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Formation of the first monoanion and dianion of stannole†

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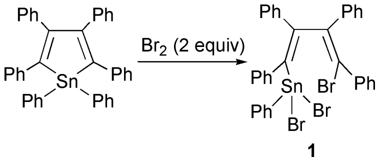
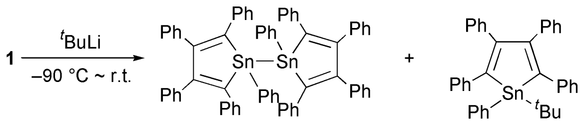
The first syntheses of mono- and dianions of stannole were accomplished by transmetallation or reduction of the novel bi(1,1-stannole).

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,f] while the germolyl anions do not show aromaticity because the negative charge localizes on the germanium.[1f,2a,c] By contrast, 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] With regard to polymer chemistry, the silole dianions were reported to be useful precursors for the synthesis of poly(1,1-silole)s having unique electronic characteristics.[5] In contrast to the well-investigated mono- and dianions of siloles and germoles, neither mono- nor dianions of stannole has been reported. We have already reported that reaction of 1,1,2,3,4,5-hexaphenylstannole with bromine gave **1** through the cleavage of a Sn–C(vinyl) bond followed by the elimination of a phenyl group (Scheme 1).[6] We report herein the first formation of stable mono- and dianions of stannole in solution at room temperature from the bi(1,1-stannole) obtained by debrominative dimerization of **1**.[7]



Scheme 1

First, we examined the synthesis of a stannole skeleton by the debrominative cyclization of **1**. Treatment of **1** with 2 equiv of *tert*-butyllithium in THF at −90 °C gave a yellow solution. After usual workup, the mixture was chromatographed to gave bi(1,1-stannole) (58%) as yellow crystals together with stannole **3** (7%) (Scheme 2). Compound **2** was proved to have a symmetrical structure by its ^{13}C NMR, and its structure was finally established by X-ray structural analysis (Fig. 1).‡ Because of the symmetric structure of **2** with respect to the Sn–Sn bond, a half moiety was refined. The length of Sn–Sn bond is normal,[8] 2.7844(7) Å. The stannole ring has nearly a planar structure. The formation of **2** is noteworthy from the standpoint of being the first example of a bi(1,1-stannole).



Scheme 2

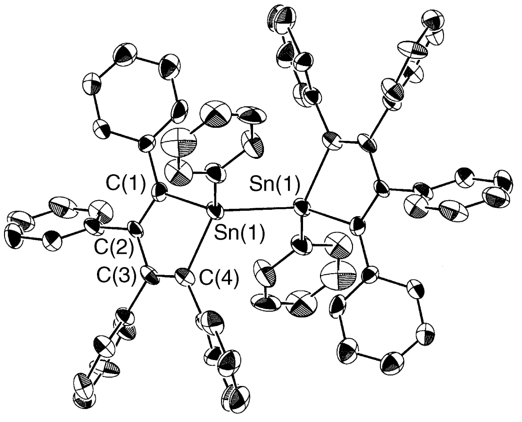
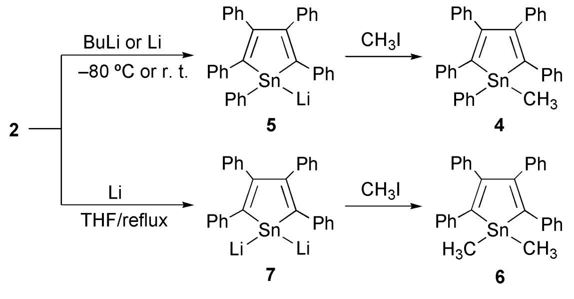


Fig. 1 ORTEP drawing of **2** with thermal ellipsoids plots (40% probability for non-hydrogen atoms). Selected bond lengths (Å) and angles (°): Sn(1)–Sn(1) 2.7844(7), Sn(1)–C(1) 2.152(7), C(1)–C(2) 1.34(1), C(2)–C(3) 1.50(1), C(3)–C(4) 1.38(1), C(4)–Sn(1) 2.146(8); C(1)–Sn(1)–C(4), 83.3(3).

Since bi(1,1-metallole)s are known to be good precursors for metalloyl anions,[1a,e,f] the formation of a stannole monoanion from **2** was examined. Reaction of **2** with butyllithium gave a red solution, suggesting the formation of a stannole monoanion. This color remained unchanged at room temperature, but immediately changed to yellow upon the addition of methyl iodide to the solution at room temperature. After usual workup, the residual mixture was chromatographed to afford 1-methyl-1-phenylstannole **4** in 42% yield (Scheme 3). The formation of **4** could be reasonably interpreted in terms of the methylation of the initially formed stannole monoanion **5**. To the best of our knowledge, the formation of **4** provides the first evidence for the formation of a stannole monoanion. Since stannole derivatives are relatively unstable on silica gel or alumina, compound **4** is likely to be isolated by chromatography in lower yield than the true yield. Compound **2** was treated with *tert*-butyllithium instead of butyllithium at low temperature and then methyl iodide was added to the reaction mixture. The ^1H NMR analysis of the reaction mixture using *p*-dimethoxybenzene as an internal standard revealed the true yields of **3** and **4** to be 76 and 86%,



Scheme 3

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† Electronic supplementary information (ESI) available: experimental details. See http://www.rsc.org/suppdata/cc/b2/b200238h/

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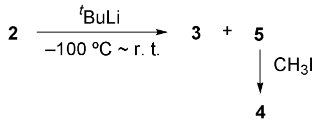
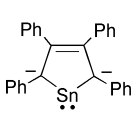
respectively, indicating quite high efficiency for the generation of **5** (Scheme 4).



