Chemistry of Heterocyclic Compounds, Vol. 37, No. 11, 2001

UNIQUE REACTIVITY OF A DIPHENYLDISILANE UNIT INCORPORATED INTO THE BICYCLIC RING SYSTEM: GENERATION OF A DISILANYLLITHIUM *via* SILICON-PHENYL BOND CLEAVAGE WITH LITHIUM*

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A bicyclic diphenyldisilane bearing two tetramethylene tethers reacts with lithium to form predominantly the disilanyllithium as a result of Si–C_{Ph} bond fission, while the pentamethylene homolog undergoes ordinary Si–Si bond cleavage to afford the expected phenylsilyllithium. The compressed Si–Si bond incorporated in the bicyclic ring system may be kinetically stabilized ("compression effect"), resulting in the unusual Si–C bond fission. When the reaction is carried out in the presence of chlorotrimethylsilane, a Calas-type reaction takes place on the phenyl rings. This result suggests that electron transfer to the phenyl group is the primary process in these bicyclic disilanes, followed by Si–Si or Si–C bond cleavage to afford the corresponding silyllithium species.

Keywords: bicyclic disilane, disilanyllithium, methylene tethers, silicon-carbon bond cleavage, silyllithium, Calas-type reaction.

Silyllithium species are quite versatile reagents for the formation of Si–Si bonds to afford oligosilanes or other compounds [1, 2]. We now describe the reactivity of disilanes bearing two oligomethylene tethers [3-6], especially focusing on the unusual formation of disilanyllithium species.

The reaction of diphenyldisilane **1** bearing two tetramethylene tethers with an excess amount of lithium followed by the addition of chlorotrime-thylsilane predominantly afforded the trisilane **2** along with the anticipated bis-disilane **3** (resulted from Si–Si bond scission) as the minor product in the ratio 8:2 (Scheme 1). Product **2** is apparently due to the disilanyllithium **4** generated by cleavage of the Si–C_{Ph} bond in such a ring system.

The Si–Si bond (2.315(1) Å [4]) in **1** compressed by two methylene tethers would kinetically suppress the bond cleavage, making the anomalous Si–C_{Ph} bond fission entropically more favored. Such kinetic stabilization may be called the "compression effect". To the best of our knowledge, there has been no example of the predominant generation of a disilanyllithium species from phenyldisilane derivatives [1, 2, 7].

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* Dedicated to professor Edmunds Lukevics on the occasion of his 65th birthday.

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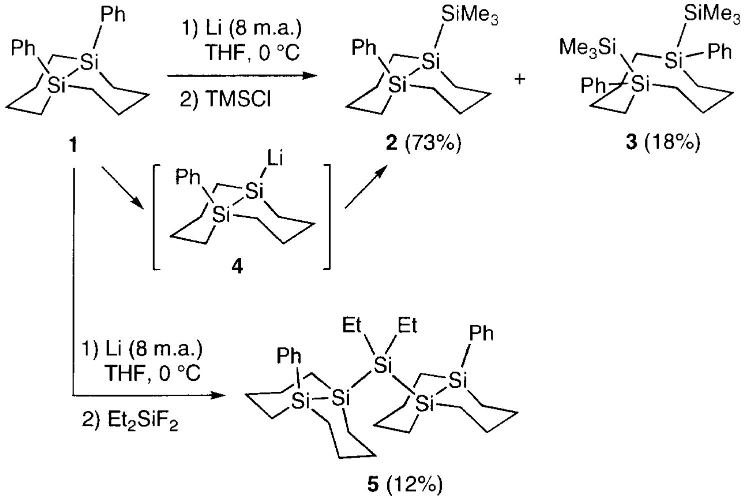
0009-3122/01/3711-1369$25.00©2001 Plenum Publishing Corporation

Scheme 1



Pentasilane **5** was obtained by the trapping of the disilanyllithium **4** with diethyldifluorosilane. The structure of **5** was confirmed by X-ray crystallography as shown in Fig. 1. The configuration of each disilane unit is syn with a C_{Ph}–Si–Si–C_{Ph} dihedral angle of *ca.* 30° [4], which implies that the configuration of the disilanyllithium **4** and the trisilane **2** is *syn* as well. It is also noted that the two Si–Si–Si–Si dihedral angles of the pentasilane moiety are 146.9(3)° and 158.12(2)°, which correspond to the deviant conformation [8].

