Generation and Trapping of 1,3-Dilithio-1,3-disila-isoindolines, the First Example of Dianions of Functionalized Silanes

Kohei Tamao,* Guang-Ri Sun and Atsushi Kawachi

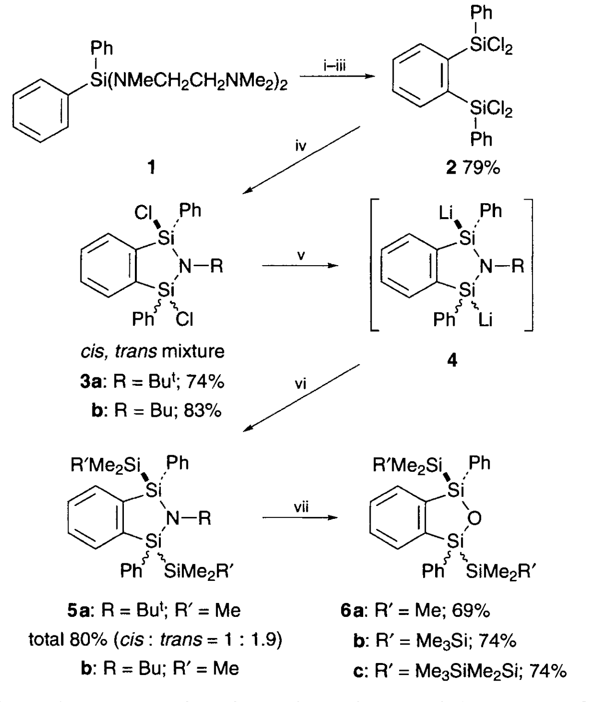
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

N-Alkyl-1,3-dichloro-1,3-disila-isoindolines are reduced with lithium naphthalenide at −78 °C to give the 1,3-dilithio derivatives which can be trapped with electrophiles.

The chemistry of silyl anions has attracted much attention recently from the synthetic and mechanistic viewpoints.[1] We have recently been engaged in a systematic study of functionalized silyl anions[2] which include (amino)phenylsilyllithiums as the first stable functionalized silyl anions[3a] and (alkoxy) phenylsilyllithiums as the silylenoid species.[2b] We now report our preliminary results on the generation and trapping of *ortho*-phenylene bis[(amino)silyllithium]s, 1,3-dilithio-1,3-disila-isoindolines, as the first examples of dianions of functionalized silanes, while some dianions of non-functionalized silicon compounds have been known.[3]

The overall transformations are summarized in Scheme 1. The precursors for the dianions **4**, 1,3-dichloro-1,3-disila-isoindoline derivatives **3**, were prepared in high yields from *ortho*-bis(phenyldichlorosilyl)benzene **2** by treatment with primary amines: **2** was obtained from a monosilyl-benzene **1** in three steps which involved the amino-group directed *ortho*-lithiation as the first key step.[4]

Typically, a *cis*/*trans* mixture of 1,3-dichloro-1,3-disila-isoindoline **3a**† with the *tert*-butyl group on nitrogen was treated with an excess amount of lithium naphthalenide in THF at −78 °C for several hours, according to our recent method,[2c] followed by treatment with trimethylchlorosilane, to form the 1,3-disilylated product **5a**.† The *trans* isomer of **5a** could be isolated pure by column chromatography on silica gel without decomposition and was characterized unambiguously by X-ray crystallography, as shown in Fig. 1.‡ The two fused rings are nearly coplanar with the approximately planar nitrogen atom and normal Si–Si bonds.§



Scheme 1 *Reagents and conditions*: i, Bu^{t}Li (1.8 equiv.), hexane, 0 °C to room temp., 2 h; ii, PhSiCl$_3$, room temp. to 50 °C, 4 h; iii, dry HCl, Et$_2$O, 0 °C, 2 h; iv, RNH$_2$ (1 equiv.), Et$_3$N (excess), THF, room temp., 10 h; v, Lithium naphthalenide (7–9 equiv.), THF, −78 °C, 3–4.5 h; vi, R′Me$_2$SiCl (5–9 equiv.), −60 °C to room temp., 1 h; vii, 0.1 mol dm^{-3} HCl, THF, room temp., 2 h

In contrast to the stable aminosilyl monoanions,[2a] the dianion **4** was rather unstable and decomposed almost completely after 3 h at 0 °C in THF.