Scheme 4

Reductive formation of **5** from **2** was also investigated. Treatment of **2** with an excess of lithium in THF at room temperature gave a dark red solution. Upon the addition of methyl iodide to this solution, the color of the reaction mixture immediately changed to yellow. After chromatography, compound **4** was obtained in 58% yield together with 1,1-dimethylstannole **6**[9] (6%). Thus, the reduction of **2** by lithium revealed evidence not only for the formation of the stannole monoanion **5** but also for the formation of the stannole dianion **7**. The formation of **6** prompted us to investigate exhaustive reduction of **2**. When a THF solution of **2** in the presence of excess lithium was refluxed and then the reaction mixture was treated with methyl iodide at room temperature, 1,1-dimethylstannole **6** was formed as a main product. Recrystallization of the crude mixture from hexane gave **6** in 23% yield (Scheme 3). The formation of **6** could be interpreted in terms of the methylation of the intermediary stannole dianion **7** resulting from the further reduction of **5**. The silole monoanion is known to be reduced to the silole dianion by lithium *via* the tetraanion.[10] To the best of our knowledge, the formation of **6** is the first evidence for the formation of a stannole dianion.

The reaction of **2** with lithium was monitored by ^{119}Sn NMR. Compound **2** (50 mg, 0.045 mmol) and lithium (20 mg, 2.88 mmol) in THF were placed in an NMR tube with C_6D_6 (as NMR lock). The color of the solution changed to dark red. The ^{119}Sn NMR signal attributable to stannole monoanion **5** (−30.3 ppm) appeared at lower field than that for **2** (−99.3 ppm in $CDCl_3$). The possible interpretation for the downfield shift of **5** compared to **2** and $Ph_3Sn^-Li^+$ (−106.7 ppm in THF) [11] in the ^{119}Sn NMR may be a partial delocalization of the negative charge into the ring as was observed in the silolyl anion.[1b] After standing the tube overnight at room temperature, an additional new small signal appeared downfield which grew gradually with concommitant disappearance of the signal for **5**. After 2 days, only the new signal assignable to stannole dianion **7** was observed at 186.7 ppm. The remarkable downfield shift of the ^{119}Sn signal for **7** is reasonably interpreted in terms of strong participation of a resonance form with stannylene character **8**, as was observed in the silole dianion showing silylene character.[1e] The central tin of the isolobal diaminostannylene **9** is known to resonate at 269 ppm.[12] The ^{13}C NMR spectrum of **7** was also measured. Compound **2** and lithium in THF–C_6D_6 was ultrasonicated to directly afford a deep red solution of **7**. In ^{13}C NMR, the signal assignable to the α-carbon in the five-membered ring was observed at 184.58 ppm judging from a large ^nJ(Sn–^{13}C) of about 320 Hz, though ^nJ(^{119}Sn–^{13}C) and ^nJ(^{117}Sn–^{13}C) could not be unfortunately estimated because of broadening. The strong downfield resonance of the α-carbon in the silole dianion was also predicted by calculation.[4b] The ^{7}Li NMR spectrum of the reaction mixture was also measured, but the assignment of signals could not be achieved because of broadening and complexity.



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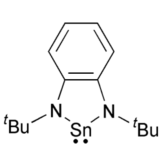

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In summary, the first stannole mono- and dianions stable in solution were successfully synthesized from the bi(1,1-stannole). These anions reacted with methyl iodide to afford the corresponding methylated stannoles. ^{119}Sn NMR studies suggest a partial delocalization of negative charge in the mono-anion and strong participation of a resonance form with stannylene character in the dianion. Further investigation on their structural analysis and application to novel tin-containing polymers are currently in progress.

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Notes and references

‡ *Crystallographic data* for **2**: $C_{34}H_{25}Sn$, M = 552.264, 0.1 × 0.1 × 0.1 mm, monoclinic, space group $P2_1/c$, a = 10.8790(5), b = 9.7350(5), c = 26.2920(13) Å, β = 109.642(2)°, V = 2622.5(2) Å^3, T = 298 K, D_c = 1.3995 g cm^{-3}, Z = 4, Mo-Kα radiation (λ = 0.71073 Å), Weisenberg scans. The non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were placed at calculated positions (d(C–H) = 0.93 Å). The final cycle of full-matrix least-squares refinement was based on 3413 observed reflections [$I > 2.00\sigma(I)$] and 316 variable parameters with R (R_w) = 0.056 (0.111). CCDC reference number 170708. See http://www.rsc.org/suppdata/cc/b2/b200238h/ for crystallographic data in CIF or other electronic format.

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