An Unexpected Elimination of Cyclopentadienide Anion in the Reaction of Silacyclohexadienes with a Bulky Aryllithium
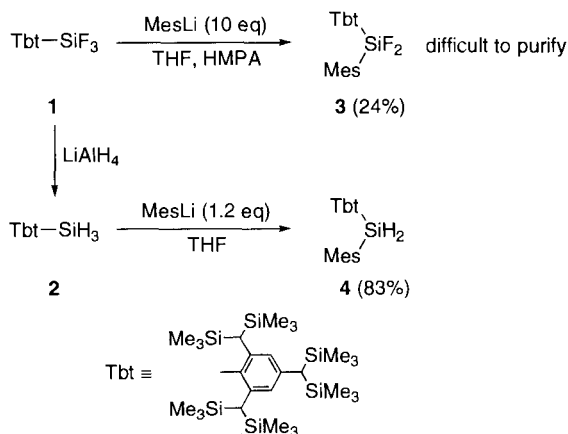
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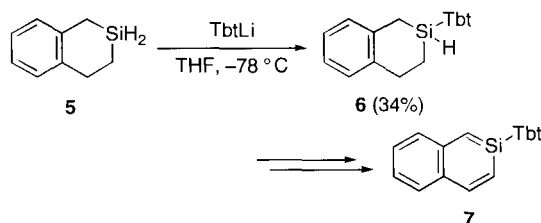
The reaction of silacyclohexadienes with an extremely hindered aryllithium, TbtLi (Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl), gave no expected Tbt-substituted silacyclohexadienes but trihydrosilane, TbtSiH$_3$, via the elimination of cyclopentadienide anion. By contrast, 1,1-difluoro-1-silacyclohexa-2,4-diene underwent a normal substitution though the yield was very low.
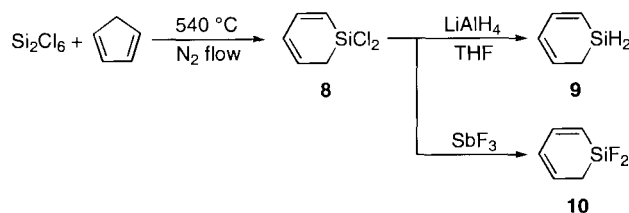
Nucleophilic substitution reactions on silicon atom are one of the most important and common class of reactions for the synthesis of various organosilicon compounds.[1] These reactions are reasonably interpreted in terms of the initial formation of a pentacoodinate silicon intermediate, which usually eliminates one of the substituents as a leaving group to give the final substitution product. In many cases halogen anions are used as leaving groups. However, in contrast to the nucleophilic substitution on carbon, even a hydride ion can serve as a leaving group though its leaving ability is relatively low. For example, we have recently showed the substitution of a hydrosilane is very useful for the introduction of a bulky substituent onto the sterically hindered silicon atom. Thus, the treatment of an overcrowded trihydrosilane, TbtSiH$_3$ (2, Tbt = 2,4,6-tris[bis(trimethylsilyl)-methyl]phenyl), with MesLi (Mes = mesityl) in THF afforded the expected dihydrosilane 4 in an excellent yield, while the nucleophilic substitution of the corresponding trifluorosilane 1 with MesLi only proceeded under much severer conditions than those for 2 in a poor yield of 3.[2]

$$Tbt{-}SiF_3 \xrightarrow[\text{THF, HMPA}]{\text{MesLi (10 eq)}} \underset{Mes}{\overset{Tbt}{>}}SiF_2 \quad \text{difficult to purify}$$

1   **3 (24%)**

↓ LiAlH$_4$

$$Tbt{-}SiH_3 \xrightarrow[\text{THF}]{\text{MesLi (1.2 eq)}} \underset{Mes}{\overset{Tbt}{>}}SiH_2$$

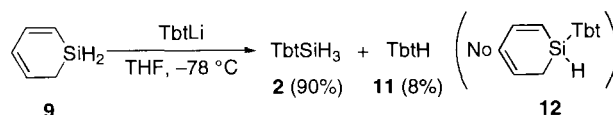**2**   **4 (83%)**

Tbt ≡

In the course of our study on highly reactive organosilicon compounds, we became interested in cyclic silanes bearing bulky substituents as suitable starting materials for the synthesis of silicon-containing cyclic π systems. This research successfully resulted in the isolation of the first stable 2-silanaphthalene 7, for which the nucleophilic substitution of the dihydrosilane 5 with TbtLi is the key step to introduce the Tbt group onto the silicon atom.[3]
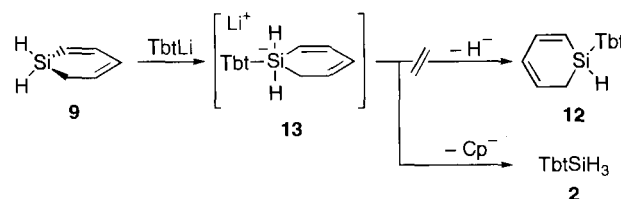

In this paper we wish to report an unusual nucleophilic substitution reaction of silacyclohexadienes with TbtLi leading to the extrusion of a cyclopentadienide anion. 1,1-Dichloro-1-silacyclohexa-2,4-diene (8) was synthesized by flow pyrolysis of hexachlorodisilane and cyclopentadiene as reported in the literature.[4,5] Treatment of 8 with LiAlH$_4$ and SbF$_3$ gave dihydrosilane 9 and difluorosilane 10,[6] respectively.

