Synthesis of Stannole Anion by Alkylation of Stannole Dianion

Masaichi Saito,* Ryuta Haga, and Michikazu Yoshioka
Department of Chemistry, Faculty of Science, Saitama University, Shimo-okubo, Sakura-ku, Saitama 338-8570

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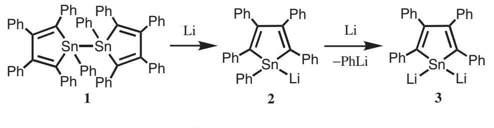
Reaction of *tert*-butylchloride with the stannole dianion first and simply prepared by the reduction of 1,1,2,3,4,5-hexaphenylstannole with lithium in ether gave 1-*tert*-butylstannole anion which was characterized by ^{1}H, ^{13}C, ^{119}Sn, and ^{7}Li NMR spectra and whose reactivities were investigated.

Recently, much attention has been focused on the anions and dianions of siloles[1] and germoles,[1f,2] heavier congeners of the cyclopentadienyl anion.[3] The structural and chemical properties of these species are of interest because these species having a novel π-electron system may possess some degree of aromaticity as predicted by theoretical calculations.[4] The degree of aromaticity of silolyl anions depends on the substituent on the silicon,[1b,1f] while the germolyl anions do not show aromaticity because the negative charge localizes on the germanium.[1f,2a,2c] On the contrary, the negative charges in the dianions of siloles and germoles significantly delocalize in the C_4M ($M = Si, Ge$) ring.[1d–f,2b,d,e] In contrast to the well-investigated mono- and dianions of siloles and germoles, neither mono- nor dianions of stannole had been reported before our project to investigate stannole mono- and dianions started. In the course of our studies on tin-containing compounds with a unique structure,[5] we have already reported the first formation of stable stannole mono- and dianions by the reduction of the novel bi(1,1-stannole) **1** (Scheme 1).[6] The intermediary stannole anion **2** which was observed by ^{119}Sn NMR spectrum and chemically trapped by methyl iodide was easily reduced to the corresponding dianion **3** in the reaction conditions with the formation of phenyllithium. Reductive elimination of a phenyl group of **2** to form **3** prompted us to investigate the method for the preparation of the stannole dianion **3** by the reduction of simple stannoles having a phenyl group on tin and the formation of a stannole anion by alkylation of **3**. We report herein the alkylation of stannole dianion **3** to afford a novel stannole anion which was characterized by ^{1}H, ^{13}C, ^{119}Sn, and ^{7}Li NMR spectra. A simple method for the synthesis of stannole dianion **3** from 1,1,2,3,4,5-hexaphenylstannole **4**[7] is also reported.



Scheme 1.

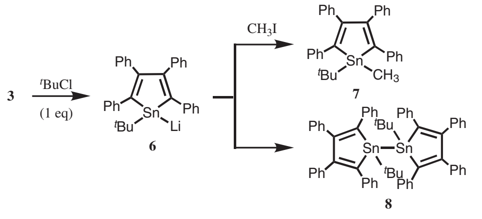
Reaction of **4** with lithium (excess) in ether at room temperature gave a deep red solution suggesting the formation of anionic species. By treatment of the reaction mixture with methyl iodide, 1,1-dimethylstannole **5** was obtained in 61% yield as a sole product suggesting the formation of stannole dianion **3** directly from **4** through reduction (Scheme 2).

Monitoring the reaction of **4** with lithium by NMR in ether–C_6D_6 showed only the signals assignable to **3**[8] and phenyllithium.[9,10] However, the signal assignable to the stannole anion **2**, a possible intermediate to **3**, was not observed. Although all the signals of ^{1}H and ^{13}C NMR spectra of **3** in ether–C_6D_6 do not appear in the same field as those in THF–C_6D_6 reported previously,[6] probably due to solvent dependency, a characteristic low-fielded signal (187.6 ppm) in ^{13}C NMR with a large tin–carbon coupling constant of about 380 Hz is assignable to the α-carbon of **3**. The ^{119}Sn NMR signal appeared as a broad signal at 131.3 ppm in ether–C_6D_6, upfield-shifted compared to that (186.7 ppm) in THF–C_6D_6,[6] although the reason for the upfield-shift in ether is still unclear. In the ^{7}Li NMR, a single resonance was observed at -1.3 ppm, suggesting the rapid intermolecular exchange of lithium cations between **3** and phenyllithium (1.4 ppm in THF–C_6D_6).

Scheme 2.

