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Sila-metalation Route to Hydrido(trialkylsilyl)silyllithiums

Takeaki Iwamoto, Junichiro Okita, Chizuko Kabuto, and Mitsuo Kira*

Department of Chemistry, Graduate School of Science, Tohoku University, Aoba-ku, Sendai 980-8578, Japan

Received April 27, 2002

Although metalation of hydrocarbons has been widely used as a convenient method for the preparation of corresponding carbanions,[1] the deprotonation of hydridosilanes (sila-metalation) forming the corresponding silyl anions is rather exceptional.[2−5] In the reaction of a hydridosilane with an alkyllithium, nucleophilic attack of the alkyl anion to silicon usually occurs to give the corresponding alkylsilane (S_N2-*Si*, path a in Scheme 1), where the hydrido group serves as a rather good leaving group. An alternative sila-metalation pathway (path b in Scheme 1) is disfavored because of the hydride character of the Si−H hydrogen; the bond polarity is $\text{Si}(\delta+)-\text{H}(\delta-)$ in contrast to the polarity of $\text{C}(\delta-)-\text{H}(\delta+)$ based on the electronegativity differences. The relative reactivity between S_N2-*Si* (path a) and sila-metalation (path b) should be modified by the substituents on silicon and the basicity of the attacking reagent.[6] Trialkylsilyl-substituted hydridosilanes are good candidates as the substrates for the selective sila-metalation because an electropositive trialkylsilyl substituent will decrease the electrophilicity of the silicon center and stabilize the silyl anion formed by the sila-metalation. In this paper, we report the achievement of the convenient sila-metalation of trialkylsilyl-substituted dihydridosilanes to give the corresponding silyllithiums, the scope and limitation of the reaction, and the structure of a hydridosilyllithium determined by X-ray crystallography.

Typically, to a THF solution (10 mL) of bis(*tert*-butyldimethylsilyl)dihydridosilane (**2a**, 0.500 g, 1.92 mmol) was added a pentane solution of *tert*-butyllithium (1.45 mol/L, 1.70 mL, 2.49 mmol) dropwise at −40 °C under argon. After the mixture was stirred for 1 h at −40 °C, an excess amount of iodomethane (1.00 g, 7.05 mmol) was added to the mixture. The usual workup gave the corresponding methylhydridosilane **3a** (0.526 g, 1.92 mmol, 100%).[7] The general reaction scheme is shown in eq 1. The results of the reactions of various dihydridosilanes with several bases are shown in Table 1. Lithium diisopropylamide (LDA) worked similarly as a base (entry 2). On the other hand, the reaction of **1a** with *n*-BuLi gave the corresponding substitution product, $(t\text{-BuMe}_2\text{Si})_2\text{Si}(\text{Bu-}n)\text{H}$, quantitatively (entry 3). Whereas the sila-metalation of bis(trialkylsilyl)dihydridosilanes **2b** and **2c** was achieved likewise by using *t*-BuLi (entries 4 and 5), the highly sterically hindered bissilyldihydridosilane **2d** reacted with neither *t*-BuLi nor LDA (entries 6 and 7). Interestingly, the sila-metalation of silyl(aryl)silane **2e** occurred satisfactorily using LDA, while the nucleophilic substitution of **2e** was the major pathway when *t*-BuLi was used (entries 8 and 9). As expected, no sila-metalation of dialkyldihydridosilane **2f** or diaryldihydridosilane **2g** occurred (entries 10−12).

Scheme 1

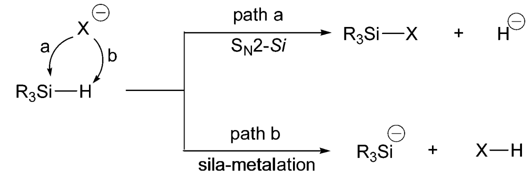
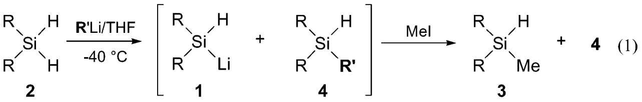


