スタンナシクロヘプタトリエニルジアニオンの合成とその反芳香族性
Synthesis of Stannacycloheptatrienyl Dianions and Their Anti-aromaticity

応用化学専攻　伊藤　正太郎
ITO Shotaro

1. Introduction

In contrast to many synthetic examples of aromatic compounds containing heavier group 14 elements,[1] studies on heavy anti-aromatics are rather limited. Matsuo's group synthesized heavy analogs of cyclobutadiene, the tetrasila- and tetragerma-cyclobutadienes, but these compounds were concluded to be non-aromatic with the charge localized structures.[2, 3] Iwamoto and his coworkers succeeded in the synthesis of the benzodisilacyclobutadiene that shows anti-aromaticity.[4] However, synthetic examples of heavier congeners of anti-aromatic compounds have been reported for only cyclobutadiene analogs. Cycloheptatrienyl anion is a seven-membered ring compound that shows anti-aromaticity with an 8π-electron system. Herein, we report the synthesis and electronic structures of a stannacycloheptatrienyl anion and a further reduced dianion species.

2. Experimental Section

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

3. Results and Discussion

Reaction of **1** with excess lithium in diethyl ether at −10 °C for 30 min followed by recrystallization of the crude product from DME and toluene yielded stannepinyl monoanion **2**. In the ^{1}H NMR spectrum of **2**, there were no significant upfield shifted signals, suggesting that **2** does not have anti-aromatic character. X-ray diffraction analysis revealed that the tin atom of **2** is highly pyramidalized, which indicates the anionic charge is strongly localized on the tin atom. This localization can be interpreted as occurring to avoid the formation of an unstable 8π-electron system.

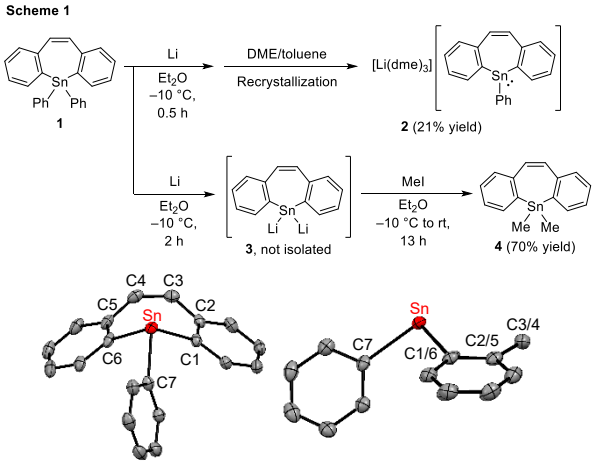


Figure 1. ORTEP drawings for **2**.

Interestingly, when a mixture of **1** and excess lithium in diethyl ether was stirred for 2 h, the color of the reaction solution turned black brown. Addition of iodomethane to this solution yielded dimethylstannepin **4**, indicating that dilithium stannacycloheptatrienide **3** was formed in the dark brown solution. Incidentally, metallolyl dianions are known to be aromatic with a 6π-electron system (Figure 2).[5] Thus, a stannepinyl dianion could be regarded as an anti-aromatic compound with an 8π-electron system. To verify this hypothesis, an electronic structure of free dianion of **3**, denoted as **3′**, was investigated by theoretical studies.

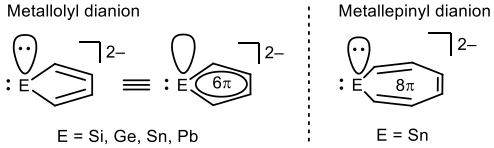
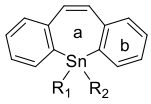


Figure 2. Metallolyl and metallepinyl dianions.

NICS(0) calculation is a useful method to evaluate aromaticity and anti-aromaticity of a molecule from a calculated chemical shift of a dummy atom at the center of a molecule. Negative NICS(0) values indicate aromaticity, while positive indicate

anti-aromaticity. The NICS(0) values of **1**, **2**, and **3′** are shown in Figure 3. The NICS(0) values of the seven-membered ring in **1** and **2** were calculated to be nearby zero, suggesting their non-aromatic characters. The benzene rings in **1** and **2** retain their aromatic nature as indicated by the negative NICS(0) values. Notably, the NICS(0) values for both the seven- and six-membered rings in **3′** are relatively large, suggesting that **3′** has a global anti-aromatic character with a 16π-electron system.