Although the reaction of dichlorosilane 8 with TbtLi only gave a complex mixture probably due to too much bulkiness of the Tbt group for nucleophlic attack to silicon, that of dihydrosilane 9 with TbtLi gave, surprisingly, Tbt-substituted *trihydrosilane* 2 in 90% yield after work up.
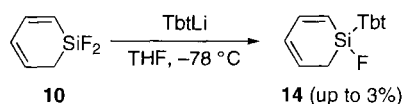

In this reaction, no expected product 12 was detected. This is in sharp contrast to the reaction of TbtLi with 5 (*vide supra*). Since the reactions of dichlorosilane 8 with various less hindered nucleophiles readily gave the corresponding substituted products,[5] the formation of trihydrosilane 2 from 9 is unique and very unusual not only for the nucleophilic substitution of silacyclohexadienes but also for that of dihydrosilanes.[7] Plausible reaction mechanism is shown below.

The most plausible intermediate of this reaction might also be the pentacoordinated dihydrosilicate **13**, as in the case of the normal substitution reaction of organosilanes. If the elimination of lithium hydride from **13** takes place silimarly to the substitution reaction of **5**, the final product should be the Tbt-substituted silacyclohexadiene **12**. However, this is not the case and the extrusion of all the carbon framework from silacyclohexadiene ring of **13** took place leading to the formation of trihydrosilane **2**. Although the mechanism of this extrusion is not clear at present, the higher leaving ability of aromatic cyclopentadienide anion $(Cp^-)^8$ than a hydride ion probably plays an important role considering the different reactivity of dihydrosilane **5** which has a framework similar to **9**.

If this mechanism is correct, the desired substituted product would be obtained when good leaving groups are introduced on the central silicon atom. Since dichlorosilane **8** cannot be substituted by TbtLi as mentioned above, substitution of less sterically hindered difluorosilane **10** was examined. Although the reaction of **10** was also very complex as in the case of **8**, careful separation of the mixture led to the detection of trifluorosilane **14**[9] containing the Tbt group.

10   **14** (up to 3%)

The very low yield of **14** is most likely due to the poor leaving ability of fluorine, the steric congestion around the central silicon atom of **10** for the nucleophilic attack with TbtLi, and the instability of **14** under separation conditions. But, we think the formation of **14** from **10** gave us important and suggestive information on the formation mechanism of the trihydrosilane **2** from **9**.

We think the unique reactivity of silacyclohexadiene **9** with TbtLi, which gave unexpected Tbt-substituted trihydrosilane **2** instead of the normal substitution product **12**, is of particular note as a new example of the characteristic reactivity of the organosilicon compounds quite different from their carbon analogues.

References and Notes

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1 Reviews: "The Chemistry of Organosilicon Compounds," ed by S. Patai and Z. Rappoport, Wiley, New York (1989), Chapter 10 and 13.

2 a) M. Unno, Ph.D. Thesis, The University of Tokyo (1988). b) H. Suzuki, Ph.D. Thesis, The University of Tokyo (1995). c) H. Suzuki, N. Tokitoh, R. Okazaki, J. Harada, K. Ogawa, S. Tomoda, and M. Goto, *Organometallics*, **14**, 1016 (1995).

3 N. Tokitoh, K. Wakita, R. Okazaki, S. Nagase, P. v. R. Schleyer, and H. Jiao, *J. Am. Chem. Soc.*, **119**, 6951 (1997).

4 Since silacyclohexadienes **8**–**10** can be obtained only as inseparable mixtures with their 2,5-diene isomers (ca. 8:1 ratio), these mixtures were used for further reactions.

5 G. Maier, G. Mihm, R. O. W. Baumgärtner, and H. P. Reisenauer, *Chem. Ber.*, **117**, 2337 (1984) and references cited therein.

6 Difluorosilane **10** has never been reported so far as we know. $^{29}Si\{^1H\}$ NMR (54 MHz, $CDCl_3$) δ −15.2 (t, J_{SiF} = 290 Hz). ^{19}F NMR (254 MHz, $CDCl_3$) δ −133.6 (br m). **10** is highly volatile and was difficult to purify.

7 Since the reaction of **9** with MesLi gave also $MesSiH_3$ (δ_{Si} = −76.9, J_{SiH} = 199 Hz), the formation of a trihydrosilane from dihydrosilane **9** may proceed regardless the bulkiness of an aryllithium employed.

8 The Cp^- anion thus formed was observed in the ^1H NMR spectrum at 5.67 ppm (THF/acetone-d_6) in agreement with that of the authentic CpLi which was synthesized from cyclopentadiene and *n*-BuLi and measured under the same conditions.

9 Spectral data of **14**: ^1H NMR (500 MHz, $CDCl_3$) δ −0.01 (s, 9H), 0.00 (s, 9H), 0.03 (s, 36H), 1.33 (s, 1H), 1.83–1.95 (m, 2H), 2.09 (br s, 1H), 2.11 (br s, 1H), 6.02–6.05 (m, 1H), 6.12–6.15 (m, 1H), 6.22 (d, J = 14 Hz, 1H), 6.26 (br s, 1H), 6.37 (br s, 1H), 6.87 (dd, J = 14, 6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.54 (q), 0.71 (q), 0.72 (q), 0.91 (q), 1.05 (q), 18.29 (dt, J_{CF} = 14 Hz), 28.16 (d), 28.53 (d), 30.60 (d), 122.01 (d), 125.62 (dd, J_{CF} = 1 Hz), 126.75 (dd, J_{CF} = 18 Hz), 127.02 (d), 130.27 (dd, J_{CF} = 2 Hz), 142.43 (dd, J_{CF} = 5 Hz), 145.76 (s), 151.62 (s), 151.94 (s), 155.97 (d, J_{CF} = 6 Hz). ^{19}F NMR (254 MHz, $CDCl_3$) δ −137.40 (t, J_{HF} = 10 Hz). LRMS (EI, 70 eV) 644 [M$^+$].