Unexpected Reaction of an Overcrowded 9,10-Dihydroanthrylchlorosilane Leading to the Formation of a Dibenzo-7-silanorbornadiene Derivative

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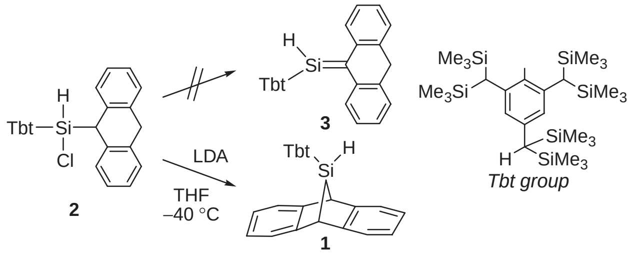
A novel and simple synthetic route for a dibenzo-7-silanorbornadiene derivative has been developed. The extremely hindered chlorosilane bearing 9,10-dihydroanthryl group, TbtRSiHCl (Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl, R = 9,10-dihydroanthryl) could be quantitatively converted into the corresponding dibenzo-7-silanorbornadiene **1** by the reaction with LDA. The molecular structure of **1** was revealed by the spectroscopic and X-ray crystallographic analyses.

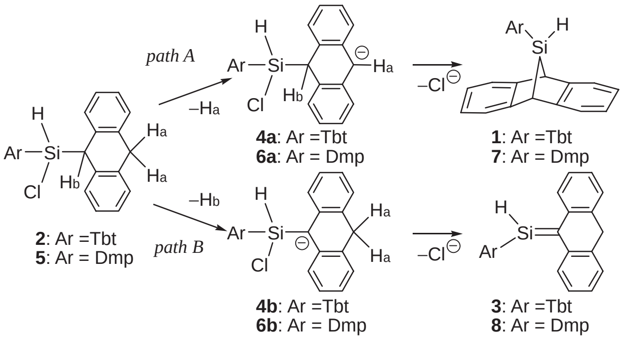
The chemistry of 7-silanorbornadienes has attracted much attention because of their strained structures and unique properties.[1–3] In addition, 7-silanorbornadienes are important species as a precursor of a silylene, since they are known to undergo thermal and photochemical dissociation to give the corresponding silylene and aromatic counterpart via retro [1 + 4] peri cyclic reaction.[3] Particularly, a 7-hydro-7-silanorbornadiene derivative has been of great interest as a precursor of not only a hydrosilylene,[4] which is an important but unprecedented species, but also a functionalized 7-silanorbornadiene derivative at 7-position.[1b,5] However, the synthesis of stable 7-silanorbornadienes are somewhat troublesome, since they should be conventionally achieved by the use of a highly reactive species, such as a transient silylene or a benzyne, with an excess amount of trapping reagents such as anthracene derivatives or siloles.[6] On the other hand, we have been interested in the synthesis and isolation of unprecedented low-coordinated species of heavier group 14 elements by taking advantage of kinetic stabilization. Recently, we have chosen the kinetically stabilized hydrosilene **3** as a target molecule[7] and examined the dehydrochlorination of the overcrowded chlorosilane **2** substituted by an extremely bulky Tbt group. Unexpectedly, however, the reaction of **2** with lithium diisopropylamide (LDA) as a base resulted in the quantitative formation of dibenzo-7-silanorbornadiene **1**, the structural isomer of **3**. We report here the synthesis and structural characterization of the new dibenzo-7-silanorbornadiene derivative **1** together with the mechanistic elucidation using theoretical calculations for the unexpected reaction of **2** with LDA giving **1**.

Chlorosilane **2** was prepared as a stable crystalline compound by the reaction of $TbtSiHCl_2$ with 9,10-dihydroanthryllithium, which was generated by the reported procedure.[8] Treatment of **2** with LDA (1.5 equiv.) in THF at −40 °C afforded dibenzo-7-hydro-7-silanorbornadiene **1** quantitatively (Scheme 1). The structure of **1** was definitely determined based on the spectroscopic and X-ray crystallographic analyses.[9] In the ^{29}Si and ^{1}H NMR spectra of **1**, characteristic signals corresponding to the central silicon atom and the hydrogen atom at the 7-position are observed at $\delta_{Si} = 35.6$ and $\delta_H = 4.83$ with the coupling constant $^{1}J_{SiH} = 207$ Hz. These spectral features of **1** are similar to those of previously reported 7-hydro-7-silanorbornadienes.[1b,5]



Scheme 1.