In contrast to the tetramethylene system, the corresponding reaction of the pentamethylene tethered homolog **6** gave the Si–Ph bond-cleaved product **7** in a lower amount than the ordinary Si–Si bond-cleaved product **8** in the ratio 4:6 (Scheme 2). It is likely that the Si–Si bond of normal length in **6** (2.340(1) Å [5, 6]) has made the Si–Si bond cleavage more favorable, supporting the existence of the compression effect in the tetramethylene case.

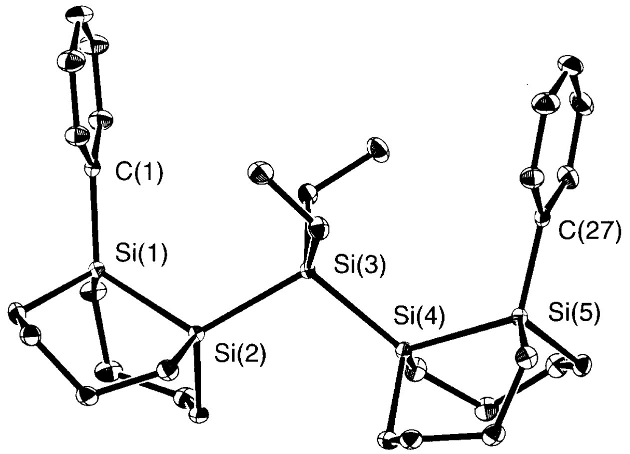
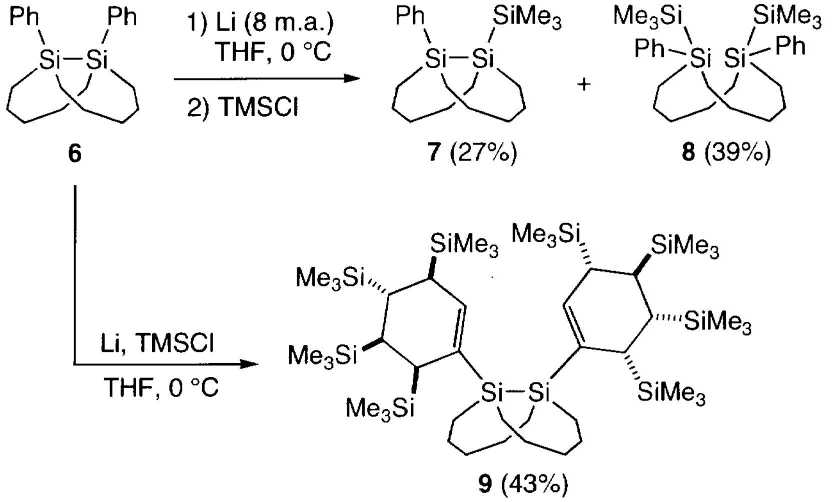


Fig. 1. X-ray structure of **5**. Selected bond lengths (Å) and torsion angles (°):
Si(1)–Si(2) 2.3242(5), Si(2)–Si(3) 2.2464(5), Si(3)–Si(4) 2.3412(5), Si(4)–Si(5) 2.3312(5), C(1)–Si(1)–Si(2)–Si(3) 28.42(6), Si(1)–Si(2)–Si(3)–Si(4) -146.93(2), Si(2)–Si(3)–Si(4)–Si(5) -158.12(2), Si(3)–Si(4)–Si(5)–C(27) -30.89(6).

