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Reversible Redox Behavior between Stannole Dianion and Bistannole-1,2-Dianion

Ryuta Haga, Masaichi Saito,* and Michikazu Yoshioka

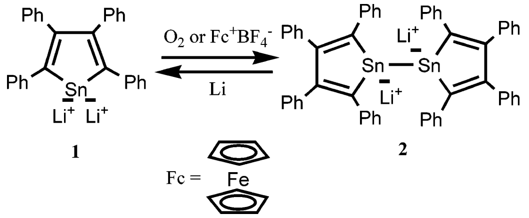
Department of Chemistry, Faculty of Science, Saitama University,
Shimo-okubo, Sakura-ku, Saitama-city, Saitama 338-8570 Japan

Received October 24, 2005; E-mail: masaichi@chem.saitama-u.ac.jp

There has been considerable recent interest in the dianions of group 14 metalloles as heavier congeners of the cyclopentadienyl anion which plays an important role in organic chemistry.[1] The negative charges in the dianions of siloles and germoles significantly delocalize in the C_4M (M=Si, Ge) ring and they were concluded to be aromatic.[2,3] Very recently, we have reported the synthesis of the first stannole dianion, which was concluded to be aromatic by the aid of NMR analysis, X-ray structural analysis and theoretical calculations.[4] Although the dianions of group 14 metalloles have been well investigated from the viewpoint of their aromaticity, there are only a few reports on the reactions of these novel aromatic compounds besides those with simple electrophiles.[5] Contrary to the dianions of group 14 metalloles, the anions of group 14 metalloles were applied in the synthesis of η^5-metallacyclopentadienyl transition metal complexes,[6] some of which showed catalytic activities. Reports on the structures of the anions of group 14 metalloles, however, are still limited.[7] Oxidative coupling of a metal anionic species is one possible method for the formation of a metal−metal bond. We have already reported the oxidation of the stannole anion to lead to the formation of a tin−tin bond, which is a novel useful method for the synthesis of bi(1,1-stannole)s.[8] Although oxidation of 1,1-dianions of group 14 metals is of considerable interest as a novel straightforward method for the synthesis of the corresponding 1,2-dianions having a metal−metal bond,[2d,9−13] redox behavior between two dianions has never been demonstrated.[14] We report herein the redox behavior between stannole dianion and bistannole-1,2-dianion (Scheme 1). The structure and aromaticity of the novel bistannole-1,2-dianion are also discussed.

The stannole dianion **1** is extremely sensitive toward air. Treatment of **1** with excess amounts of oxygen gave a complex mixture. To find the most suitable quantity of oxygen, the reaction of **1** with oxygen was monitored by NMR spectroscopy. By the treatment of **1** with 0.5 equiv of oxygen in THF at room temperature, the color of the solution turned from bright red to dark violet. The ^{119}Sn NMR spectrum of the resulting reaction mixture showed two signals at 195 and −81 ppm, assignable to the remaining **1** and **2**, respectively. The ^{1}H NMR spectra change in the reaction of **1** with oxygen is shown in Figure 1. Addition of an equivalent of oxygen to the solution of **1** gave **2** exclusively, judging from the ^{1}H NMR spectrum of the resulting solution, the color of which was deep blue (Figure 1). The ^{119}Sn NMR spectrum revealed only one signal at −81 ppm due to **2** with a coupling constant of 3962 Hz, resulting from an Sn−Sn bond. The signal of **2** appeared in upper field than that of **1**, but similar to that of $Ph_3Sn^-Li^+$ (−105.3 ppm in THF).[13b] The ^{7}Li signals of **2** were observed at about 0 ppm, suggesting that the Li cations should be in an environment similar to that in common organolithium compounds.[15] These NMR data suggest that the negative charge of **2** should localize on the tin atom, and hence compound **2** should be nonaromatic. The bistannole-1,2-dianion **2** was isolated as deep-black powder in 94% yield.[16] These results revealed clean generation of **2** by the oxidation of **1**. The oxidation of **1** with an equimolar amount of ferrocenium tetrafluoroborate in THF also gave 1,2-dianion **2** nearly quantitatively, as estimated by NMR spectra.[17]