The unexpected formation of **1** in this reaction should be worthy of note as a novel synthetic route for a dibenzo-7-silanorbornadiene. It can be considered that **1** is formed by the initial deprotonation of H_a (Scheme 2) of **2** followed by the simple S_N2 reaction at the central silicon atom (path A). If H_b proton was abstracted in the initial stage of the reaction of **2** with LDA, silene **3** would be generated (path B). Theoretical calculations for the model compounds, **5**–**8**, which have a 2,6-dimethylphenyl (Dmp) group instead of a Tbt group, indicate that the H_b proton has slightly higher acidity than that of the H_a proton probably due to the α effect of a silicon atom (**6b** is more stable than **6a** by ca. 1.3 kcal/mol).[10] In addition, theoretical calculations for the model reactions, i.e., the reaction of **5** with NH_2Li leading to the formation of 7-silanorbornadiene **7** or hydrosilene **8** together with NH_3 and LiCl, indicate that the formation of **7** is an exothermic reaction of ca. 4 kcal/mol, but that of **8** is an endothermic reaction of 16 kcal/mol. That is, the heat of formation of **7** should sufficiently make up for the unfavorable deprotonation at 10-position (H_a) of **2**. Taking into consideration of these results, the considerable steric hindrance around the central silicon atom should be an indispensable qualification for the generation of a dibenzo-7-silanorbornadiene to prevent deprotonation of the α proton of the central silicon atom. It can be concluded that the quantitative formation of dibenzo-7-silanorbornadiene **1** in the reaction of **2** with LDA is most likely due to the kinetic effect of the extremely bulky Tbt group.[11]



Scheme 2.

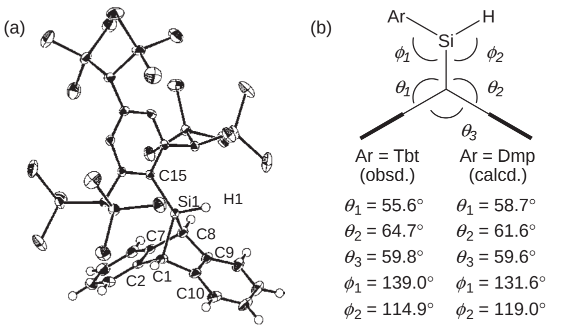
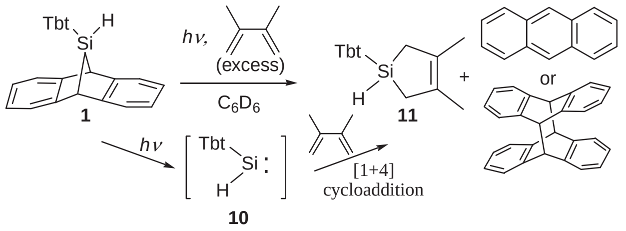


Figure 1. (a) ORTEP drawing of **1** (50% probability). The hydrogen atoms of the Tbt group were omitted for clarity. (b) Depiction of dibenzo-7-silanorbornadienes **1** (observed) and **7** (calculated) from C1–C8 axis.



Scheme 3.

Although a 7-hydro-7-silanorbornadiene skeleton has been already structurally characterized so far,[6] we found unique structural features of **1**. The structural parameters of **1** revealed by X-ray crystallographic (Figure 1a) analysis are also similar to those of the previously reported dibenzo-7-silanorbornadiene (**9**),[6d,12] which has two Dmp groups on the silicon atom at 7-position. Interestingly, dihedral angles θ_1 (Figure 1b) of the dibenzo-7-silanorbornadiene moiety of **1** is smaller than θ_2 despite of the steric repulsion due to the very bulky Tbt group, while **9** shows a symmetric structure as expected (the corresponding θ_1 and θ_2 are almost the same values in **9**). Although the reason is unclear at present, similar tendencies are found in the theoretically optimized structural parameters of the less hindered model compound **7**,[10] indicating that the smaller θ_1 values and the larger θ_2 values observed in **1** may not be due to the steric reason but to somewhat attractive interaction between the Tbt group and the aromatic moiety. On the other hand, ϕ_1 is larger than ϕ_2 in **1** (Figure 1b) most likely due to the steric repulsion between the bulky Tbt group and the dibenzo-7-silanorbornadiene moiety.

When the C_6D_6 solution of **1** was irradiated by the medium- or low-pressure Hg lamp in the presence of 2,3-dimethyl-1,3-butadiene (DMB) at room temperature, [1 + 4]-cycloadduct **11** was obtained in 36 or 50% yield, respectively, together with anthracene and/or anthracene-photodimer, indicating the photochemical generation of hydrosilylene **10** (Scheme 3).[9,13] Thus, 7-hydro-dibenzo-7-silanorbornadiene **1** was proved to be a good precursor of the corresponding hydrosilylene **10**.

This work was supported by Grant-in-Aid for Scientific Research (Nos. 17GS0207 and 18750030) and the 21st Century COE Program, Kyoto University Alliance for Chemistry, from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 For recent topics on 7-silanorbornadienes, see: a) O. S. Volkova, M. B. Taraban, V. F. Plyusnin, T. V. Leshina, M. P. Egorov, O. M. Nefedov, *J. Phys. Chem. A* **2003**, *107*, 4001. b) J. Schuppan, B. Herrschaft, T. Müller, *Organometallics* **2001**, *20*, 4584. c) M. B. Taraban, A. I. Kruppa, O. S. Volkova, I. V. Ovcharenko, R. N. Musin, T. V. Leshina, E. C. Korolenko, K. Kitahara, *J. Phys. Chem. A* **2000**, *104*, 1811. d) M. B. Taraban, O. S. Volkova, A. I. Kruppa, V. F. Plyusnin, V. P. Grivin, Y. V. Ivanov, T. V. Leshina, M. P. Egorov, O. M. Nefedov, *J. Organomet. Chem.* **1998**, *566*, 73. e) I. M. Magin, P. A. Purtov, A. I. Kruppa, T. V. Leshina, *J. Phys. Chem. A* **2005**, *109*, 7396.

