

論文内容要旨

論文題目 Synthesis of Two-Dimensionally Extended Hetero- π -Conjugated Molecules and Their Properties

(二次元的に拡張された含典型元素 π 共役分子の創製とその性質)

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Introduction

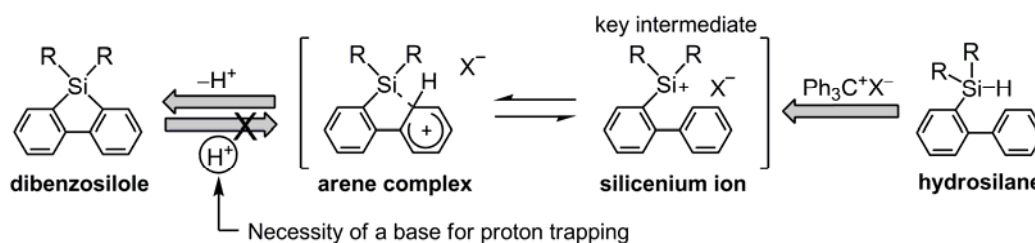
Introduction of the main group element into π -conjugated systems is currently receiving much attention because it gives the electronic perturbation to photoelectronic properties of π -conjugated molecules. Silole, a silicon-containing cyclopentadiene, has a significant low-lying LUMO, and π -extended silole derivatives involving spiro-type and ladder-type molecules have desirable properties, such as high fluorescence quantum yields and high glass-transition temperatures. Because of these advantages, further extension or modification of the silole framework is intriguing. For the effective synthesis of these compounds, however, a new synthetic methodology for siloles is desired, and the developments have been reported recently. Despite the recent remarkable progress in this field, synthesizable silicon-containing π -conjugated skeletons are limited to one-dimensionally extended ladder-type silafluorenes at most. The development of a new type of synthetic methodology will be a keystone for the further progression to two-dimensionally extended derivatives. So during my Ph.D. work, I developed new synthetic methodology for constructing the two-dimensionally extended silicon and other heteroatom-containing π -conjugated molecules.

Development of a Sila-Friedel–Crafts Reaction

The Friedel–Crafts reaction is a well-known method for the direct substitution of an aromatic ring. On the other hand, the sila-Friedel–Crafts reaction, i.e., Friedel–Crafts-type silylation involving a

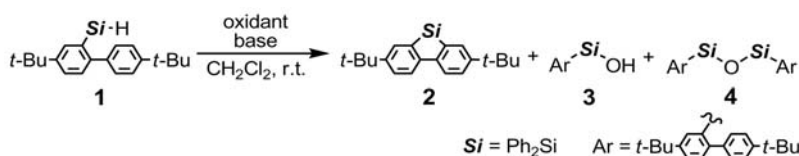
silicenium ion as an intermediate, occurs only with electron rich aromatic rings such as a ferrocene and a pyrrole. However, in the case of a nonactivated aromatic ring such as benzene, the conversion of the reaction markedly decreases. Thus, the sila-Friedel–Crafts reaction has not been used as a versatile synthetic method to date. Meanwhile, this reaction has great potential to construct a dibenzosilole framework. The basic strategy is shown in Scheme 1. The reaction of hydrosilane with a trityl cation is a useful method for the generation of a silicenium ion, which should spontaneously form the arene complex. The dibenzosilole would be obtained by deprotonation from this species. The presence of a base is necessary in this reaction to prevent the reverse reaction.

Scheme 1. Strategy for the Intramolecular Sila-Friedel–Crafts Reaction



The reaction of hydrosilane **1** with trityl perchlorate and 2,6-lutidine in dichloromethane at room temperature gave dibenzosilole **2** in 52% yield. Silanol **3** and disiloxane **4** were also formed as side products (Table 1, entry 1). This moderate conversion may be due to deactivation of the intermediate by coordination of a perchlorate anion to the silicenium ion. Changing the counteranion to tetrakis(pentafluorophenyl)-borate significantly increased the conversion yield of **2** to 84% (entry 2). This reaction was very sensitive to the choice of base, and no bases other than 2,6-lutidine worked well (entry 3–6). The reasons for the high efficiency of 2,6-lutidine are still unclear, but the bulkiness and basicity of 2,6-lutidine should be important in this reaction.

