

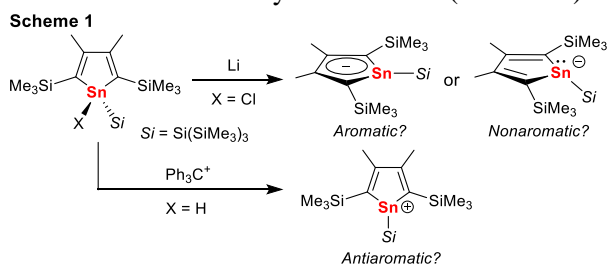
芳香族性/反芳香族性を有するスタンノールアニオン/カチオンの合成検討

Synthetic Studies of Stannole Anions/Cations Exhibiting
Aromatic/Antiaromatic Characters応用化学専攻 北村 浩平
KITAMURA Kohei

1. Introduction

Many studies have been conducted on "heavy" aromatic compounds by replacing one or more skeletal carbon atoms in aromatic compounds with heavier group 14 elements.¹ Not only heavier benzenes but also heavier non-benzenoid compounds have attracted increasing attention. Among them, heavy analogues of Cp^- have been considered to be nonaromatic due to their pyramidalized E center and C–C bond alternation in the five-membered rings.² However, Kovács and Müller *et al.* recently reported the synthesis of aromatic silole³ and germole⁴ anions with a planar structure. In this case, introduction of silyl groups on the α -carbons of the metallole ring is considered to be the key point to realize the aromatic metallole anions. With these results in mind, the author investigated whether an aromatic stannole anion could be synthesized.

In contrast, research on heavy antiaromatics are rather limited. Most of them have been focused on heavy analogues of cyclobutadiene.⁵ With regard to other antiaromatic species, heavy cyclopentadienyl cations (Cp^+) are predicted to be antiaromatic.⁶ However, no successful synthesis of such species have been reported so far.⁷ To shed light on the aromaticity/antiaromaticity of tin analogues of Cp^-/Cp^+ , the author also tackled to synthesize a stannole cation with silyl substituents (Scheme 1).



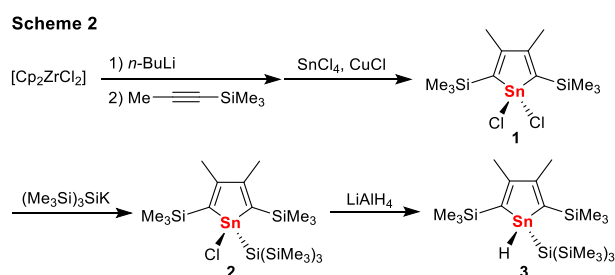
2. Experimental Section

All manipulations were carried out under an inert atmosphere by using standard Schlenk techniques or in a glovebox. Isolable products were characterized by NMR, X-ray diffraction, and elemental analyses.

3. Results and Discussion

Synthesis of starting materials

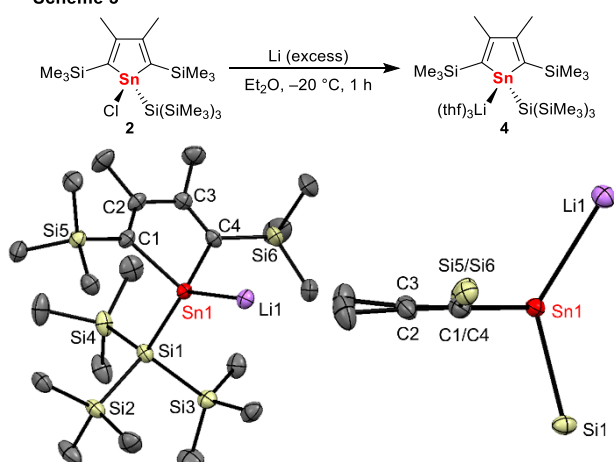
Reaction of an *in situ* generated zirconacycle with SnCl_4 in the presence of CuCl in hexane gave dichlorostannole **1**. Introduction of a bulky $\text{Si}(\text{SiMe}_3)_3$ substituent on the tin atom was achieved by using $(\text{Me}_3\text{Si})_3\text{SiK}$ to obtain (chloro)(silyl)stannole **2**. The subsequent hydride reduction by LiAlH_4 in Et_2O at room temperature yielded hydrostannole **3**.

A tin analogue of cyclopentadienyl anion

Reaction of **2** with excess lithium in diethyl ether at $-20\text{ }^\circ\text{C}$ for 1 h afforded a deep red suspension. Hexane was added to the suspension, and insoluble materials were removed by filtration. Further recrystallization from hexane and THF yielded stannole anion **4** (26% yield). The X-ray diffraction study revealed that **4** has remarkable C–C bond alternation in the stannole ring with the C–C bond distances of 1.362(4), 1.489(4), and 1.363(4) Å. Furthermore, the tin atom is highly pyramidalized, and the angle between the vector from the centroid

of the stannole ring to the tin atom and the Sn–Si bond is ca. 104° . These structural features indicate the anionic charge is strongly localized on the tin atom. The $^{119}\text{Sn}\{^1\text{H}\}$ signal of **4** appeared at $\delta -130.6$, which is considerably high-field shifted compared to that of **2** ($\delta 101.3$). Additionally, the $^{13}\text{C}\{^1\text{H}\}$ NMR signals of the α - and β -carbons ($\delta 180.2, 156.9$) were low-field shifted in comparison to those of **2** ($\delta 159.8, 146.2$), confirming that the negative charge is localized on the tin atom also in solution. Thus, unlike the related silole and germole anions, **4** was concluded to be nonaromatic, probably because the Sn–C bonds are longer than Si–C and Ge–C bonds, which ends in smaller aromatic stabilization energy.