Scheme 2



The reaction of **6** and lithium in the presence of chlorotrimethylsilane afforded the polysilylated compound **9**, whose X-ray structure is shown in Fig. 2. The result is reminiscent of the Calas reaction that aromatic compounds such as biphenyl or naphthalene undergo with magnesium in HMPA in the presence of chlorotrimethylsilane to give polysilylated compounds [9, 10].

Thus, this result demonstrates that the lithium cleavage of phenyldisilane would be initiated by electron transfer from lithium to phenyl groups like the Calas reaction. The resulting radical anion intermediate undergoes subsequent reaction by either Si–C_{Ph} bond cleavage to afford the disilanyllithium species or Si–Si bond cleavage to afford the monosilyllithium species. The former would be predominant due to the kinetic stabilization of the Si–Si bond by the compression effect.

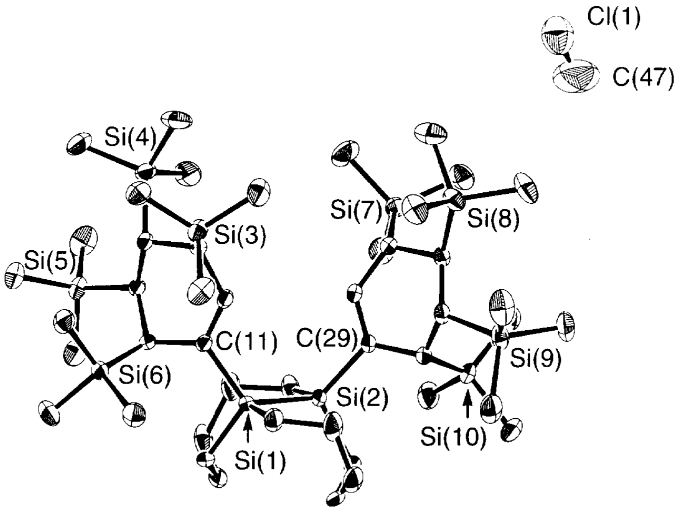


Fig. 2. X-ray structure of $\mathbf{9}\cdot 1/2\mathrm{CH_2ClCH_2Cl}$. Selected bond length (Å) and torsion angle (°): Si(1)–Si(2) 2.373(1), C(11)–Si(1)–Si(2)–C(29) 58.4.

EXPERIMENTAL

Instruments used in NMR measurements were as follows: ^{1}H (270 MHz), ^{13}C (67.94 MHz), ^{29}Si (53.67 MHz). NMR spectra were recorded on a JEOL JNM-EX 270 spectrometer; ^{1}H (300 MHz). NMR spectra were recorded on a Varian Mercury 300 spectrometer. ^{1}H and ^{13}C chemical shifts were referenced to internal benzene-d$_6$ (^{1}H δ 7.20 and ^{13}C δ 128.00 ppm). ^{29}Si chemical shifts were referenced to external Me_4Si (0 ppm).

Column chromatography was performed using silicagel (Kieselgel 60, 70-230 mesh, Merck) with hexane as eluent.

Reaction of 1,6-Diphenyl-1,6-disilabicyclo[4.4.0]decane (1) with Lithium. The oil dispersion of lithium (30 %) was washed with hexane three times and dried in vacuo. To a suspension of lithium (42.7 mg, 6.2 mmol) in THF (1.5 ml) was added **1** (243 mg, 0.75 mmol) at 0°C under an Ar atmosphere, and the resulting mixture was stirred for 4 h to give a red suspension. The silyllithium solution was added dropwise through a glass filter, in order to remove excess lithium metal, to a solution of chlorotrimethylsilane (0.95 ml, 7.5 mmol) in THF (1.0 ml). The resulting mixture was stirred for 4 h, concentrated, and quenched with water. The mixture was extracted with Et_2O three times, the collected organic layer was washed with brine and dried over $MgSO_4$, and the organic solvents were evaporated. The residue was subjected to column chromatography. The fractions were concentrated under reduced pressure to give trisilane product **2** in 73% yield (175 mg, 0.55 mmol) as a colorless liquid and the ring-opened product **3** in 18% yield (63.4 mg, 0.13 mmol) as colorless crystals.