Table 1. Intramolecular Sila-Friedel–Crafts Reaction



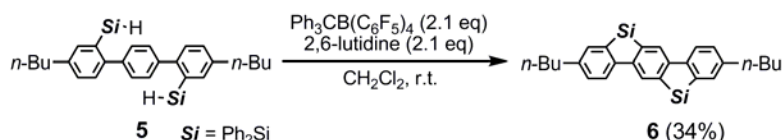
entry	oxidant	base	% yield ^a			
			1	2	3	4
1	Ph ₃ CClO ₄	2,6-lutidine	0	52	23	25
2	Ph ₃ CB(C ₆ F ₅) ₄	2,6-lutidine	0	84	12	4
3	Ph ₃ CB(C ₆ F ₅) ₄	proton sponge	100	0	0	0
4	Ph ₃ CB(C ₆ F ₅) ₄	pyridine		– ^b		
5	Ph ₃ CB(C ₆ F ₅) ₄	DTBMP ^c	100	0	0	0
6 ^d	Ph ₃ CB(C ₆ F ₅) ₄	diisopropylethylamine	50	0	0	0

^a Estimated by ¹H NMR. ^b A complex mixture was obtained. ^c DTBMP = 2,6-di-*tert*-butyl-4-methylpyridine. ^d An unidentified compound was generated.

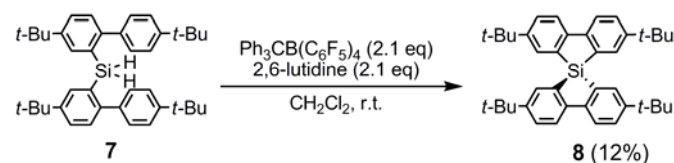
Application of an Intramolecular Sila-Friedel–Crafts Reaction

The intramolecular sila-Friedel–Crafts reaction afforded a dibenzosilole in a good yield under mild conditions. Therefore, I applied this reaction to the synthesis of π -extended dibenzosilole derivatives. The intramolecular sila-Friedel–Crafts reaction of 2,2''-bis(diphenylsilyl)-1,1':4',1''-terphenyl **5** afforded the corresponding ladder-type silafluorene **6** (Scheme 2). This result suggests that the

Scheme 2.



Scheme 3.

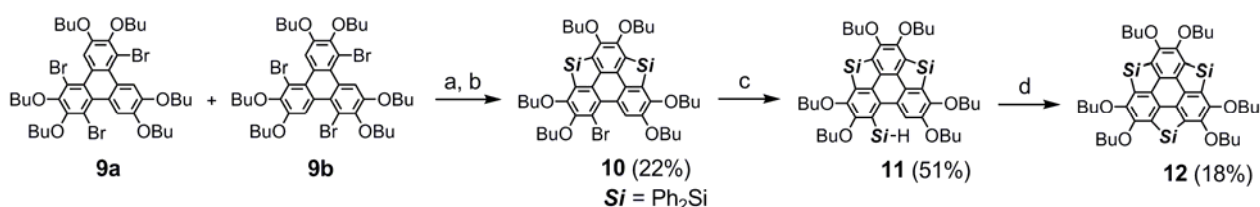


sila-Friedel–Crafts reaction is applicable to intramolecular double cyclization. In addition, spirosilane **8** could be synthesized by using dihydrosilane **7** as a precursor (Scheme 3). Thus, the sila-Friedel–Crafts reaction is useful as a new method for multistep C–Si bond formation on the same silicon atom.

Synthesis of Two-Dimensionally Extended Silole

Sumanene is known as one of the partial skeleton of C_{60} . The silicon analogue of sumanene, trisilasumanene has attracted much attention as both a sumanene analogue and a novel π -extended silole derivative. However, trisilasumanene is considered difficult to synthesize using conventional methods. Thus, I applied the intramolecular sila-Friedel–Crafts reaction to the synthesis of trisilasumanene. Starting from an isomeric mixture of tribromotriphenylene **9**, doubly cyclized monobromide **10** was synthesized in two steps, including a dual sila-Friedel–Crafts reaction (Scheme 4). Transformation to the precursor **11** was achieved by lithiation of **10** followed by the addition of diphenylsilane in 51% yield. Finally, the intramolecular sila-Friedel–Crafts reaction was applied again to **11**, and trisilasumanene **12** was obtained in 18% yield.

Scheme 4. Synthesis of Trisilasumanene **12**^a



^a (a) (i) *n*-BuLi (2.0 equiv), THF, -78°C , (ii) Ph_2SiCl_2 , r.t., (iii) LiAlH_4 , reflux; (b) $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, 2,6-lutidine, CH_2Cl_2 , r.t.; (c) *t*-BuLi (2.0 equiv), Et_2O , -78°C , (ii) Ph_2SiH_2 , reflux; (d) $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, 2,6-lutidine, CH_2Cl_2 , r.t..

