Organometallics **1994,** *13,* 4683−4685

Synthesis and Characterization of Dilithium 1,2-Disilaacenaphthenediide

Wataru Ando,* Takatsugu Wakahara, and Takeshi Akasaka

Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305, Japan

Shigeru Nagase

Department of Chemistry, Faculty of Education, Yokohama National University, Yokohama 240, Japan

Received October 6, 1994®

*Summary: Reaction of 1,2-dichloro-1,2-diisopropyl-1,2-disilaacenaphthene (**1**) with excess lithium resulted in formation of the corresponding dilithium 1,2-disilaacenaphthenediide (**2**) as the 1,2-dilithiodisilane. On treatment with methyl iodide and methanol, **2** was converted into the corresponding 1,2-dimethyl- and 1,2-dihydro-1,2-disilaacenaphthene derivatives, respectively. NMR spectroscopic analysis and theoretical investigation strongly support the dilithiodisilane structure (**2a**) in which the negative charge is localized on the silicon atom and one lithium atom interacts with one silicon atom, respectively. The measurement of the Si−Li coupling at low temperature shows that a Si−Li bond has a partial covalency.*

Renewed interest in the reactivity, structure, and bonding of organolithium compounds has increased remarkably in recent years.[1] Dilithium compounds such as 1,2-dilithioethane formed by reduction of a carbon−carbon double bond are known to have interesting structures.[2] Meanwhile, there has been no report so far concerning reduction of a silicon−silicon double bond to afford a 1,2-dilithiodisilane. Weidenbruch and coworkers reported ESR spectra assigned to the disilene anion radicals.[3] West et al. carried out one-electron reduction of isolable disilenes by means of cyclic voltammetry.[4] However, direct dilithiation of a 1,2-dihalodisilane without formation of a disilene has not yet been achieved. One of the best candidates for generation of a 1,2-dilithiodisilane[5] might be 1,2-dichloro-1,2-diisopropyl-1,2-disilaacenaphthene (**1**). The particular advantage of **1** is that the two silicon atoms in **1** are fixed at the distance of a silicon−silicon single bond[6] and hence a silicon−silicon double bond cannot be formed. We report herein the synthesis and characterization of the 1,2-dilithiodisilane **2**, derived from dilithiation of 1,2-dichloro-1,2-disilaacenaphthene (**1**).

Scheme 1

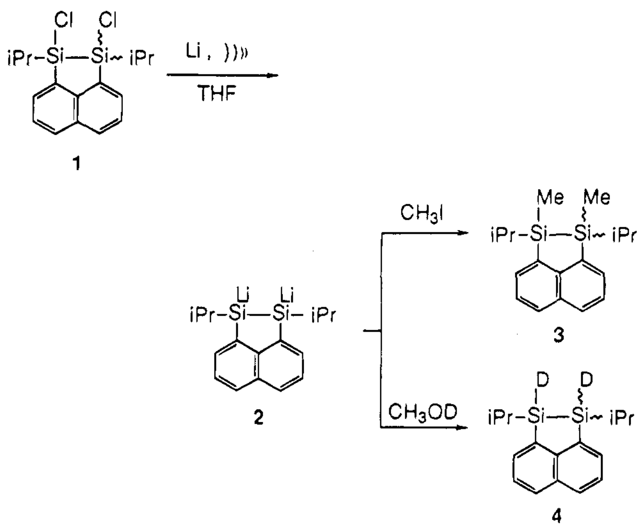


Table 1. ^{1}H NMR Chemical Shifts for Dianion 2 and Related Species

compd	H-3,8	H-4,7	H-5,6	compd	H-2	H-3	H-4
1^{a,b}	7.92	7.58	8.01	**5**^{b}	7.61	7.37	7.29
4^{a,b}	7.70	7.33	7.68	**6**^{b}	7.57	7.18	7.17
3^{a,b}	7.80	7.43	7.74				
2^{b}	7.07	6.46	6.46	**7**^{c}	7.33	6.98	6.88

^{a} Transform. ^{b} In THF-d_8, internal Me$_4$Si as standard. ^{c} In THF, cyclohexane used as reference.[14]

1 (0.100 g, 0.296 mmol) and excess lithium (0.100 g, 14.4 mmol) in THF was sonicated for 30 min at room temperature under an argon atmosphere to afford a dark blue solution. After removal of the unreacted lithium, addition of an excess of CH$_3$I to this solution afforded 1,2-dimethyl-1,2-diisopropyl-1,2-disilaacenaphthene (**3**)[6a,7] in 80% yield. On treatment of this solution with CH$_3$OD, quantitative formation of 1,2-dideuterio-1,2-diisopropyl-1,2-disilaacenaphthene (**4**) was observed (Scheme 1). The formation of **3** and **4** clearly reveals that dichlorodisilane **1** was readily reduced with lithium to afford dilithium 1,2-disilaacenaphthenediide (**2**).[8] The

---

® Abstract published in *Advance ACS Abstracts,* November 15, 1994.

