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 silvlene 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 7position.^{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 molecule⁷ 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 com-

pound by the reaction of TbtSiHCl₂ 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 ²⁹Si and ¹HNMR 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 ¹J_{SiH} = 207 Hz. These spectral features of **1** are similar to those of previously reported 7-hydro-7-silanorbornadienes.^{1b,5}

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 NH₂Li leading to the formation of 7-silanorbornadiene 7 or hydrosilene 8 together with NH₃ 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



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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.



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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 7position. 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 mediumor low-pressure Hg lamp in the presence of 2,3-dimethyl-1,3butadiene (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**.

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