Aromaticity

DOI: 10.1002/ange.200501632

The Aromaticity of the Stannole Dianion**

Masaichi Saito, Ryuta Haga, Michikazu Yoshioka, Kazuya Ishimura, and Shigeru Nagase*

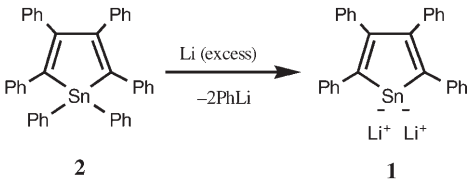
In the last decade, much attention has been focused on the anions and dianions of siloles[1] and germoles,[1f,2] which are heavier congeners of the cyclopentadienyl anion.[3] The degree of aromaticity of silolyl anions depends on the substituent,[1b,f] while the germolyl anions do not show aromaticity because the negative charge is localized on the germanium atom.[1f,2a,2c] In contrast, the negative charges in the dianions of siloles and germoles are significantly delocalized in the C_4M (M = Si, Ge) ring and they were concluded to be aromatic.[1d–f,2b,2d,2e,4] The aromatic delocalization in these dianions was evidenced by NMR studies, calculations, and X-ray crystal structural analyses, which showed no alternation of the C–C bonds within the ring. In contrast to the well-investigated mono- and dianions of siloles and germoles, neither mono- nor dianions of stannoles had been reported before we undertook a study of such species a few years ago.

[*] Assoc. Prof. Dr. M. Saito, R. Haga, Prof. Dr. M. Yoshioka
Department of Chemistry, Faculty of Science
Saitama University
Shimo-okubo, Saitama City, Saitama 338-8570 (Japan)
Fax: (+81) 48-858-3700
E-mail: masaichi@chem.saitama-u.ac.jp
Dr. K. Ishimura, Prof. Dr. S. Nagase
Department of Theoretical Molecular Science
Institute for Molecular Science
Myodaiji, Okazaki, Aichi 444-8585 (Japan)

[**] This work was partially supported by Grants-in-Aid for Young Scientists (B) No. 17750032 (M.S.) and the Nanotechnology Support Project from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. M.S. acknowledges a research grant from Toray Science Foundation. R.H. thanks the Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

In the course of our studies on the synthesis of tin-containing aromatic compounds,[5] mono- and dianions of stannoles were revealed as fascinating synthetic targets because these species are potential intermediates for the synthesis of tin-containing aromatic compounds. Recently, we reported the synthesis of compound **1** by the reduction of bi(1,1′-pentaphenylstannole)[6] or hexaphenylstannole with the concomitant formation of phenyllithium.[7] The dianion in **1** was characterized by ^{1}H, ^{13}C, and ^{119}Sn NMR spectroscopy and chemical trapping with methyl iodide. However, the formation of phenyllithium prevented the isolation of **1** in a pure form as well as the estimation of its aromaticity by using ^{7}Li chemical shifts[4b,8] because of the intermolecular exchange of lithium cations. Herein, we report the isolation of compound **1** and the crystallographic and theoretical studies of its aromaticity.

The reduction of hexaphenylstannole **2**[9] with excess lithium in ether at room temperature gave **1** and phenyllithium. Refluxing the reaction mixture for 14 h completely decomposed phenyllithium,[10] and **1** was obtained as deep-red crystals in 98% yield (Scheme 1).



Scheme 1. Synthesis of stannole dianion **1** by the reduction of hexaphenylstannole **2**.

The structure of **1** was determined by X-ray analysis. As shown in Figure 1, two lithium atoms lie above and below the stannole ring. Each lithium atom is coordinated to the stannole ring in an η^5 fashion and is also coordinated to an ether molecule. Each unit molecule of **1** contains a benzene molecule in a unit cell. η^5-Bonded lithium atoms were also found in the lithium salts of the dianions of tetraphenylgermole[2d] and tetramethylsilole.[1e,f] The C2–C3 bond significantly shortens to 1.442(5) Å from 1.511(6) Å in **2**.[9b] On the contrary, the C1–C2 and C3–C4 bonds significantly lengthen to 1.422(6) and 1.446(6) Å, respectively, from 1.352 Å in **2**.[9b] The stannole ring is almost planar and the C–C distances within the ring are nearly equal, ranging from 1.422(6) to 1.446(6) Å, which suggests a considerable aromatic character of dianion in **1**.