Similarly, **3b** with the less bulky butyl group on nitrogen could also be transformed into **5b** *via* **4**. However, **5b** decomposed upon attempted chromatographic isolation and was converted by acid hydrolysis into the corresponding stable cyclic disiloxane derivative **6a** in *ca.* 70% overall yields.† The dianion **4** could be trapped with other electrophiles such as chloro-oligosilanes to form eventually the *ortho*-bis(oligosilanyl)benzenes **6**, which are otherwise hardly accessible. Each stereoisomer of **6** was isolated pure by HPLC and fully characterized.†

There are two points to be noted further. (1) For the generation of dianion **4**, lithium naphthalenide may be the reductant of choice. In comparison, reduction of **3** with lithium powder at 0 °C in THF, under the standard condition for generation of the aminosilyl monoanions,[1a,5] resulted in the formation of a complex mixture of products which involved **6** in only 20% yield or less, due to the instability of the dianion. (2) The cyclic disila-isoindoline skeleton seems to be essential for the high yield formation of the dianion. For example, we have examined similar reactions of an acyclic *ortho*-bis{(amino)(chloro)silyl}benzene **7** with lithium naphthalenide, but obtained only a complex mixture of products here again.

The dianions should be useful for two-direction derivatizations in, for example, the synthesis of new organosilicon materials.[6] Importantly, the products have functional groups on silicon atoms, ready for further functional group transformations.

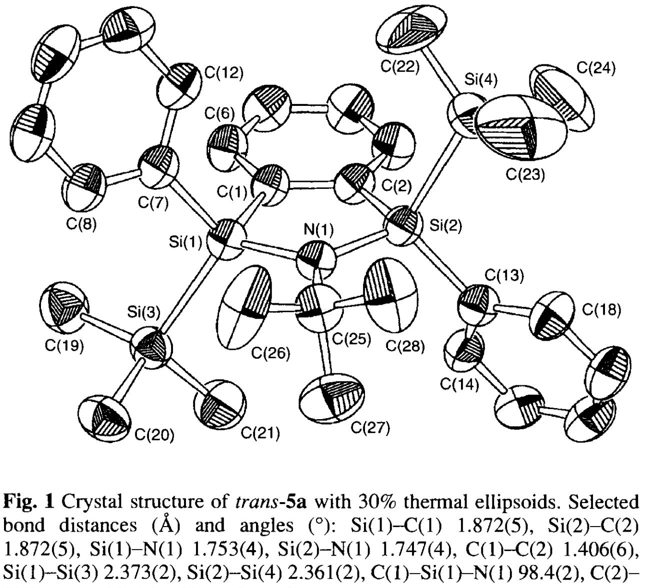
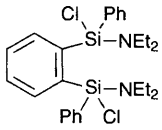


Fig. 1 Crystal structure of *trans*-**5a** with 30% thermal ellipsoids. Selected bond distances (Å) and angles (°): Si(1)–C(1) 1.872(5), Si(2)–C(2) 1.872(5), Si(1)–N(1) 1.753(4), Si(2)–N(1) 1.747(4), C(1)–C(2) 1.406(6), Si(1)–Si(3) 2.373(2), Si(2)–Si(4) 2.361(2), C(1)–Si(1)–N(1) 98.4(2), C(2)–Si(2)–N(1) 98.6(2), Si(1)–C(1)–C(2) 114.2(3), Si(2)–C(2)–C(1) 114.0(3), Si(1)–N(1)–Si(2) 114.4(2), Si(1)–N(1)–C(25) 122.6(3), Si(2)–N(1)–C(25) 123.0(3).



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We thank the Ministry of Education, Science, and Culture, Japan, for a Grant-in-Aid (No. 05453137) and Shin-Etsu Chemical Co., Ltd. for a gift of some chlorosilanes.

Received, 5th June 1995; Com. 5/03608I

Footnotes

† All new compounds gave satisfactory analytical and/or spectral data.