Structure and Optical Property of Trisilasumanene **12**

The crystal structure of **12** is shown in Figure 1. It is known that sumanene and its sulfur analogue, trithiasumanene, have a bowl-shaped structure with bowl depths of 1.11 and 0.65 Å, respectively. The difference between the bowl depths is attributed to the larger covalent radius of the sulfur atom. X-ray structural analysis of trisilasumanene **12** indicated that the main framework was almost planar.

To elucidate the electronic structure, the UV-vis absorption spectrum of trisilasumanene **12** was measured in dichloromethane. An intense absorption band of **12** ($\lambda_{\max} = 299$ nm, $\log \varepsilon = 4.67$) was slightly red-shifted from that of 2,3,6,7,10,11-hexabutoxytriphenylene (**13**) ($\lambda_{\max} = 280$ nm, $\log \varepsilon = 5.09$) and sumanene ($\lambda_{\max} = 278$ nm). In addition, a weak absorption band was observed in the longer wavelength region (>350 nm) in **12**. This longer wavelength absorption was mainly attributed to the HOMO–LUMO transition of **12**, and it suggested the existence of a $\sigma^*-\pi^*$ conjugation on the silicon atoms. In the emission spectrum, **12** showed a blue fluorescence in dichloromethane solution ($\lambda_{\max} = 427$ nm) and in the solid state ($\lambda_{\max} = 447$ nm).

Chart 1. Structures of Sumanene and Its Main-Group Analogues, Trithiasumanene and Trisilasumanene

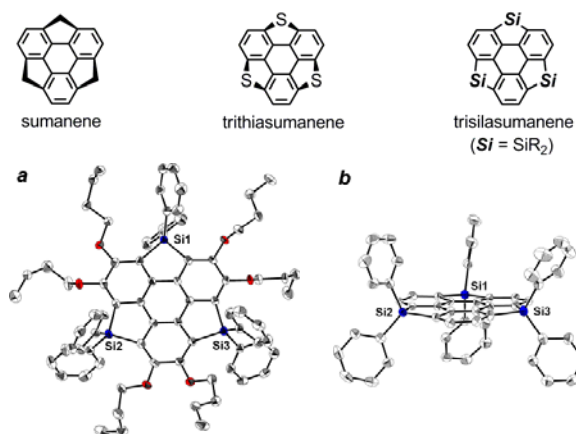
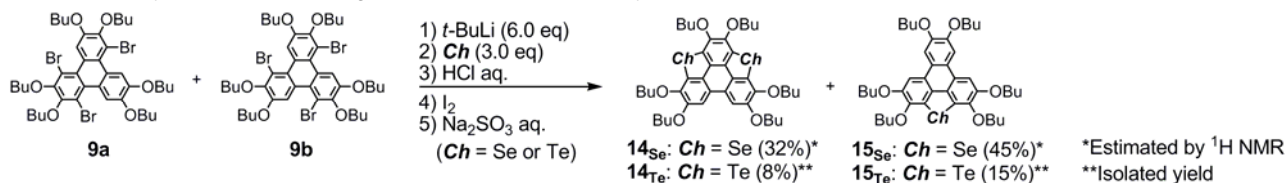


Figure 1. (a) Top view and (b) side view of the crystal structure of trisilasumanene **12**. In (b), the six butoxy groups have been omitted for the sake of clarity.

Synthesis of Chalcogenophene Derivatives Utilizing Intramolecular Cyclization

By applying the intramolecular cyclization methodology to the synthesis of chalcogeno-containing π -conjugated molecules, syntheses of chalcogenophene-fused triphenylene derivatives **14** and **15** were also achieved (Scheme 5).

Scheme 5. Synthesis of chalcogenophene-fused triphenylene derivatives **14** and **15**



Conclusion

An intramolecular sila-Friedel–Crafts reaction was developed and applied to the synthesis of dibenzosilole derivatives. This reaction proceeds under mild conditions to afford the target in relatively high yield, indicating its availability as a versatile synthetic method. The synthesis of trisilasumanene, a silicon analogue of sumanene, was achieved using the present reaction. Such an intramolecular cyclization methodology was found to be effective for the construction of other two-dimensionally expanded π -conjugated molecules containing main group elements.