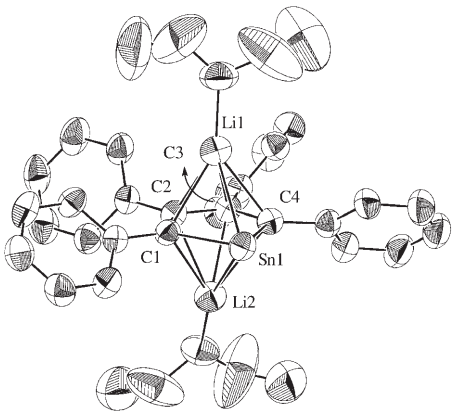


Figure 1. ORTEP drawing of **1** with thermal ellipsoid plots (40% probability for non-hydrogen atoms). All hydrogen atoms and a benzene molecule are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1-C1 2.179(4), C1-C2 1.422(6), C2-C3 1.442(5), C3-C4 1.446(6), C4-Sn1 2.133(4), Sn1-Li1 2.758(8), Sn1-Li2 2.769(8); C1-Sn1-C4 77.43(15).

To aid in understanding the structure of **1**, the geometry of unsolvated **1** was optimized with the hybrid density functional theory at the B3LYP[11] level by using Huzinaga's (433321/43321/421; DZP) basis set and a polarization d function ($\xi = 0.183$) for Sn[12] and 6-31G(d) for C,[13,14] H,[15] and Li.[14,16,17] Two different dilithio complexes were found to be minima (Figure 2). One of these (**1a**), which corresponds closely to

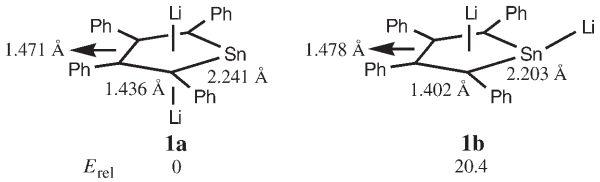
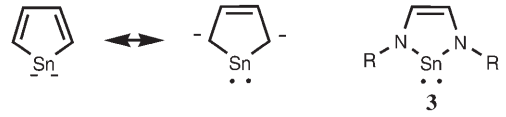


Figure 2. Geometry optimization and relative energies of **1a** and **b**.

the X-ray crystal structure, is of C_2 symmetry with both lithium atoms η^5-coordinated to the aromatic ring. The other structure (**1b**) is of C_1 symmetry with one lithium atom bonded to the tin atom and the other bonded in an η^5 fashion to the ring. The structure **1a** was calculated to be more stable than **1b** by 20 kcal mol^{-1}. The calculated C–C distances within the ring of **1a** are nearly equal (1.436 and 1.471 Å), which suggests a considerable aromatic delocalization of the negative charges in **1a**. The calculated structure of **1a** is in good agreement with the X-ray crystal structure of **1** (Figure 1). According to the natural population analysis, the α carbon atoms are considerably negatively charged (−0.713) in **1a**. This finding suggests the large contribution of a resonance form with stannylene character, as indicated in dianions of siloles and germoles, although the natural population analyses of these dianions were not reported. The β carbon atoms are also negatively charged (−0.273) in **1a**, whereas the α (−0.415) and β (−0.030) carbon atoms of **2** are less negatively charged than those of **1a**, which suggests a considerable delocalization of negative charges into the stannole ring.

The NMR spectroscopic analysis of **1** was also carried out. The ^{119}Sn signal for **1** ($\delta = 163.3$) appeared at a lower field than that for **2** ($\delta = -88$ ppm in $CDCl_3$), which reflects the strong contribution of a resonance form with stannylene character in **1** consistent with the natural population analysis of **1a**. The central tin atom of the isolobal diaminostannylene **3** (Scheme 2) is known to resonate at about $\delta = 240$ ppm.[18] However, the ^{13}C NMR signal assignable to the α carbon atom in the five-membered ring ($\delta = 187$ ppm) was observed at a lower field than that for **2** ($\delta = 143$ ppm in $CDCl_3$). This result is contrary to the low-frequency resonance predicted by the natural population analysis and the major resonance contribution. The signal arising from the β carbon atom in the



3

Scheme 2. Mesomeric forms of diaminostannylene **3**.

five-membered ring appeared at a higher field than that for **2** ($\delta = 133$ vs. 155 ppm).