Scheme 1



The dark-black crystals of $2[Li^+(12\text{-crown-}4)]_2$ suitable for X-ray analysis were obtained by recrystallization from THF/benzene in the presence of 12-crown-4 at −33 °C.[18] The ORTEP drawing and the selected bond lengths and angles of $2[Li^+(12\text{-crown-}4)]_2$ are shown in Figures 2 and 3, respectively. The dilithium salt of **2** has well-separated ion pairs with the distance of Sn−Li of 5.90 Å, suggesting no interaction between the tin and the lithium atoms. The stannole rings in $2[Li^+(12\text{-crown-}4)]_2$ are arranged in gauche conformation and are nearly planar. Contrary to the stannole dianion **1**,[4b] bond alternation in the C−C bond is observed in the five-membered ring (the bond distances of C(1)−C(2), C(2)−C(3), and C(3)−C(4) are 1.361(4), 1.473(4), and 1.378(4) Å, respectively), indicating that the 1,2-dianion **2**, the first X-ray-characterized tin analogue of the cyclopentadienyl anion, has considerable diene character (Figure 3), as do other anions of group 14 metalloles.[7] The pyramidalization at the tin center is clearly evidenced by the angle between the C_4Sn plane and the Sn−Sn bond of 110 °. The Sn−Sn distance of 2.9059(5) Å is longer than that of 1,1′-diphenylbistannole (2.785(2) Å)[4a] but is similar to that of 1,2-dilithiotetraphenyldistannane (2.905(3) Å).[13a]

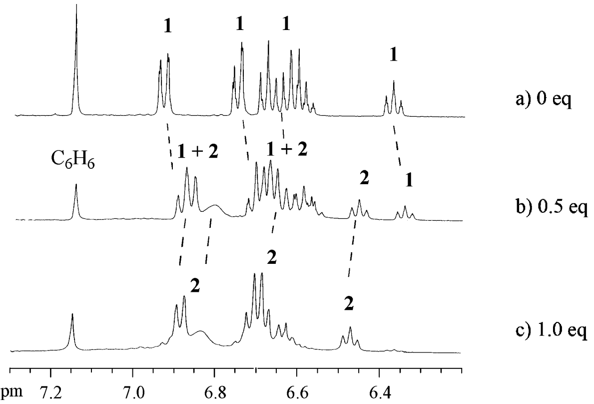


Figure 1. ^{1}H NMR spectral change by the reaction of **1** with oxygen; (a) stannole dianion **1** without oxygen; (b) 1:1 mixture of **1** and **2** resulting from the reaction of **1** with 0.5 equiv of oxygen; (c) 1,2-dianion **2** resulting from the reaction of **1** with 1 equiv of oxygen.

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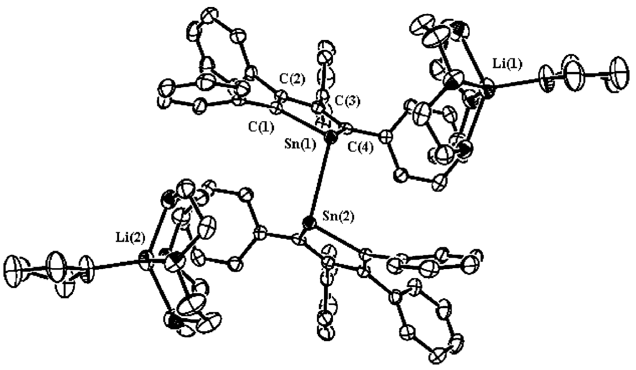

Figure 2. ORTEP drawing of **2**[Li$^+$(12-crown-4)]$_2$ with thermal ellipsoid plots (40% probability for non-hydrogen atoms). All hydrogens and a benzene molecule were omitted for clarity.

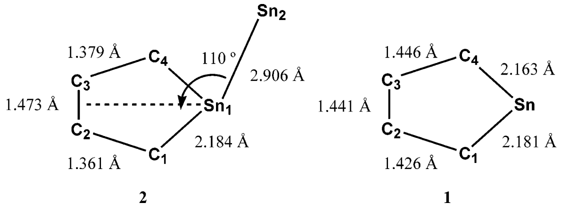

Figure 3. Comparison of the structures of **2** and **1**.