[1] Wardell, J. L. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 1, p 109.

[2] Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985,** *24,* 353.

[3] (a) Weidenbruch, M.; Kramer, K.; Schaefer, A.; Blum, J. K. *Chem. Ber.* **1985,** *118,* 107. (b) Weidenbruch, M.; Kramer, K.; Peters, K.; Schnering, H. G. *Z. Naturforsch.* **1985,** *40B,* 601. (c) Weidenbruch, M.; Thom, K.-L. *J. Organomet. Chem.* **1986,** *308,* 177.

[4] West, R.; Shepherd, B. D. *Chem. Lett.* **1988,** 183.

[5] Recently, Boudjouk et al. reported the synthesis of bis(1-lithio-1-silacyclopentadienide): Hong, J.-H.; Boudjouk, P.; Castellino, S. *Organometallics* **1994,** *13,* 3387.

[6] (a) Chernyshev, E. A.; Komalenkova, N. G.; Klochkova, T. A.; Schepinova, S. A.; Mosin, A. M. *Zh. Obshch. Khim.* **1971,** *41*(1), 122. The Si−Si bond length is 2.34 Å in 1,1,2,2-tetramethyl-1,2-disilaacenaphthene. (b) Ando, W.; Imai, S.; Wakahara, T.; Akasaka, T. Unpublished results. The Si−Si bond length is 2.33 Å in 1,1,2,2,5,5,6,6-octamethyl-1,2,5,6-tetrasilapyracene.

[7] The tetramethyl derivative has already been prepared: Kiely, J. S.; Boudjouk, P. *J. Organomet. Chem.* **1979,** *182,* 173.

[8] On the time course of the reaction of **1** with excess lithium, it has been observed that the reaction mixture first turns dark red, followed by change to the dark blue color of **2**. The dark red solution can be stabilized by addition of tetramethylenediamine (TMEDA). Details will be reported in due course.

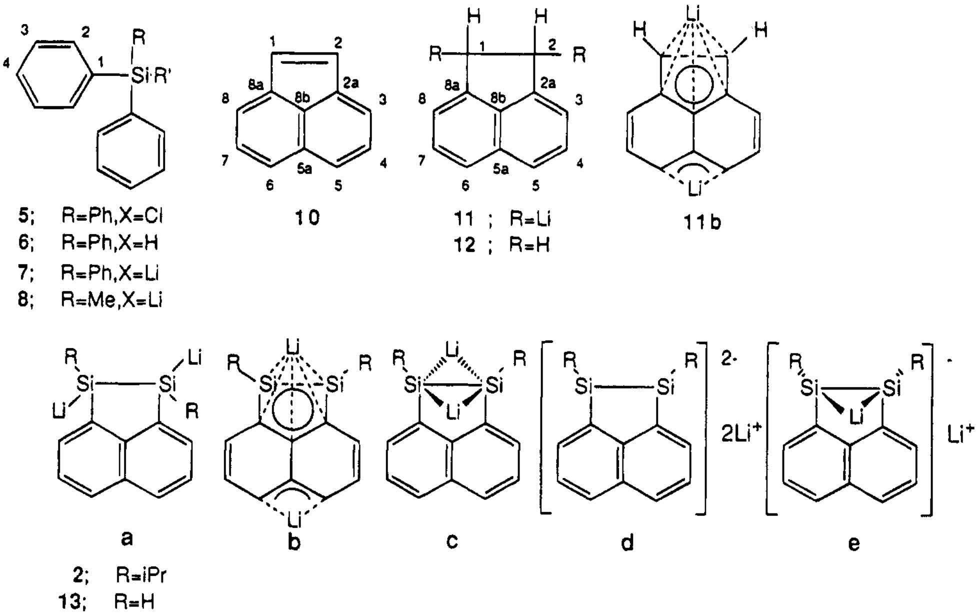
0276-7333/94/2313-4683$04.50/0

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

compd	C-3,8	C-4,7	C-5,6	C-2a,8a	C-5a	C-8b	compd	C-1	C-2	C-3	C-4
$1^{a,b}$	133.86	126.81	132.02	136.23	133.91	146.42	$5^{c,e}$	137.4	135.5	128.0	129.9
$4^{a,b}$	134.22	125.53	129.63	137.60	133.65	147.70	$6^{c,e}$	133.7	136.1	128.4	130.1
$3^{a,b}$	132.79	126.11	129.72	142.64	133.96	147.54					
2^{b}	126.91	117.21	123.88	172.94	136.05	148.90	$7^{d,e}$	145.0	136.1	127.5	128.4

[a] Transform. [b] In THF-d_8, internal Me_4Si as standard. [c] In THF, internal Me_4Si as standard. [d] In THF, external Me_4Si as standard. [e] Reference 15.

