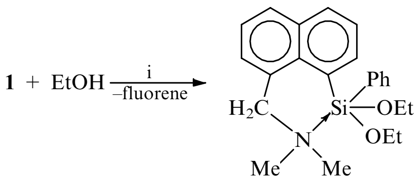
Scheme 2 *Reagents and conditions*: i, THF, two-fold excess aldehyde, 2 days at 20 °C, 30 min of heating, **3** (72%).

It should be mentioned that protolysis of the C9–Si bond under the action of such weak electrophiles as alcohol is not characteristic of silylated fluorenes. It is likely that the Si←N coordination in compound **1** results in the additional polarisation of the C9–Si bond and facilitates desilylation.



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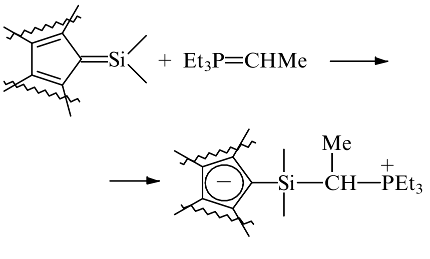
Scheme 3 *Reagents and conditions*: i, benzene, two-fold excess alcohol, 30 min, **4** (≈ 100%).

We also studied the reaction of compound **1** with triethylethylidene-λ^5-phosphane. As has been shown previously, this reaction in the case of silafulvenes,[7] dibenzosilafulvenes[6,13] and [8-(dimethylamino)methyl-1-naphthyl]phenylsilanethione[14] results in the formation of betaines (Scheme 4).

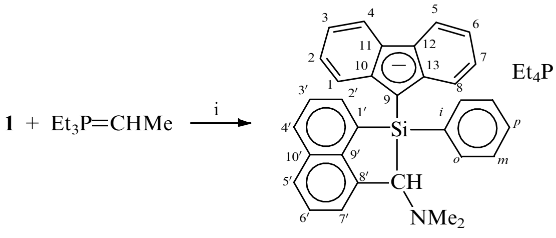
We failed to detect the formation of a stable betaine in the case of compound **1**, and the derivative of silaacenaphthene **5** is formed (Scheme 5).



Scheme 4

The silanethione reported by Corriu[14] acts similarly under thermodynamically-controlled conditions.

The spectral data obtained and the chemical behaviour observed allow one to assert that compound **1**, which can be formally considered as the derivative of dibenzosilafulvene, has a zwitterionic nature.



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Scheme 5 *Reagents and conditions*: i, all-sealed evacuated device (10^{-3} Torr), technique of breaking membranes and tubes, equimolar amounts of reagents, THF, 20 °C, 10 h, **5** (≈ 100%).

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