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Editor's Choice

Synthesis, Structure, and Reaction of Tetraethyldilithiostannole

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Reduction of tetraethyldiphenylstannole **3** with lithium afforded tetraethyldilithiostannole **2**, and its considerable aromatic character was evaluated by X-ray diffraction analysis and theoretical calculations. Reaction of **2** with *t*-butyl chloride provided 1,1′-dilithiobistannole **4**. This reaction mode is different from that of dilithiotetraphenylstannole **1** and is of considerable interest.

For a decade, dialkaline-metallated siloles and germoles have received considerable attention as novel carbocyclic aromatic compounds with a heavier group 14 element.[1] The aromatic delocalizations in these derivatives were evidenced by NMR studies, theoretical calculations, and X-ray structural analyses that showed no alternation of the C–C bonds within the planar ring.[2–4] The substituents (alkyl or aryl groups) of the carbon atoms in the aromatic five-membered rings have little effect on degree of aromaticity of these dialkaline-metallated metalloles as well as their reactivities.[2,3] In the course of our studies on the synthesis of tin-containing aromatic compounds, we have already reported the synthesis and structure of dilithiotetraphenylstannole **1** (Chart 1).[5] Based on its molecular structure and theoretical calculations, compound **1** is concluded to be the first tin-containing carbocyclic aromatic compound.[5b,6] Reactions of **1** with alkyl, aryl, or metallyl halides gave the corresponding lithiotetraphenylstannoles.[7] In contrast, there have been no reports on the structure and reactivity of a dilithiostannole with alkyl substituents on the carbon atoms of the five-membered ring. We report herein the synthesis and structure of tetraethyldilithiostannole **2** and its unique reactivity, which is different from that of **1**.

The tetraethyldilithiostannole **2** was obtained by the reduction of 1,1-diphenylstannole **3**[8] with lithium through reductive cleavage of the Sn–Ph bonds, as in the synthesis of the dilithiotetraphenylstannole **1** (Scheme 1).[5b,9] Reduction of 1,1-diphenylstannole **3** with lithium proceeded cleanly to afford phenyllithium and a new compound which had a stannole skeleton, as evidenced by NMR spectroscopy. After heating the reaction mixture at 80 °C for 22 h, phenyllithium completely decomposed and **2** was obtained as black-yellow crystals in 57% yield.

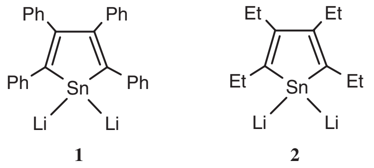
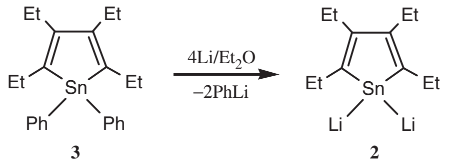


Chart 1. Dilithiostannoles, **1** and **2**.



Scheme 1. Synthesis of tetraethyldilithiostannole **2**.

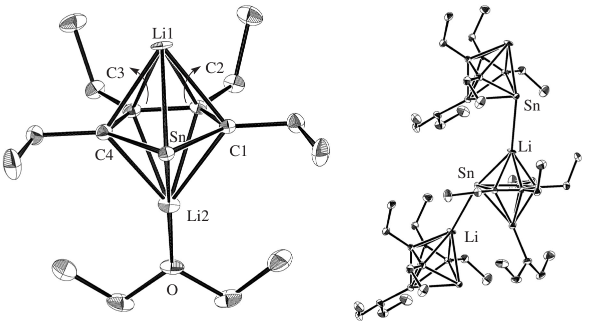
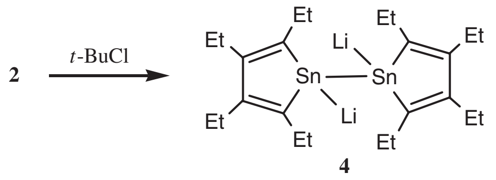


Figure 1. ORTEP drawings of tetraethyldilithiostannole **2** with thermal ellipsoids plots drawn at 40% probability for non-hydrogen atoms. Selected bond lengths (Å): Sn–Li1, 2.657(5); Sn–Li2, 2.741(6).

The molecular structure of **2** was established by X-ray diffraction analysis. The ORTEP drawing of **2** is shown in Figure 1.[9] One lithium atom is coordinated by an ether molecule and the stannole ring in an η^5-fashion, whereas the other lithium atom is coordinated by the stannole ring in an η^5-fashion and a tin atom of another dilithiostannole molecule in an η^1-fashion with the intermolecular distance between the tin and the lithium atoms of 2.748(5) Å, making a polymeric chain in the solid state (Figure 1), whereas such interactions were not found in **1**.[5b] The stannole ring is planar with the sum of the internal angles of 539.9°. The C–C bonds of the starting **3** differ (1.346(4), 1.510(4), and 1.344(4) Å), indicating 1,3-diene character.[9] In contrast, the C–C distances within the ring are almost equal (1.404(4), 1.455(4), and 1.404(5) Å), as was observed in the aromatic dilithiotetraphenylstannole **1**, suggesting that the tetraethyldilithiostannole **2** has also considerable aromatic character.