Chart 1



5; R=Ph,X=Cl
6; R=Ph,X=H
7; R=Ph,X=Li
8; R=Me,X=Li

10

11 ; R=Li
12 ; R=H

11b

2; R=iPr
13; R=H

Table 3. ^{29}Si NMR Chemical Shifts for Dianion 2, Related Species, and Other Silyl Anions

$1^{a,b}$	2^{b}	$3^{a,b}$	$4^{a,b}$	$5^{c,d}$	$6^{c,d}$	$7^{c,d}$	$8^{c,d}$	$9^{b,e}$
8.99	−1.24	−14.23	−30.38	−15.3	−17.7	−30.0	−22.1	25.10

[a] Transform. [b] In THF-d_8, internal Me_4Si as standard. [c] Reference 14. [d] In THF, external Me_4Si as standard. [e] Reference 17.

Table 4. ^{13}C NMR Chemical Shifts for Carbanions 11 and Related Species

compd	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
11^{a}	81.0	95.8	128.4	85.3	124.7	148.8	137.1
12^{b}	30.1	118.6	127.1	121.9	145.0	131.4	139.1

[a] In THF, cyclohexane used as reference.[19] [b] In CCl_4, internal Me_4Si as standard.[20]

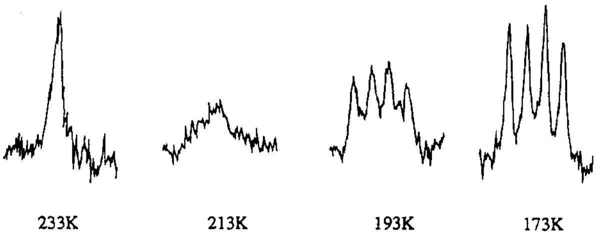


Figure 1. Low-temperature ^{29}Si NMR spectra of **2** in THF-d_8.

half-life period of disappearance of **2** in THF is 13.5 h at 30 °C. Since each of the compounds **1**, **3**, and **4** has two stereoisomers, their NMR spectra show the paired chemical shifts.[9] NMR measurement of the lithiated solution however, showed the existence of a single product.

In order to shed light on the structure of **2**, detailed NMR measurements were carried out.[10] The chemical shifts of the aromatic protons in **2**, in comparison with those of the corresponding disilanes (**1**, **3**, and **4**), are shifted upfield around 0.85−1.55 ppm (Table 1). Upfield shifts of the ^{13}C NMR signals for C-3−C-8 atoms are also seen, as shown in Table 2. The most important factor affecting the upfield chemical shifts of the proton and carbon resonances in **2** and **7** (Chart 1) is thought to be the presence of a negative charge on the silicon atom.[11] The ^{29}Si NMR chemical shift for **2** was observed at −1.24 ppm, a large downfield shift compared to the resonances of other silyl anions.[12,13] Interestingly, the ^{29}Si resonance for **2**, however, is upfield from that of lithium 1-*tert*-butyl-2,3,4,5-tetraphenyl-1-silacyclopentadienide (**9**) (Table 3).[14]

Comparison of the NMR data of **2** with those of its carbon analogue **11**, summarized in Table 4, reveals a characteristic feature.[15,16] On the basis of the ^{1}H and ^{13}C NMR chemical shifts, Edlund et al. reported the structure of dilithium acenaphthenediide (**11**; Chart 1), in which one lithium cation coordinates on the five-membered ring, while the other one is located between the C-5 and C-6 positions. The electronic structure of **11** is described in terms of a partly localized π-electronic

---

(9) The major products are tentatively assigned as *trans* forms.

(10) All ^{1}H and ^{13}C chemical shifts were assigned by means of ^{1}H, ^{13}C, H−H NOESY, H−C COSY, H−C COLOC, and ^{13}C INVGATE NMR measurements.

(11) Buncel, E.; Venkatachalam, T. K.; Eliasson, B.; Edlund, U. *J. Am. Chem. Soc.* **1985**, *107*, 303.

(12) Olah, G. A.; Hunadi, R. J. *J. Am. Chem. Soc.* **1980**, *102*, 6989.

(13) Edlund, U.; Lejon, T.; Pyykkö, P.; Venkatachalam, T. K.; Buncel, E. *J. Am. Chem. Soc.* **1987**, *109*, 5982.

(14) Boudjouk, P.; Hong, J.-H. *J. Am. Chem. Soc.* **1993**, *115*, 5883.