***cis*-1-Phenyl-6-trimethylsilyl-1,6-disilabicyclo[4.4.0]decane (2)**: ^{1}H NMR spectrum (270 MHz, C_6D_6), δ, ppm: 7.62 (2H, d, *J* = 7.6 Hz, phenyl); 7.2-7.3 (3H, m, phenyl); 1.6-1.9 (8H, m, methylene), 1.08 (4H, m, methylene); 0.95 (4H, m, methylene); 0.11 (9H, s, Me). ^{13}C NMR spectrum (67.9 MHz, C_6D_6), δ, ppm: 139.03, 134.67, 128.92, 128.11, 26.69, 26.56, 13.77, 10.50-0.98 (Me). ^{29}Si NMR spectrum (53.7 MHz, C_6D_6), δ, ppm: -16.81, -25.42, -52.40. Found, %: C 64.08; H 9.50. $C_{17}H_{30}Si_3$. Calculated, %: C 64.07; H 9.49. Electron impact mass spectrum, *m/z*: 318 $[M]^+$, 245 $[M-SiMe_3]^+$.

1,6-Diphenyl-1,6-bis(trimethylsilyl)-1,6-disilacyclodecane (3). Colorless crystals; mp 102°C. ^{1}H NMR spectrum (300 MHz, C_6D_6), δ, ppm: 7.48 (4H, dd, *J* = 7.5 Hz, phenyl); 7.2-7.28 (6H, m, phenyl); 1.7 (8H, m, methylene); 1.2 (8H, m, methylene); 0.17 (18H, s, Me). ^{13}C NMR spectrum (67.9 MHz, C_6D_6), δ, ppm: 137.68, 134.45, 128.59, 128.12, 25.50, 8.90-1.29 (Me). ^{29}Si NMR spectrum (53.7 MHz, C_6D_6), δ, ppm: -16.73, -19.59. Found, %: C 66.74; H 9.47. $C_{26}H_{44}Si_4$. Calculated, %: C 66.59; H 9.46. Electron impact mass spectrum, *m/z*: 468 $[M]^+$, 395 $[M-SiMe_3]^+$.

Bis(6-phenyl-1,6-disilabicyclo[4.4.0]decan-1-yl)diethylsilane (5). The silyllithium reagent was prepared as described above from lithium (564 mg, 24.4 mmol) and **1** (964 mg, 2.99 mmol). To a solution of diethyldifluorosilane (376 mg, 1.01 mmol) in THF (30 ml) the silyllithium solution was added dropwise through a glass filter, and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated and quenched with water. The mixture was extracted with Et_2O three times, the collected organic layer was washed with brine and dried over $MgSO_4$, and the solvents were evaporated. The residue was subjected to column chromatography and the solvent was removed under reduced pressure to give 99.6 mg (0.17 mmol; 12%) of **5** as colorless crystals; mp 108-109°C. ^{1}H NMR spectrum (270 MHz, C_6D_6), δ, ppm: 7.63 (4H, dd, *J* = 7.8 Hz, phenyl), 7.2-7.3 (6H, m, phenyl), 1.45-1.95 (16H, m, methylene), 0.95-1.20 (16H, m, methylene), 0.92 (6H, t, *J* = 7.6 Hz, α-H of the ethyl group), 0.71 (4H, q, *J* = 7.6 Hz, β-H of the ethyl group). ^{13}C NMR spectrum (67.9 MHz, C_6D_6), δ, ppm: 139.48, 134.58, 128.89, 128 (overlapped), 26.62, 26.55, 13.81, 12.69, 10.86, 4.41. ^{29}Si NMR spectrum (53.7 MHz, C_6D_6), δ, ppm: -25.82, -28.15, -47.99. Found, %: C 66.33; H 9.21. $C_{32}H_{52}Si_5$. Calculated, %: C 66.59; H 9.08. GS mass spectrum, *m/z*: 576 $[M]^+$, 331 $[M-(one\ disilane\ unit)]^+$.