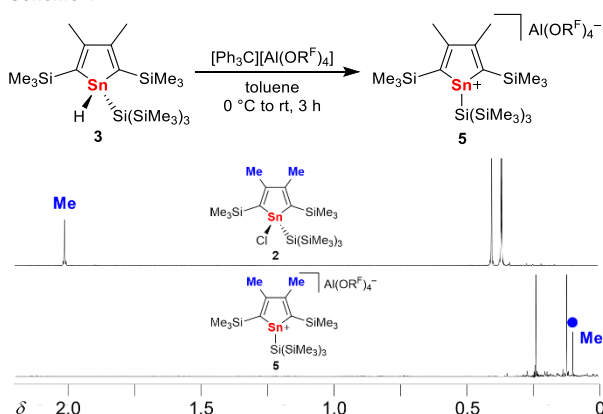
Scheme 3

Figure 1. ORTEP drawings for **4**.

A tin analogue of cyclopentadienyl cation

Reaction of **3** with $[\text{Ph}_3\text{C}][\text{Al}(\text{OR}^{\text{F}})_4]$ ($\text{OR}^{\text{F}} = \text{OC}(\text{CF}_3)_3$) in toluene at 0°C to room temperature for 3 h gave a biphasic reaction mixture. The ^1H NMR spectrum of the upper non-polar phase revealed the formation of Ph_3CH , suggesting that the desired hydride abstraction from **3** took place.

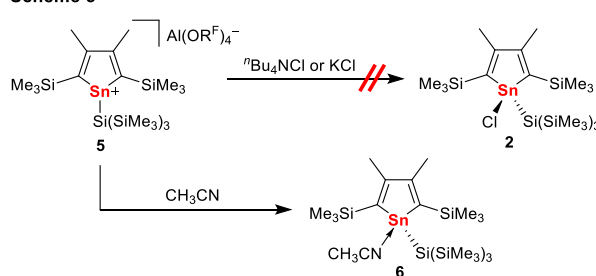
Scheme 4

Figure 2. ^1H NMR spectra of **2** and **5**.

Moreover, in the ^1H NMR spectrum of the lower viscous phase, the signal of the methyl groups on the five-membered ring exhibited a notable upfield shift ($\delta 0.10$) compared to those of **1–3** ($\delta 1.72\text{--}2.11$), which may be attributable to the paramagnetic ring current. Unfortunately, $^{119}\text{Sn}\{^1\text{H}\}$ NMR spectrum of **5** could not be measured because of its low solubility in common organic solvents.

Since single crystals of the stannole cation **5** suitable for X-ray study could not be obtained so far, trapping experiments were performed to confirm the formation of **5**. Although treatment with Cl^- sources failed to give **2**, the addition of acetonitrile to a solution of **5** suggested the generation of adduct **6** on the basis of the signal of the acetonitrile ($\delta 0.71$) downfield shifted in comparison with that of free acetonitrile in C_6D_6 ($\delta 0.58$).

Scheme 5



4. Conclusion

Novel stannole anion and cation were synthesized. Anion **4** was concluded to be nonaromatic on the basis of the NMR and X-ray diffraction studies, whereas the antiaromaticity of cation **5** was supported by the ^1H NMR spectrum.

References

- (1) Sekiguchi, A.; Lee, V. Y. *Angew. Chem., Int. Ed.* **2007**, *46*, 6596–6620.
- (2) (a) Tilley, T. D. *et al. J. Am. Chem. Soc.* **1996**, *118*, 10457–10468. (b) Tilley, T. D. *et al. Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1887–1890.
- (3) Kovács, I.; Nyulászi, L. *et al. Chem. Commun.* **2017**, *53*, 11064–11067.
- (4) Müller, T. *et al. Chem. Eur. J.* **2019**, *25*, 10858–10865.
- (5) (a) Matsuo, T.; Tamao, K. *et al. Science* **2011**, *331*, 1306–1309. (b) Iwamoto, T. *et al. Angew. Chem., Int. Ed.* **2017**, *56*, 1543–1552.
- (6) Schleyer, P. von R. *et al. Organometallics* **1997**, *16*, 1543–1552.
- (7) Olah, G. A. *et al. J. Am. Chem. Soc.* **1992**, *114*, 7737–7742.

Presentations

- (1) ICCOC-GTL-16, P28 (2019).
- (2) 100th CSJ Annual Meeting, 1H2-52 (2020).