(15) Eliasson, B.; Edlund, U. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1837.

(16) Hunter, D. H.; Stothers, J. B. *Can. J. Chem.* **1973**, *51*, 2884.

Table 5. Relative Charge Densities of 13 and Difference of Chemical Shifts in 2a and 11b

	Δ for charge densities[a,b]				**2a**		**11b**
position in **13**	**13a**	**13b**	**13c**	**13d**	$\Delta\delta(^{29}\mathrm{Si})$[c]	$\Delta(\delta^{13}\mathrm{C})$[c]	$\Delta\delta(^{13}\mathrm{C})$[d]
1, 2	−0.503	−0.682	−0.471	−1.593	−10.23		+50.9
2a,8a	+0.155	−0.107	+0.031	+0.253		+36.71	−20.3
3, 8	−0.084	−0.127	+0.015	−0.128		−6.95	−22.8
4, 7	+0.021	+0.06	−0.006	−0.084		−9.60	+1.3
5, 6	−0.055	−0.448	+0.011	−0.198		−8.14	−36.6
	0[e]	26.1[e]	75.9[e]				

[a] **13** vs **14**. [b] Charge from natural population analysis. [c] **2a** vs **1**. [d] **11b** vs **12**. [e] Relative energy in kcal/mol; calculated at the HF/3-21G* level.

system.[15,17] In contrast to the case of **11**, NMR data for **2** support localization of the negative charge on the silicon atoms which is well-known on the basis of theoretical[18a] as well as experimental studies.[18b] The rationalization for these observations may also be that the structure of **2** is distinct from that of **11**. In order to obtain further information on the structure of **2**, a low-temperature ^{29}Si NMR measurement to observe a scalar ^{29}Si−^{7}Li coupling was carried out. In the ^{29}Si NMR spectrum of **2**, a well-resolved quartet with $^{1}J_{^{29}\mathrm{Si}^{7}\mathrm{Li}}$ = 43.5 Hz at 173 K in THF-d_8 was observed (Figure 1). Similar $^{1}J_{^{29}\mathrm{Si}^{7}\mathrm{Li}}$ coupling constants, 51 and 38.6 Hz, are known for Ph_3SiLi at 173 K in THF[10] and $(Me_3Si)_3SiLi(THF)_3$ at room temperature in toluene-d_8,[19] respectively. These observations indicate that **2** has at least a partial covalency at low temperature.

In the ^{7}Li NMR spectrum of **2**, a single peak at 5.79 ppm appeared at 183 K in THF-d_8.

The experimental findings for **2** were confirmed by theoretical calculations at the HF/3-21G* level.[20] Dilithium 1,2-dihydro-1,2-disilaacenaphthenediides (**13a**–**d**; Chart 1) correspond to energy minima, and **13a** is the most stable. The relative charge densities based on the natural population analysis of **13a**–**d** and $\Delta\delta(^{29}\mathrm{Si}_{\mathrm{SiLi-SiCl}})$ and $\Delta\delta(^{13}\mathrm{C}_{\mathrm{SiLi-SiCl}})$ in **2** are summarized in Table 5. The results in Table 5 reveal that **2a** and **2d** might be considered. **2b**–**d** and **2e**, however, can be easily ruled out by means of the ^{29}Si−^{7}Li coupling measurement and the low-temperature ^{7}Li NMR measurement, respectively.

The spectral analysis and theoretical investigation support structure **2a** as the best representation of dilithium 1,2-disilaacenaphthenediide (**2**). Interestingly, this is in contrast with dilithium acenaphthenediide, for which the structure **11b** is favored. We are presently exploring the reactivity of **2**.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan. We thank Shin-Etsu Chemical Co. Ltd. for a gift of organosilicon reagents. Ab initio calculations were carried out using the Gaussian 92 program.

Supplementary Material Available: Text giving complete spectral and analytical data for **1**–**4** and figures giving ^{1}H, ^{13}C, ^{13}C INVGATE, ^{29}Si, ^{7}Li, H−H NOESY, H−C COSY, and H−C COLOC NMR spectra for **2** (11 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; ordering information is given on any current masthead page.

OM940774M

---

(17) (a) Minsky, A.; Meyer, A. Y.; Hafner, K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 3975. (b) Becker, B. C.; Huber, W.; Schnieders, C.; Mullen, K. *Chem. Ber.* **1983**, *116*, 1573.

(18) (a) Edlund, U.; Buncel, E. In *Prog. Phys. Org. Chem.* Taft, R. W., Ed.; Wiley: New York, 1993; Vol. 19, p 254. (b) Sooriyakumaran, P.; Boudjouk, P. *J. Organomet. Chem.* **1984**, *271*, 289.

(19) Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 2694.

(20) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039.