The pentamethylene analogues **7** and **8** were obtained in a similar manner to **2** and **3** in 27% and 39% yield, respectively as colorless liquid.

***cis*-1-Phenyl-7-trimethylsilyl-1,7-disilabicyclo[5.5.0]dodecane (7).** ^{1}H NMR spectrum (300 MHz, C_6D_6), δ, ppm: 7.63 (2H, dd, *J* = 7.2 Hz, phenyl); 7.20-7.26 (3H, m, phenyl); 1.75-1.89 (8H, m, methylene); 1.60-1.73 (4H, m, methylene); 1.09-1.18 (2H, m, methylene); 0.61-0.96 (4H, m, methylene); 0.02 (9H, s, Me). ^{13}C NMR spectrum (67.9 MHz, C_6D_6), δ, ppm: 140.31, 134.67, 128.76, 128.09, 33.31, 23.28, 21.88, 13.32, 9.86, -1.23 (Me). ^{29}Si NMR spectrum (53.7 MHz, C_6D_6), δ, ppm: -9.89, -15.73, -34.89. Found, %: C 65.69; H 9.89. $C_{19}H_{34}Si_3$. Calculated, %: C 65.82; H 9.88. Electron impact mass spectrum, *m/z*: 346 $[M]^+$.

1,7-Diphenyl-1,7-bis(trimethylsilyl)-1,7-disilacyclododecane (8). ^{1}H NMR spectrum (300 MHz, C_6D_6), δ, ppm: 7.49 (4H, dd, *J* = 7.8 Hz, phenyl); 7.22-7.33 (6H, m, phenyl); 1.54 (12H, m, methylene); 0.95-1.10 (8H, m, methylene); 0.17 (18H, s, Me). ^{13}C NMR spectrum (67.9 MHz, C_6D_6), δ, ppm: 137.61, 134.55, 128.58, 128.07, 34.50, 21.47, 8.96, -1.11 (Me). ^{29}Si NMR spectrum (53.7 MHz, C_6D_6), δ, ppm: -17.73, -19.74. Found, %: C 67.57; H 9.57. $C_{28}H_{48}Si_4$. Calculated, %: C 67.66; H 9.73. Electron impact mass spectrum, *m/z*: 496 $[M]^+$.

***cis*-1,7-Bis[3',4',5',6'-tetrakis(trimethylsilyl)cyclohexen-1-yl]-1,7-disilabicyclo[5.5.0]undecane (9).** To a suspension of lithium (108 mg, 15.6 mmol) in THF (2.0 ml) were added a solution of **6** (702 mg, 2.00 mmol) and chlorotrimethylsilane (1.27 ml, 10.0 mmol) in THF (6.0 ml) at 0 °C, and the resulting mixture was stirred for 5 h under Ar atmosphere. To the reaction mixture was added an additional 2.0 ml of chlorotrimethylsilane, and the resulting mixture was stirred overninght. The reaction mixture was quenched by successive addition of isopropyl alcohol and water. The mixture was extracted with Et_2O three times, the collected organic layer was washed with brine and dried over $MgSO_4$, and the solvents were evaporated. The residue was subjected to column chromatography (eluent hexane) and the solvent was removed under reduced pressure to give **9** (886 mg, 0.93 mmol; 47%) as colorless crystals: m.p 223 °C. ^{1}H NMR spectrum (270 MHz, C_6D_6), δ, ppm: 6.09 (4H, d, *J* = 5.7 Hz, Si–C=CH); 2.52 (2H, d, *J* = 2.7 Hz, Si–CH(TMS)–); 2.21 (2H, dd, *J* = 8.4, 5.7 Hz, Si–CH–CH(TMS)–); 1.98-2.04 (4H, m, methylene); 1.63-1.79 (10H, m, overlapping methylene protons in the methylene tethers with methyne protons in the cyclohexenylrings); 1.18-1.26 (4H, m, methylene); 0.72-0.82 (2H, m, methyne, 0.36 (18H, s, Me); 0.35 (18H, s, Me); 0.31 (18H, s, Me); 0.27 (18H, s, Me). ^{13}C NMR spectrum (67.9 MHz, C_6D_6), δ, ppm: 141.25, 139.72, 32.87, 32.66, 31.38, 31.24, 25.12, 23.89, 23.56, 18.10, 14.92, 4.06 (Me), 2.74 (Me), 1.82 (Me), 1.15 (Me). ^{29}Si NMR spectrum (53.7 MHz, C_6D_6), δ, ppm: 4.01, 2.53, 1.40, -0.58, -5.59. Found, %: C 58.68; H 11.03. $C_{46}H_{102}Si_{10}$. Calculated, %: C 59.02; H 10.98.