2 a) M. N. Paddon-Row, S. S. Wong, K. D. Jordan, *J. Am. Chem. Soc.* **1990**, *112*, 1710. b) M. N. Paddon-Row, K. D. Jordan, *J. Chem. Soc., Chem. Commun.* **1988**, 1508. c) J. A. Hawari, D. Griller, *Organometallics* **1984**, *3*, 1123.

3 a) T. Sanji, T. Mori, H. Sakurai, *J. Organomet. Chem.* **2006**, *691*, 1169. b) A. Sekiguchi, S. S. Zigler, R. West, J. Michl, *J. Am. Chem. Soc.* **1986**, *108*, 4241. c) M. B. Taraban, O. S. Volkova, V. F. Plyusnin, A. I. Kruppa, T. V. Leshina, M. P. Egorov, O. M. Nefedov, *J. Phys. Chem. A* **2003**, *107*, 4096. d) P. P. Gasper, R. West, in *The Chemistry of Organic Silicon Compounds*, ed. by Z. Rappoport, Y. Apeloig, Wiley, Chichester, **1998**, Vol. 2, pp. 2463–2568. e) M. Kako, S. Oba, R. Uesugi, S. Sumiishi, Y. Nakadaira, K. Tanaka, T. Takada, *J. Chem. Soc., Perkin Trans. 2* **1997**, 1251.

4 Transition-metal complexes of a hydrosilylene have been reported, see: a) B. V. Mork, T. D. Tilley, A. J. Schultz, J. A. Cowan, *J. Am. Chem. Soc.* **2004**, *126*, 10428. b) T. Watanabe, H. Hashimoto, H. Tobita, *Angew. Chem., Int. Ed.* **2004**, *43*, 218. c) T. Watanabe, H. Hashimoto, H. Tobita, *J. Am. Chem. Soc.* **2006**, *128*, 2176.

5 A. Kawachi, M. Okimoto, Y. Yamamoto, *Chem. Lett.* **2005**, *34*, 960.

6 For examples, see: a) W. C. Joo, J. H. Hong, S. B. Choi, H. E. Son, C. H. Kim, *J. Organomet. Chem.* **1990**, *391*, 27. b) Y. L. Pan, J. H. Hong, S. B. Choi, P. Boudjouk, *Organometallics* **1997**, *16*, 1445. c) H. Sakurai, H. Sakaba, Y. Nakadaira, *J. Am. Chem. Soc.* **1982**, *104*, 6156. d) H. Sakurai, K. Oharu, Y. Nakadaira, *Chem. Lett.* **1986**, 1797.

7 A number of theoretical studies and trapping reactions of transient hydrosilenes have been reported. For examples, see: a) H. Ottosson, *Chem.—Eur. J.* **2003**, *9*, 4144. b) W. J. Leigh, R. Boukherroub, C. Kerst, *J. Am. Chem. Soc.* **1998**, *120*, 9504. c) C. J. Bradaric, W. J. Leigh, *Organometallics* **1998**, *17*, 645.

8 a) P. W. Rabideau, D. M. Wetzel, C. A. Husted, J. R. Lawrence, *Tetrahedron Lett.* **1984**, *25*, 31. b) H. Stamm, P. Y. Lin, A. Sommer, A. Woderer, *Tetrahedron* **1989**, *45*, 2571.

9 All the new compounds here obtained showed satisfactory spectral data. Experimental procedures, compound data, and crystal data of **1** (CCDC 620514) are described in Supporting Information, which is available electronically on the CSJ Journal web site; http://www.csj.jp/journals/chem-lett/.

10 Theoretical calculations were performed at the B3PW91/6-31+G(d) level without ZPE corrections. It is difficult to take the solvent effect into the calculations, since the calculations containing solvent molecules should be highly complicated.

11 Reaction of a less hindered chlorosilane, (9,10-dihydroanthryl)-MesSiHCl, with LDA under the same conditions afforded a complicated mixture containing no dibenzo-7-silanorbornadiene derivative.

12 M. Kako, M. Mori, K. Hatakenaka, S. Kakuma, Y. Nakadaira, M. Yasui, F. Iwasaki, *Tetrahedron* **1997**, *53*, 1265.

13 a) A. Kawachi and Y. Yamamoto have recently reported the trapping reaction of the hydrosilylene, Mes(H)Si:, generated by the photoirradiation of the corresponding 7-hydro-dibenzo-7-silanorbornadiene, see: The 86th Annual Meeting of the Chemical Society of Japan, Abstr., No. 3F4-12, **2006**. b) Heating of the toluene-d_8 solution of **1** at 150 °C in the presence of DMB resulted in no reaction. c) Relatively low yields of **11** under these conditions are probably due to the over-photoreaction of resulting **11**.