Synthesis of **5a** and **6a**: To a solution of lithium napthalenide, prepared from 43 mg (6.1 mmol) of Li and 787 mg (6.1 mmol) of naphthalene in THF (8 ml) at room temp. for 5 h, was added a solution of **3a** (300 mg; 0.7 mmol) in THF (3 ml) at −78 °C. The mixture was stirred at −78 °C for 4.5 h. To the silyl anion mixture was added Me_3SiCl (1.2 ml) at −60 °C, followed by stirring at room temp. for 1 h. After condensation, dilution with hexane and filtration, the filtrate was concentrated and subjected to column chromatography on silica gel (hexane–EtOAc 50 : 1, R_f = 0.15) to give **5a** (282 mg, 80%) as an isomeric mixture in a *cis* : *trans* ratio of 1 : 1.9). Recrystallization from hexane gave the pure *trans* isomer: Mp 178.5–179.5 °C: ^1H NMR (270 MHz, [$^2H_6$]benzene: δ 0.404 (s, 18 H), 1.281 (s, 9 H), 7.176–7.309 (m, 8 H), 7.540 (dd, *J* 5.4 and 3.2 Hz, 2 H) and 7.822–7.857 (m, 4 H). ^{13}C NMR (67.8 MHz): δ 0.88, 35.67, 53.26, 128.84, 129.18, 130.01, 133.39, 136.44, 142.28 and 147.98. ^{29}Si NMR (53.7 MHz, [$^2H_8$]THF): δ −6.4 and −20.3. In a similar experiment, the crude product was treated with 0.1 mol dm^{-3} hydrochloric acid (0.2 ml) in THF (6 ml) at room temp. for 2 h. Usual work-up and column chromatography on silica gel (hexane–EtOAc 50 : 1, R_f = 0.15) gave **6a** in 69% overall yield as a *cis* : *trans* 1 : 1 mixture. Each isomer was separated by HPLC on silica gel (hexane–EtOAc 90 : 1). *trans*: ^1H NMR (270 MHz, [$^2H_6$]benzene): δ 0.135 (s, 18 H), 7.234–7.304 (m, 6H), 7.325 (dd, *J* 5.4 and 3.2 Hz, 2H), 7.756 (dd, *J* 5.4 and 3.2 Hz, 2 H), 7.861 (dd, *J* 5.1 and 1.6 Hz, 4 H). ^{13}C NMR (67.8 MHz): δ −2.08, 128.34, 129.26, 129.89, 132.44, 133.82, 138.71, 147.96. HRMS: Calc. for $C_{24}H_{32}OSi_4$: *m/z* 448.15308. Found: *m/z* 448.15378. *cis*: ^1H NMR (270 MHz, [$^2H_6$]benzene): δ 0.299 (s, 18 H), 7.101−7.135 (m, 6H), 7.299 (dd, *J* 5.4 and 3.0 Hz, 2H), 7.607 (dd, *J* 5.7 and 2.2 Hz, 4 H), 7.710 (dd, *J* 5.4 and 3.0 Hz, 2 H). ^{13}C NMR (67.8 MHz): δ −1.67, 128.20, 129.24, 129.71, 132.38, 133.86, 138.73 and 147.80. HRMS: Calc. for $C_{24}H_{32}OSi_4$: *m/z* 448.15308. Found: *m/z* 448.15549.

‡ *Crystal data* for **5a** (colourless crystal from hexane): $C_{28}H_{41}NSi_4$, M = 503.98, prismatic (0.5 × 0.4 × 0.4 mm), monoclinic, space group $P2_1/n$ (no. 14) with a = 10.388(2), b = 17.466(1), c = 17.021 Å, V = 3049.9(6) Å^3, Z = 4, D_c = 1.097 g cm^{-3}, $F(000)$ = 600, μ(Cu-Kα) = 19.15 cm^{-1}, λ = 1.54178 Å, 20 °C, $2\theta_{max}$ = 120.1°. Measurements: Rigaku AFC7R diffractometer, scan type ω–2θ. A total of 4990 reflections was measured and of these 4701 were unique: No absorption correction was made; the data were corrected for Lorentz and polarization effects. The structure was solved by heavy-atom Patterson methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on 3292 reflections observed with $I > 3.00\sigma(I)$. R = 0.077 and R_w = 0.090. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ **5** exhibits two absorption maxima in UV spectrum λ_{max} (cyclohexane) at 217 nm (ε 39 500 dm^3 mol^{-1} cm^{-1}) and 262 nm (ε 4270) characteristic of a combination of the σ(Si–Si)–π and n(N)–σ(Si–Si) conjugations in (amino)(phenyl)disilanes:[5] further detailed analysis of these conformationally fixed cyclic sytems may shed new light on the electronic properties.

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