X-ray Single Crystal Structural Analysis of 5. Intensity data were collected at -100°C on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated MoK radiation to a maximum 2υ value of 54.0°. A total of 18×3.0° oscillation images each being exposed for 24 min were collected. The data were corrected for Lorentz polarization and secondary extinction effects. The crystal ctructure was solved by direct methods (SAPI91), and expanded using Fourier techniques (DIRDIF94). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions and refined isotopically. All calculations were performed using the teXsan crystallographic package from the Molecular Structure Corp.

X-ray Single Crystal Structural Analysis of 9·1/2CH$_2$ClCH$_2$Cl. Crystals suitable for X-ray analysis were obtained by recrystallizing from 1,2-dichloroethane. Intensity data were collected at -100°C on a Rigaku RAXIS-IV imaging plate area detector with graphite monochromated MoK radiation to a maximum 2υ value of 55.1°. A total of 19×5.5° oscillation images each being exposed for 120 min were collected. The data were corrected for Lorentz polarization effects. The crystal structure was solved by Patterson methods (SIR92), and expanded using Fourier techniques (DIRDIF94). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included at calculated positions and were not refined. All the calculations were performed using the teXsan crystallographic package from the Molecular Structure Corp.

SUPPLEMENTARY MATERIAL

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 165139 (**5**) and 16540 (**9**·1/2CH$_2$ClCH$_2$Cl). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk. or www:http://www.ccdc.cam.ac.uk.

Acknowledgement

Financial support by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan (09239103) is gratefully acknowledged.

REFERENCES

1. K. Tamao and A. Kawachi, *Adv. Organomet. Chem*., **38**, 1 (1995).
2. P. D. Lickiss and C. M. Smith, *Coord. Chem. Rev*., **145**, 75 (1995).
3. K. Tamao and M. Kumada, *J. Organomet. Chem*., **31**, 35 (1971).
4. K. Tamao, M. Terada, H. Tsuji, and A. Toshimitsu, submitted for publication.
5. K. Tamao, H. Tsuji, M. Terada, M. Asahara, S. Yamaguchi, and A. Toshimitsu, *Angew. Chem*., **112**, 3425 (2000).
6. K. Tamao, H. Tsuji, M. Terada, M. Asahara, S. Yamaguchi, and A. Toshimitsu, *Angew. Chem*., Int. Ed. **39**, 3287 (2000).
7. A. L. Allred, R. T. Smart, and D. A. Van Beek, Jr., *Organometallics*, **11**, 4225 (1992).
8. J. Michl and R. West, *Acc. Chem. Res*., **33**, 821 (2000).
9. J. Dunogues, R. Calas, and N. Duffaut, *J. Organomet. Chem*., **20**, P20 (1969).
10. J. Dunogues, R. Calas, C. Biran, and N. Duffaut, *J. Organomet. Chem*., **23**, C50 (1970).