Reaction of 1,2-dianion **2** with lithium in THF gave stannole dianion **1** nearly quantitatively, as evidenced by NMR spectroscopy.[19]

In summary, the oxidation of the stannole dianion **1** leads to the formation of a tin−tin bond to afford the 1,2-dianion **2**. Controlling the amount of oxidant is essential for clean oxidation of the stannole dianion to form the 1,2-dianion. This result exhibits the stepwise and controlled synthesis of oligo- and polymeric metalloles could be possible to control their properties. The 1,2-dianion **2**, a tin analogue of the cyclopentadienyl anion, has nonaromatic nature, as evidenced by NMR and X-ray analyses. By reduction the 1,2-dianion **2** is reversed to the stannole dianion **1**. The redox reaction between the stannole dianion and the bistannole-1,2-dianion can be controlled to be reversible.

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Supporting Information Available: Experimental procedure for the reactions of **1** with oxygen (excess and 0.5 equiv) and **2** with lithium; assignments of ^{13}C and ^{119}Sn signals of a 1:1 mixture of **1** and **2** (Figures S1 and 2); refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and CIF for **2**.

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(16) Experimental procedure for the preparation of **2**: Oxygen used was dried over activated molecular sieves and taken by a gas-tight syringe. To a THF (0.6 mL) solution of stannole, dianion **1** (37 mg, 0.076 mmol) was added, oxygen dried, over activated molecular sieves (1.8 mL, 0.074 mmol; 1 atm, 298.15 K). The resulting deep-blue solution was degassed by freeze−pump−thaw cycles and sealed. After removal of insoluble materials by filtration, the filtrate was concentrated in a glovebox. The residue was washed with hexane to give **2** (34 mg, 94%). **2**: ^{1}H NMR-(400 MHz, THF−C_6D_6) δ 6.45−6.50(m, 2H), 6.60−6.75(m, 12H), 6.77−6.95(m, 6H); ^{13}C NMR(101 MHz, THF−C_6D_6) δ 120.83(d), 123.05(d), 126.43(d), 126.58(d), 129.75(d), 132.49(d), 146.43(s), 146.51(s), 151.40-(s, J(Sn−C) = 34 Hz), 182.67(s, J(Sn−C) = 158, 407 Hz); ^{119}Sn NMR-(149 MHz, THF−C_6D_6) δ −81.4(J(Sn−Sn) = 3962 Hz); ^{7}Li NMR(156 MHz, THF−C_6D_6) δ 0.08. The elemental analysis and measurement of mass spectroscopy of **2** could not be carried out because of its extremely high reactivity toward water and oxygen.

(17) Reaction of **1** with ferrocenium tetrafluoroborate: A THF (0.5 mL) solution of **1** (24 mg, 0.049 mmol) with C_6D_6 (0.2 mL) for NMR lock was placed in a 5 mm NMR tube in a glovebox. To the solution was added ferrocenium tetrafluoroborate (13 mg, 0.048 mmol), and the resulting deep-blue solution was degassed by freeze−pump−thaw cycles and sealed. The NMR spectra showed the nearly quantitative formation of **2** as well as the complete disappearance of the signals for **1**.

(18) Crystals suitable for X-ray diffraction were obtained by recrystallization of a THF/benzene solution of **2** in the presence of 12-crown-4 at −33 °C in a glovebox. The crystal was mounted in a glass capillary. The intensity data were collected at −120 °C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and graphite monochromator. Crystal data of **2**[Li$^+$(12-crown-4)]$_2$: Formula, $C_{86}H_{94}Li_2O_{10}Sn_2$, FW = 1538.91, Crystal Dimension 0.15 × 0.10 × 0.10, Monoclinic, $C2/c$, $a = 35.223(3)$ Å, $b = 11.1137(9)$ Å, $c = 25.776(2)$ Å, $\beta = 130.960(3)°$, $V = 7619.8(11)$ Å^3, $Z = 4$, $D_{calcd} = 1.342$ g cm^{-3}. $R_1 = 0.038$ ($I > 2\sigma(I)$, 5593 reflections), w$R_2 = 0.109$ (for all reflections) for 7523 reflections and 451 parameters. GOF = 0.945.

(19) To gain more insight into the redox behavior between stannole dianion **1** and bistannole-1,2-dianion **2**, voltammetric measurement was attempted in a glovebox under the conditions: working electrode: glassy carbon, pseudo-reference electrode: platinum wire, and counter electrode: platinum wire using a THF solution of $Bu_4N^+PF_4^-$ (0.1 mol/L) as an electrolyte. However, stannole dianion **1** was decomposed in the electrolyte, and the redox potential of **1** could not be estimated.

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