

カリックスおよびチアカリックス[4]アレーンテトリレン化合物の  
合成・構造および反応性  
Synthesis, Structures and Reactivities of Calix- and Thiacalix[4]arene  
Tetrylene Compounds

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### 1. Introduction

Divalent species of Si, Ge, Sn, and Pb, which are heavier analogs of carbene, are called tetrylenes and show interesting structures and reactivities which cannot be observed with carbenes. Although tetrylenes are highly reactive, they have been successfully isolated by the aid of kinetic stabilization by introducing bulky substituents and/or thermodynamic stabilization with Lewis bases or heteroatom substituents having a lone pair. Among the tetrylene derivatives, tetrylene dichalcogenolates are particularly difficult to be synthesized, because, unlike carbon and nitrogen substituents, each of the chalcogen substituents has only one bulky protecting group. Recently, Aldridge's and Power's groups reported the synthesis of tetrylene dichalcogenolates by using very bulky boroxo ( $R_2BO^-$ ) and aryloxo ( $ArO^-$ ) substituents.<sup>1</sup> However, reported examples of tetrylene dichalcogenolates are still limited in number, especially for the Pb analogs.<sup>1a</sup>

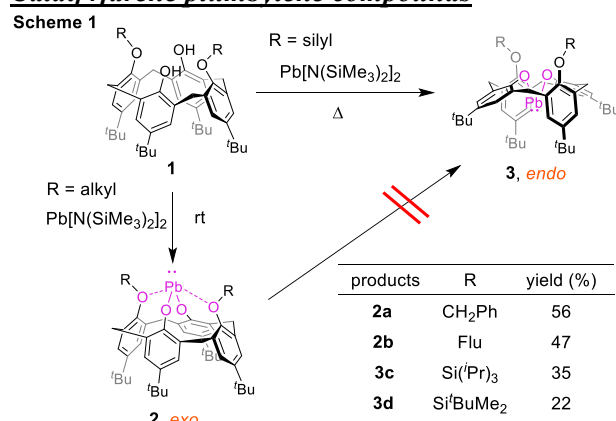
In this study, the author selected calix[4]arenes as a supporting ligand for tetrylenes, because their bulkiness can be fine-tuned by changing the protecting groups on the phenolic oxygen atoms. Although some calix[4]arene-germylenes and -stannylenes have been synthesized by Parkin *et al.*,<sup>3</sup> related plumblylenes still remains to be developed.

### 2. Experimental Section

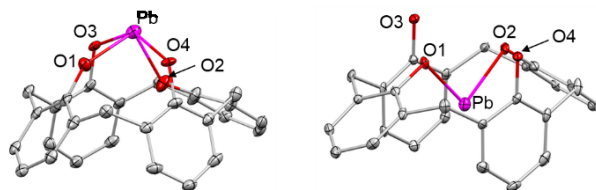
All manipulations were performed under an argon atmosphere by using standard Schlenk techniques or in a glovebox. New compounds were characterized by NMR, X-ray diffraction (XRD), and elemental analyses.

### 3. Results and Discussion

#### Calix[4]arene plumblylene compounds



Treatment of calix[4]arenes, in which two of the OH groups are protected by R groups (R = CH<sub>2</sub>Ph, 9-fluorenyl (Flu), Si<sup>i</sup>Pr<sub>3</sub>, Si<sup>i</sup>BuMe<sub>2</sub>), and Pb[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> at room temperature or under heating conditions resulted in the formation of **2** and **3**, where the Pb atoms are situated outside and inside the cavity of the calixarene, respectively (Scheme 1). Selectivity of these two isomers seems to be controlled by the bulkiness of the R groups; the *exo* isomers were formed with less bulky carbon substituents, while the *endo* isomers were selectively generated with bulky silyl substituents. The *exo* to *endo* isomerization of **2b** did



**Figure 1.** Molecular structures of **2b** (left) and **3d** (right). The R groups on the O3/4 atoms and <sup>t</sup>Bu substituents are omitted.

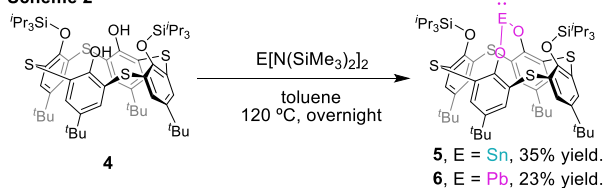
not proceed even by heating at 140 °C in C<sub>6</sub>H<sub>5</sub>Cl for 15 h, which is in sharp contrast to the fact that the related Ge analogs with the *exo* form are easily transformed into the corresponding *endo* isomers by heating.<sup>2</sup>

The XRD study revealed that **2** and **3** have cone type structures similar to those of the corresponding Sn analogs.<sup>2</sup> The distances between the Pb and O3/4 atoms are *ca.* 2.9 Å in **2**, while those between the Pb and the carbon atoms of the benzene rings are *ca.* 3.0 Å in **3**. These results suggest that the empty *p* orbital of the Pb atom in **2** and **3** is weakly coordinated by the lone pairs of the O3/4 atoms and the  $\pi$ -electrons of the benzene rings, respectively.