Table 1. Reactions of Various Dihydridosilanes with Bases



entry	dihydridosilane **2**	base (**R′**Li)	yields of products **3**	 **4**
1	$(t\text{-BuMe}_2\text{Si})_2\text{SiH}_2$ (**2a**)	*t*-BuLi	100 (**3a**)	0
2	**2a**	$i\text{-Pr}_2\text{NLi}$	88 (**3a**)	0
3	**2a**	*n*-BuLi	0	100 (**4a**)
4	$(\text{Me}_3\text{Si})_2\text{SiH}_2$ (**2b**)	*t*-BuLi	100 (**3b**)	0
5	$(i\text{-Pr}_2\text{MeSi})_2\text{SiH}_2$ (**2c**)	*t*-BuLi	97 (**3c**)	0
6	$(i\text{-Pr}_3\text{Si})_2\text{SiH}_2$ (**2d**)	*t*-BuLi	0[a]	0
7	**2d**	$i\text{-Pr}_2\text{NLi}$	0[a]	0
8	$(t\text{-BuMe}_2\text{Si})(\text{Tol})\text{SiH}_2$[b] (**2e**)	*t*-BuLi	21 (**3e**)	67 (**4e**)
9	**2e**	$i\text{-Pr}_2\text{NLi}$	97 (**3e**)	0
10	Pr_2SiH_2 (**2f**)	*t*-BuLi	0	100 (**4f**)
11	Ph_2SiH_2 (**2g**)	*t*-BuLi	0	88 (**4g**)
12	**2g**	$i\text{-Pr}_2\text{NLi}$	0	80 (**4g′**)

[a] Hydridosilane **2d** was recovered. [b] Tol = 4-methylphenyl.

Hydridosilyllithium **1a** was isolated as air- and moisture-sensitive, but thermally stable, colorless crystals.[8] The ^{7}Li resonance in **1a** appeared at 2.0 ppm, suggesting that the lithium ion is not free but exists as a contact ion-pair in toluene.[9] The $^1J(^{29}\text{Si}-^1\text{H})$ coupling constant of 75 Hz for **1a** is much smaller than that for tris(*tert*-butyldimethylsilyl)silane (147 Hz),[10] indicating that the s-character of the silicon orbital of the Si−H bond in **1a** is much less than that in **2a** due to the electropositive lithium substituent in **1a**.

X-ray analysis showed that **1a** is dimeric in the solid state,[11] where two lithium atoms bridge between anionic silicon atoms forming a parallelogram, and each lithium atom is coordinated by one THF molecule (Figure 1). The Si−H hydrogens are in the plane of the parallelogram but are disordered.[13,14] The Si−H- - -Li distances in **1a** are 1.95(5)−1.96(5) Å, which are close to the distances calculated for the inverted SiH_3Li (1.911 Å)[15] and those observed in 1,2-dilithio-1,1,2,2-tetrakis(dimethylsilyl)-ethane (2.00−2.33 Å);[16] the agostic interactions are suggested to exist between lithium and hydrogen atoms in **1a**.[17−19]

The reaction of $(t\text{-BuMe}_2\text{Si})_2\text{GeH}_2$ with *t*-BuLi in THF afforded the corresponding germyllithium, $(t\text{-BuMe}_2\text{Si})_2\text{GeHLi}$ (**5**), in quantitative yield.[20,21] A single crystal of **5** was found to have a dimeric structure similar to that of **1a**.

Application of the functional silyl anions prepared by sila-metalation to organic synthesis is in progress.

Acknowledgment. This work was supported by the Ministry of Education, Culture, Sports, Science, and Technology of Japan

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* To whom correspondence should be addressed. E-mail: mkira@si.chem.tohoku.ac.jp.

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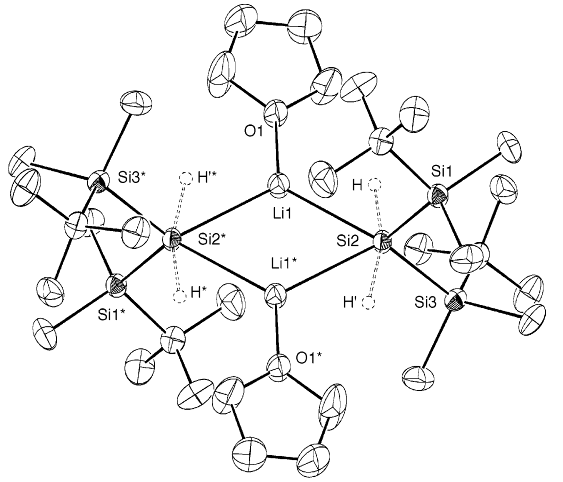

Figure 1. ORTEP view of hydridosilyllithium **1a**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and angles (deg): Si1−Si2 2.3480(9), Si2−Si3 2.3453(8), Si2−Li1 2.644(4), Si2−Li1* 2.667(4), Si2−H 1.44(5), Si2−H′ 1.47(5), H−Li1 1.95(5), H′−Li1* 1.96(5), Si1−Si2−Si3 108.03(3), Li1−Si2−Li1* 67.6(1), Si2−Li1−Si2* 112.3(2).

(Grants-in-Aid for Scientific Research (B) No. 11440185 (M.K. and T.I.)) and for the Encouragement of Young Scientists No. 12740336 (T.I.).