The observed values of **1** are in good agreement with the calculated values of $\delta = 207$ and 138 ppm, respectively (Table 1).[19] The high-frequency resonance of the α carbon

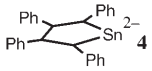
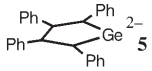
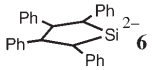
Table 1: Calculated and measured chemical shifts for **1**.

	C_α	C_β	Li
Calculated	206.69	138.15	−6.30
Experimental	187.68	133.46	−4.36

atom could be explained by the paramagnetic contribution of a tin–carbon bond.[20] The ^{7}Li NMR signal attributable to **1** was observed at $\delta = -4.36$ ppm; the calculation predicted $\delta = -6.30$ ppm (Table 1). This appreciable low-frequency resonance is evidently caused by the strong shielding effect of the diatropic ring current resulting from the 6π-electron system, and hence the stannole dianion in **1** is concluded to have considerable aromatic character.[4b,8]

The nucleus-independent chemical shift (NICS) value of $\delta = -5.96$ ppm[19] calculated at 1.0 Å above the ring (non-weighted mean of the heavy-atom coordinate) of non-lithium-coordinated **4** also suggests that the stannole dianion in **1** should be aromatic (Table 2).[21] The origin of the aromaticity

Table 2: NICS(1) calculation for **4**–**6**.

Compound	NICS(1)/ppm
 **4**	−5.96
 **5**	−6.26
 **6**	−6.30

of **1** could be reasonably interpreted in terms of the delocalization of negative charges of the tin out-of-plane p orbital into the LUMO of the butadiene moiety (Figure 3).[22] However, the degree of aromaticity of **1** is smaller than those of the germanium and silicon analogues, judging from the NICS(1) values of non-lithium-coordinated dianions **4**–**6** (Table 2).

In summary, the lithium salt **1** of a stannole dianion was isolated and characterized by NMR and X-ray crystal structural studies, and the related calculations were carried out. The stannole dianion has a planar structure with almost equal C–C distances within the ring, and hence the negative

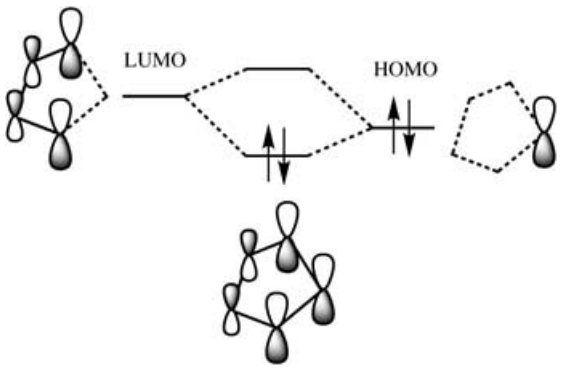


Figure 3. Orbital correlation between butadiene and tin dianion moieties.

charges considerably are delocalized in the ring. The strong low-frequency resonance arising from the diatropic ring current from the 6π-electron system was observed by ^{7}Li NMR spectroscopy. Compound **1** is concluded to be the first tin-containing carbocyclic aromatic compound.

Experimental Section

Synthesis of **1**: Ether (10 mL) was added to a mixture of **2** (971 mg, 1.54 mmol) and lithium (103 mg, 14.8 mmol), and the resulting suspension was refluxed for 17 h. Insoluble materials were removed by filtration, and the filtrate was concentrated in a glove box. The residue was washed with hexane to give **1** (741 mg, 98%); ^{1}H NMR (400 MHz, Et_2O/C_6D_6): $\delta = 6.61$–6.68 (m, 4H), 6.75–6.82 (m, 12H), 6.88–6.93 ppm (m, 4H); ^{13}C NMR (101 MHz, Et_2O/C_6D_6): $\delta = 121.90$ (d), 124.09 (d), 127.17 (d), 127.21 (d), 128.43 (d), 132.64 (d), 133.46 (s, J(Sn,C) = 29 Hz), 144.18 (s, J(Sn,C) = 14 Hz), 150.57 (s, J(Sn,C) = 34 Hz), 187.68 ppm (s, J(Sn,C) = 375, 393 Hz); ^{119}Sn NMR (149 MHz, Et_2O/C_6D_6): $\delta = 163.3$ ppm; ^{7}Li NMR (156 MHz, Et_2O/C_6D_6): $\delta = -4.36$ ppm. An elemental analysis and the measurement of the melting point of **1** could not be carried out because of its extremely high reactivity toward water.