The <sup>207</sup>Pb NMR signals for the *exo* and *endo* isomers are observed at *ca.*  $\delta$  110 and 570 ppm, respectively. These signals are in a lower-field region than those of Power's diaryloxyplumbylene ( $\delta$  1070.3)<sup>1b</sup>, suggesting that the Pb atoms in **2** and **3** are also coordinated by the OR and aryl groups, respectively, in solution.

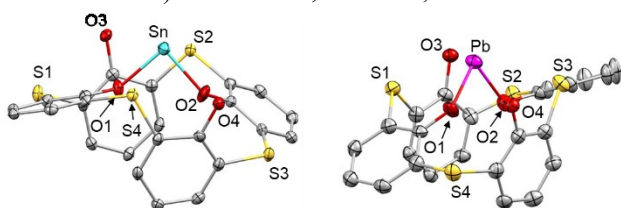
### Thiacalix[4]arene tetrylene compounds

Scheme 2



Thiacalix[4]arene **4** was next selected as the ligand for tetrylenes, because the larger ring size of **4** was expected to prevent the coordination of the O3/4 atoms and the benzene rings. Treatment of **4** with E[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> (E = Sn, Pb) at 120 °C resulted in the formation of diaryloxystannylene **5** and -plumbylene **6** as colorless and yellow crystals, respectively (Scheme 2).

The XRD analysis revealed that **5** and **6** have distorted and partial cone structures, respectively. The distances between the Sn and O3/4 atoms in **5** are 3.25/3.54 Å, while those between the Pb and O3/4 atoms in **6** are 3.60/2.94 Å. These distances are shorter than the sums of van der Waals radii (Sn–O: 3.69 Å, Pb–O: 3.54 Å). In solution, however, **6** was shown to



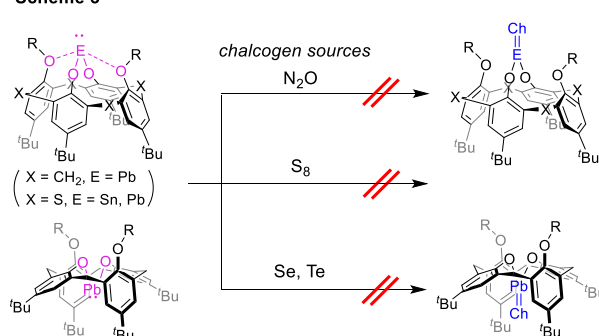
**Figure 2.** Molecular structures of **5** (left) and **6** (right). The Si<sup>*i*</sup>Pr<sub>3</sub> and <sup>*t*</sup>Bu substituents are omitted.

adopt a C<sub>2</sub>-symmetric type structure on the basis of the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra.

The <sup>119</sup>Sn{<sup>1</sup>H} and <sup>207</sup>Pb NMR signals for **5** and **6** are observed at  $\delta$  –358.6 and 1210.4, respectively. These signals are in a low-field region compared to those of the corresponding calix[4]arene tetrylenes (Sn:  $\delta$  –665.6, Pb:  $\delta$  124.2), and in a similar region to those of the Lewis base-free diaryloxy stannylene<sup>3</sup> and plumbylene.<sup>1b</sup> Therefore the interaction between the Sn/Pb and O3/4 atoms in **5** and **6** is considered to be much weaker than in **2**.

### Reactivity of tetrylenes

Scheme 3



Heavier analogs of ketones were expected to be obtained from the reactions of **2**, **3**, **5** or **6** with various chalcogen sources. Unfortunately, however, all attempts have been unsuccessful so far even under heating conditions (Scheme 3). The low reactivity of these tetrylenes could be ascribed to the electron donation from the adjacent O1/2 atoms and the coordination of the O3/4, S atoms and Ar groups toward the vacant *p* orbital of the Sn and Pb atoms in spite of the above-mentioned NMR features of **5** and **6**.

### 4. Conclusion

*exo/endo*-Calix[4]arene–plumbylenes **2**, **3**, and thiacalix[4]arene–stannylene **5**, –plumbylene **6** have been synthesized and characterized by NMR and XRD.

### 5. References

- (1) (a) Aldridge, S. *et al. Angew. Chem., Int. Ed.* **2019**, *58*, 4847–4851. (b) Power, P. P. *et al. Inorg. Chem.* **2013**, *52*, 3054–3062. (2) Parkin, G. *et al. Tetrahedron* **2007**, *63*, 10826–10833. (3) Boyle, J. T. *et al. Dalton. Trans.* **2012**, *41*, 9349–9364.

### 6. Presentation List

- (1) 99<sup>th</sup> CSJ Annual Meeting IPA-145 (2019). (2) 46<sup>th</sup> Symp. Main Group Element Chem. P-28 (2019). (3) 13<sup>th</sup> Int. Conf. Heteroatom Chem. PP-50 (2019).