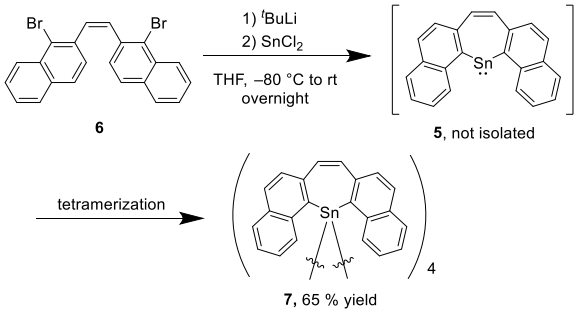
	NICS(0) values (a)	(b)
1 (R_1, R_2 = Ph)	0.07	–8.83
2 (R_1= Ph, R_2 = lone pair)	0.24	–7.09
3′ (R_1, R_2 = lone pair)	7.73	7.00

Figure 3. The NICS(0) values of **1**, **2**, and **3′**.

However, **3** could not be isolated due to its thermal instability and byproducts. To resolve these problems, π-extended derivative **5** with a Sn(II) center was designed. π-Extension would enhance the stability of the target dianionic species. More importantly, reduction of **5** generate no byproducts.

^{t}BuLi was added dropwise to a THF solution of dibromostilbene derivative **6** at −80 °C, then the mixture was treated with $SnCl_2$ to obtain tetramer **7** that arises from tetramerization of **5**.

Scheme 2



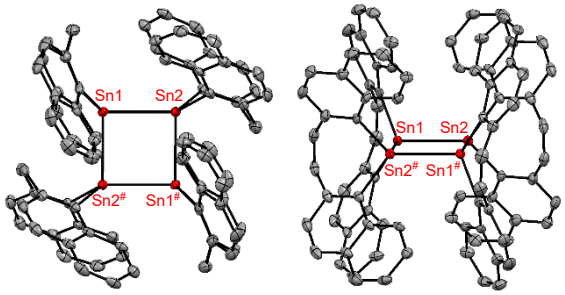
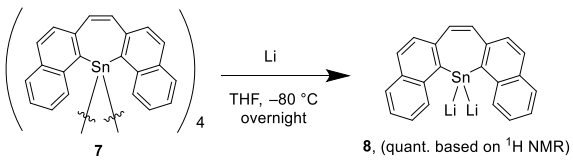


Figure 4. ORTEP drawings for **7**.

Treatment of **7** with excess lithium in THF at −80 °C afforded dilithium stannacycloheptatrienide **8** as a thermally stable black purple powder quantitatively based on the ^{1}H NMR spectrum. The drastic difference of stability between **3** and **8** is ascribed to the naphthalene units that induce kinetic and thermodynamic stabilization by steric protection around the tin atom and delocalization of anionic charges of the tin atom, respectively. The ^{1}H NMR signals of **8** were found in a characteristic high-field region ranging from 6.79 to 4.18 ppm. These high-field shifted signals of **8** can be attributable to its anti-aromatic nature arising from paramagnetic ring current. NICS(0) values of **8** were calculated to be 8.60 for the seven-membered ring, and 9.00, 12.5 for the six-membered rings. These results suggest that **8** has a global anti-aromatic character with a 24π-electron system. Importantly, this interpretation is also supported by the high-field shifts of ^{1}H NMR signals of **8**.

Scheme 3



4. Conclusion

Stannacycloheptatrienyl anion and dianions were synthesized. Monoanion **2** was concluded to be non-aromatic on the basis of the NMR and X-ray diffraction studies. Anti-aromaticity of dianion **8** was supported by the NMR and theoretical studies.

5. References

1) Lee, V. Y. and Sekiguchi, A. *Angew. Chem., Int. Ed*. **2007**, *46*, 6596–6620. 2) Matsuo, T. and Tamao, K. *et al. Science* **2011**, *331*, 1306–1309. 3) Matsuo, T. *et al. Chem. Commun.* **2018**, *54*, 2200–2203. 4) Iwamoto, T. *et al. Angew. Chem., Int. Ed*. **2017**, *56*, 13829–13832. 5) Saito M. *Acc. Chem. Res.* **2018**, *51*, 160–169.

6. Presentations

1) The 65th Symp. on Organomet. Chem. P2-10 (2018). 2) 99th CSJ Annual Meeting 3D1-33 (2019). 3) The 13th ICHAC, OC10A (2019) (20 min. English oral session). 4) ICOC-GTL-16, P61 (2019). 5) The 30th Symp. on Physical Organic Chemistry 2P125 (2019).