Supporting Information Available: Tables of crystal data, structure solution, and refinement, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and ORTEP drawings for **1a** and **5** (PDF) and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Wardwell, J. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, S. G. W., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press Ltd.: Oxford, 1982; Chapter 2, pp 43−120 and references therein.

(2) For recent reviews on silyl anions, see: (a) Kawachi, A.; Tamao, K. *Adv. Organomet. Chem.* **1995**, *38*, 1. (b) Lickiss, P. D.; Smith, C. M. *Coord. Chem. Rev.* **1995**, *145*, 75. (c) Belzner, J.; Dehnert, U. In *The Chemistry of Organic Silicon Compounds*; Apeloig, Y., Rappoport, Z., Eds.; John Wiley & Sons: Chichester, 1998; Vol. 2, Chapter 14, p 779. (d) Sekiguchi, A.; Lee, V. Y.; Nanjo, M. *Coord. Chem. Rev.* **2000**, *210*, 11.

(3) Metalation of a hydridosilane with potassium hydride has been evidenced to proceed not by direct deprotonation but via a pentacoordinate silicon intermediate resulting from the nucleophilic attack of hydride to the silicon atoms. Corriu, R. J. P.; Guerin, C. *J. Chem. Soc., Chem. Commun.* **1980**, 168. Brefort, J. L.; Corriu, R.; Guérin, C.; Henner, B. *J. Organomet. Chem.* **1989**, *370*, 9.

(4) Trichlorosilyl anion was produced by the apparent deprotonation of trichlorosilane with trialkylamines: (a) Benkeser, R. A.; Foley, K. M.; Grutzner, J. B.; Smith, W. E. *J. Am. Chem. Soc.* **1970**, *92*, 697. (b) Bernstein, S. C. *J. Am. Chem. Soc.* **1970**, *92*, 699. (c) Benkeser, R. A. *Acc. Chem. Res.* **1971**, *4*, 94 and references therein.

(5) The reaction of $KSiH_3$ with $(H_3Si)_2SiH_2$ giving a mixture of H_3SiSiH_2K, $(H_3Si)_2SiHK$, and $(H_3Si)_3SiK$ has been proposed to be initiated by the deprotonation of $(H_3Si)_2SiH_2$ by H_3SiK. (a) Bürger, H.; Eujen, R.; Marsmann, H. C. *Z. Naturforsch., B: Chem. Sci.* **1974**, *29B*, 149. (b) Feher, F.; Freund, R. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 561.

(6) Theoretical calculations at the B3LYP/6-31G(d) level have shown that the charges on the central silicon (α_{Si}) and the Si−H hydrogen (α_H) of R_2SiH_2 are strongly dependent on R. α_{Si} values are +0.501, +0.369, and +0.056, respectively, and α_H values are −0.087, −0.084, and −0.046, respectively, for R = CH_3, Ph, and SiH_3. In comparison to CH_3 and Ph, the SiH_3 group reduces α_{Si} and increases α_H significantly, indicating that the electrophilicity of the central silicon is reduced and the acidity of the Si−H hydrogen is increased by the introduction of silyl substituents as R groups in R_2SiH_2.

(7) Even when **2a** was treated with 2 equiv of *t*-BuLi, the corresponding 1,1-dilithiosilane was not produced.

(8) **1a**: colorless crystals; ^{1}H NMR (C_7D_8, δ) 0.20 (s, 1H, Si−H), 0.24 (brs, 6H, SiMe), 0.32 (brs, 6H, SiMe), 1.04 (s, 18H, *t*-Bu), 1.22−1.31 (m, 4H, THF), 3.50−3.54 (m, 4H, THF); ^{13}C NMR (C_7D_8, δ) 0.3, 1.4 (SiMe), 18.2 ($C(CH_3)_3$), 25.3 ($C(CH_3)_3$), 28.2 (THF), 69.0 (THF); ^{29}Si NMR (C_7D_8, δ) −188.8 (SiHLi, *J*(Si−H) = 75 Hz), 4.5 (*t*-BuMe$_2$Si); ^{7}Li NMR (C_7D_8, δ) 2.01 (brs, $\nu_{1/2}$ = 9.3 Hz).

(9) In THF-d_8, ^{7}Li resonance of **1a** was found at 0.62, suggesting the solvated monomeric structure of **1a**. For the solvent effects on the ^{7}Li resonances, see: (a) Heine, A.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. *Inorg. Chem.* **1993**, *32*, 2694. (b) Nanjo, M.; Sekiguchi, A.; Sakurai H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 741.