To synthesize a stannole anion from the dianion **3**, the alkylation of **3** was studied. Since the reaction of **3** with methyl iodide gave dimethylated compound **5**, *tert*-butyl chloride was chosen as a bulkier alkylating reagent than methyl iodide. When *tert*-butyl chloride was added to an ether solution of **3** at room temperature, the color of the solution turned from deep red to bright red. By the treatment of the reaction mixture with methyl iodide, 1-*tert*-butyl-1-methylstannole **7**[11] was obtained in 55% yield suggesting the formation of stannole anion **6** by alkylation of **3** (Scheme 3). The formation of **6** from **3** was reasonably explained in terms of electron transfer mechanism, as observed in the reaction of a tributylstannyl anion with *tert*-butyl halides.[12] The reaction of **3** with of *tert*-butyl chloride followed by exposure of the reaction mixture to the air without treatment of methyl iodide gave bi(1,1-stannole) **8**[13] in 27% yield. Since a silyl anion is known to oxidize by NO^{+} to a silyl radical,[14] the formation of **8** is reasonably interpreted in terms of dimerization of 1-*tert*-butylstannole radical resulting from air oxidation of **6**.

Monitoring the reaction of **3** with *tert*-butyl chloride by



Scheme 3.

NMR was also carried out. In ^{119}Sn NMR there appeared only one signal for stannole anion **6**[15] at 30.4 ppm with the complete disappearance of the signal for **3**. In ^{13}C NMR a characteristic low-fielded signal (170.66 ppm) with a large tin–carbon coupling constant of about 113 Hz assignable to the α-carbon in **6** was observed. In ^{7}Li NMR a single resonance was observed at 0.92 ppm, suggesting the the rapid intermolecular exchange of lithium cations between **6** and lithium chloride.

In summary, stannole dianion **3** was synthesized by reduction of 1,1,2,3,4,5-hexaphenylstannole **4** with lithium. This is a convenient method for the synthesis of stannole dianion **3** because **4**[7] is easily prepared. Reaction of **3** with *tert*-butyl chloride gave stannole anion **6**, a tin-analogue of cyclopetadienyl anion. The anion **6** was characterized by ^{1}H, ^{13}C, ^{119}Sn, and ^{7}Li NMR spectra. Further investigation on aromaticity of **6** is currently in progress.

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8 **3**: ^{1}H NMR (400 MHz, ether–C_6D_6) δ 6.56–6.58 (m, 4H), 6.73–6.74 (m, 6H), 6.80–6.83 (m, 4H), 6.96–6.98 (m, 6H); ^{13}C NMR (101 MHz, ether–C_6D_6) δ 121.83 (d), 124.01 (d), 126.98 (d), 127.13 (d), 128.53 (d), 132.73 (d), 134.27 (s), 144.12 (s), 150.79 (s), 187.66 (s, $J_{\text{Sn-C}} = 366$, 388 Hz); ^{119}Sn NMR (149 MHz, ether–C_6D_6) δ 131.3; ^{7}Li NMR(156 MHz, ether–C_6D_6) δ -1.3.

9 The ^{1}J(Sn–C) in α-carbon of **4** was reported to be 213 and 223 Hz in Ref. 7b.

10 Although monitoring the reaction of **4** with lithium by NMR in THF–C_6D_6 also showed the signals assignable to **3** and phenyllithium, the reaction did not proceed cleanly.

11 **7**: mp 75–80 °C (decomp)(methylene chloride+methanol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.60 (s, 3H), 1.22 (s, 9H), 6.77–6.79 (m, 4H), 6.83–6.85 (m, 4H), 6.93–6.98 (m, 8H), 7.04–7.08 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ -10.57(q), 29.90(s), 30.68(q), 124.86(d), 125.58(d), 127.18(d), 127.74(d), 129.09(d), 130.44(d), 141.01(s), 143.62(s), 145.41(s), 154.47(s). Anal. Calcd for $C_{33}H_{32}Sn$: C, 72.42; H, 5.89. Found: C, 72.43; H, 5.51. The ^{1}J(Sn–C) in α-carbon could not be estimated because of broading.

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13 **8**: mp 270–300 °C (decomp)(recrystallized from methylene chloride). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (s, 18H), 6.80–6.84 (m, 8H), 6.87–7.04 (m, 32H); ^{13}C NMR(101 MHz, $CDCl_3$) δ 31.64(q), 35.21(s), 124.90(d), 125.64(d), 127.20(d), 127.74(d), 129.56(d), 130.65(d), 140.90(s), 143.51(s), 148.46(s), 154.23(s). Anal. Calcd for $C_{64}H_{58}Sn_2$: C, 72.21; H, 5.49. Found: C, 71.54; H, 5.37. The ^{1}J(Sn–C) in α-carbon could not be estimated because of low solubility.

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15 **6**: ^{1}H NMR (400 MHz, ether–C_6D_6) δ 1.25 (s, 9H), 6.61–6.78 (m, 12H), 6.80–6.83 (m, 4H), 6.88–6.90 (m, 4H); ^{13}C NMR (101 MHz, ether–C_6D_6) δ 28.64(s), 33.71(q), 122.22(d), 124.04(d), 126.80(d), 127.07(d), 129.35(d), 131.59(d), 145.05(s), 150.35(s), 151.78(s), 170.66 (s, $J_{\text{Sn-C}} = 113$ Hz); ^{119}Sn NMR (149 MHz, ether–C_6D_6) δ 30.4; ^{7}Li NMR (156 MHz, ether–C_6D_6) δ 0.92.