In the ^{7}Li NMR of **2** in THF–C_6D_6 at room temperature, only one sharp signal was observed at −5.2 ppm, in the region similar to that of **1** (−4.4 ppm),[5b] suggesting that **2** has considerable aromatic character and exists as a monomer with two solvated lithium atoms on the stannole ring in solution.

To aid in understanding the structure of **2**, theoretical calculations were performed.[10] The optimized structure of unsolvated **2** is also planar and the calculated C–C distances



Scheme 2. Formation of 1,1′-dilithiobistannole **4** from **2**.

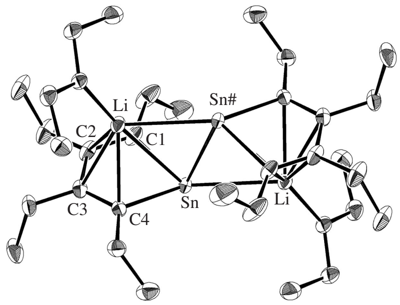


Figure 2. ORTEP drawings of 1,1′-dilithiobistannole **4** with thermal ellipsoids plots drawn at 40% probability for non-hydrogen atoms. Selected bond lengths (Å): Sn–Li, 2.879(4); Sn#–Li, 2.907(4); C1–C2, 1.367(4); C2–C3, 1.486(4); C3–C4, 1.370(3).

within the ring of **2** are nearly equal (1.435 and 1.469 Å), which is consistent with the X-ray measured values. The considerably negative NICS(1)[11] values of a free stannole dianion were calculated to be −6.89 and −7.24 ppm, suggesting that the dilithiostannole **2** is also aromatic, as are other group 14 dilithiometalloles.[1c,5]

Next, reactivity of **2** was investigated. Reaction of **1** with *t*-butyl chloride gave the corresponding lithiostannole with a *t*-butyl group on the tin atom.[7a] Reaction of **2** with *t*-butyl chloride provided the sole product having a stannole skeleton, as evidenced by NMR spectroscopy (Scheme 2).[9] Recrystallization of the reaction product afforded 1,1′-dilithiobistannole **4**, instead of the corresponding *t*-butyl-substituted lithiostannole, in 93% yield, the structure of which was determined by X-ray diffraction analysis (Figure 2). The electron transfer from **2** to *t*-butyl chloride would occur to provide anion radical **5**, which would react not with the resulting *t*-butyl radical but with another anion radical **5**, leading to the formation of **4** (Scheme S1, see Supporting Information). Alternatively, halophilic reaction of **2** toward *t*-butyl chloride would occur to give chlorolithiostannole **6**, which would react with **2** to afford **4**.

The X-ray diffraction analysis of **4** revealed that the two stannole rings are oriented in an anti fashion through the tin–tin bond (Figure 2).[9] Each lithium atom is coordinated by an ether molecule and the stannole rings in η^6-fashions. The Sn–Sn distance is 2.9652(3) Å, which is slightly longer than those of 1,2-dilithiotetraphenyldistannane (2.905(3) Å)[12] and dilithium salt of bistannole 1,1′-dianion **7** (2.9059(5) Å) (Chart 2).[13] In contrast to **7** having the planar stannole rings, the stannole rings of **4** slightly deviate from planarity and angle between the C1–C2–C3–C4 and C1–Sn–C4 planes is 14°. As found for **7**, there is remarkable alternation of the C–C bonds in the stannole rings, suggesting that the stannole rings of **4** have considerable 1,3-diene character.

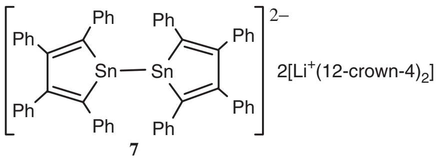


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Chart 2. 1,1′-Dilithiooctaphenylbistannole **7**.

In summary, tetraethyldilithiostannole **2** has also considerable aromatic character, as observed in dilithiotetraphenylstannole **1**. However, the reactivity of **2** toward *t*-butyl chloride is different from that of **1**. This difference probably arises from different steric enviroment around the tin atoms.[14]

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14 According to the natural population analysis of unsolvated **2**, the tin atom is positively charged (+0.25), whereas the α- and β-carbons are negatively charged (−0.74 and −0.29, respectively).[5b] These trends are essencially the same as those in **1**, and hence the electronic effect seems less important for the different reactivity.