(10) The smaller *J*(Si−H) value in Mes_2SiHLi as compared to that in Mes_2SiH_2 has been reported: Roddick, D. M.; Heyn, R.; Tilley, T. D. *Organometallics* **1989**, *8*, 324.

(11) Recrystallization from hexane gave single crystals of **1a** suitable for data collection. All of the diffraction measurements were carried out on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystallographic data for **1a**: formula, $C_{24}H_{62}Si_6Li_2\cdot(C_4H_8O)_2$; formula weight, 677.36; colorless prism; crystal dimensions 0.30 × 0.35 × 0.40 mm; monoclinic; space group $P2_1/c$ (No. 14); cell dimensions, $a = 11.8427(4)$ Å; $b = 15.943(1)$ Å; $c = 12.7700(4)$ Å; $\beta = 107.467(4)°$; $V = 2299.9(2)$ Å^3; $Z = 2$; $D_{calc} = 0.978$ g/cm^3; temperature −123.0 °C. A total of 16 981 reflections were collected, of which 5185 reflections were independent. The number of parameters was 199. The structure was solved by the direct method and refined by the full matrix least-squares on F^2 using SHELXL-97.[12] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final *R* value calculated for 3959 reflections ($I > 2\sigma(I)$) was 0.055, and the wR2 for all of the reflections was 0.162. The value of GOF was 1.039.

(12) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; Universität Göttingen: Germany, 1997.

(13) As shown in Figure 1, the disorder is confined to the Si−H hydrogens H and H′; each of the hydrogens occupies two sites bound to Li1 and Li1* with a refined occupancy ratio of 48.8(4):51.2(4).

(14) While no detailed structural parameters are given, Schleyer et al. have predicted a similar dimeric structure with significant interactions between hydrogen and lithium atoms in $(SiH_3Li)_2$ by theoretical calculations: Sannigrahi, A. B.; Kar, T.; Niyogi, B. G.; Hobza, P.; Schleyer, P. v. R. *Chem. Rev.* **1990**, *90*, 1061.

(15) Schleyer, P. v. R.; Clark, T. *J. Chem. Soc., Chem. Commun.* **1986**, 1371.

(16) (a) Sekiguchi, A.; Ichinohe, M.; Takahashi, M.; Kabuto, C.; Sakurai, H. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1533. (b) Ichinohe, M.; Sekiguchi, A.; Takahashi, M.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 1905.

(17) Very recently, Wiberg et al. reported the X-ray analysis of $(t\text{-}Bu_3Si)_2SiHK(C_6H_6)_2$, which exists as a monomer with significant Si−H- - -K interactions in the solid state. Wiberg, N.; Niedermayer, W.; Nöth, H.; Warchold, M. *J. Organomet. Chem.* **2001**, *628*, 46.

(18) For X-ray analysis of other related hydridosilylmetals with short SiH- - -metal distances, see: (a) Ring, M. A.; Ritter, D. M. *J. Phys. Chem.* **1961**, *65*, 182. (b) Pritzkow, H.; Lobreyer, T.; Sundermeyer, W.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 216. (c) Goldfuss, B.; Schleyer, P. v. R.; Handschuh, S.; Hampel, F.; Bauer, W. *Organometallics* **1997**, *16*, 5999 and references therein.

(19) A recent study has shown that close H- - -Li contacts are not necessarily an indication of the agostic interactions: Scherer, W.; Sirsch, P.; Shorokhov, D.; McGrandy, G. S.; Mason, S. A.; Gardiner, M. G. *Chem.-Eur. J.* **2002**, *8*, 2324. As suggested by a referee, a more detailed study of the structure using a combined high-resolution X-ray and neutron diffraction method is required to elucidate the agostic interactions.

(20) The abstraction of Ge−H hydrogens to give the corresponding germyl anions has been a well-known process, in contrast to sila-metalation. For a recent review, see: Armitage, D. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, S. G. W., Stone, F. G. A., Abel, E. W., Eds; Pergamon Press Ltd.: Oxford, 1982; Chapter 9.1, p 1 and references therein.

(21) **5**: ^{1}H NMR (C_6D_6, δ) −0.55 (s, 1H, Ge−H), 0.44 (s, 6H, SiMe), 0.55 (s, 6H, SiMe), 1.18 (s, 18H, *t*-Bu), 1.22−1.28 (m, 4H, THF), 3.59−3.63 (m, 4H, THF); ^{13}C NMR (C_6D_6, δ) 1.3, 2.5 (SiMe), 18.6 ($C(CH_3)_3$), 25.3 ($C(CH_3)_3$), 28.4 (THF), 68.6 (THF); ^{29}Si NMR (C_6D_6, δ) 12.5 (*t*-BuMe$_2$Si). See the Supporting Information for the X-ray data of **5**.

JA026705D