Crystal data for **1**: Crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a solution of **1** in ether performed in a glove box. The crystal was mounted in a glass capillary. Data for the X-ray crystallographic analysis were collected on Mac Science DIP3000 diffractometers with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 298 K. The structure was solved by direct methods by using SIR[23] and refined with full-matrix least-squares procedures on F^2 (SHELXL-97).[24] The non-hydrogen atoms were refined anisotropically except for the disordered carbon atoms (see below), and all the hydrogen atoms were placed at calculated positions (d(C-H) = 0.96 Å). Disorder around one of the ether molecules was found. The occupancies of the disordered ether carbon atoms were fixed as 0.50:0.50 and the corresponding hydrogen atoms were not placed. Formula $C_{36}H_{35}Li_2O_2Sn$, C_6H_6, $M_r = 710.34$, crystal dimension $0.40 \times 0.40 \times 0.20$ mm^3, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 10.8280(6)$, $b = 13.3290(7)$, $c = 15.2920(10)$ Å, $\alpha = 104.449(3)$, $\beta = 94.865(3)$, $\gamma = 113.249(3)°$, $V = 1921.6(2)$ Å^3, $\rho_{calcd} = 1.228$ g cm^{-3}, $R1 = 0.057$ ($I > 2\sigma(I)$, 5247 reflections), $wR2 = 0.169$ (for all reflections) for 6519 reflections and 423 parameters, GOF = 1.146. CCDC-271622 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: May 12, 2005
Published online: September 12, 2005

Keywords: anions · aromaticity · carbocycles · NMR spectroscopy · tin

[1] a) W.-C. Joo, J.-H. Hong, S.-B. Choi, H.-E. Son, C. H. Kim, *J. Organomet. Chem.* **1990**, *391*, 27; b) J.-H. Hong, P. Boudjouk, *J. Am. Chem. Soc.* **1993**, *115*, 5883; c) J.-H. Hong, P. Boudjouk, S. Castellino, *Organometallics* **1994**, *13*, 3387; d) U. Bankwitz, H. Sohn, D. R. Powell, R. West, *J. Organomet. Chem.* **1995**, *499*, C7; e) R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig, T. Mueller, *J. Am. Chem. Soc.* **1995**, *117*, 11608; f) W. P. Freeman, T. D. Tilley, G. P. A. Yap, A. L. Rheingold, *Angew. Chem.* **1996**, *108*, 960; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 882; g) W. P. Freeman, T. D. Tilley, L. M. Liable-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **1996**, *118*, 10457.

[2] a) P. Dufour, J. Dubac, M. Dartiguenave, Y. Dartiguenave, *Organometallics* **1990**, *9*, 3001; b) J.-H. Hong, P. Boudjouk, *Bull. Soc. Chim. Fr.* **1995**, *132*, 495; c) W. P. Freeman, T. D. Tilley, F. P. Arnold, A. L. Rheingold, P. K. Gantzel, *Angew. Chem.* **1995**, *107*, 2029; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1887; d) R. West, H. Sohn, D. R. Powell, T. Müller, Y. Apeloig, *Angew. Chem.* **1996**, *108*, 1095; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1002; e) S.-B. Choi, P. Boudjouk, J.-H. Hong, *Organometallics* **1999**, *18*, 2919.

[3] For examples of reviews, see: a) E. Colomer, R. J. P. Corriu, M. Lheureux, *Chem. Rev.* **1990**, *90*, 265; b) J. Dubac, C. Guérin, P. Meunier in *The Chemistry of Organic Silicon Compounds* (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, p. 1961; c) M. Saito, M. Yoshioka, *Coord. Chem. Rev.* **2005**, *249*, 765.

[4] a) B. Goldfuss, P. von R. Schleyer, F. Hampel, *Organometallics* **1996**, *15*, 1755; b) B. Goldfuss, P. von R. Schleyer, *Organometallics* **1997**, *16*, 1543.

[5] a) M. Saito, M. Nitta, M. Yoshioka, *Organometallics* **2001**, *20*, 749; b) M. Saito, N. Henzan, M. Nitta, M. Yoshioka, *Eur. J. Inorg. Chem.* **2004**, 7437.

[6] M. Saito, R. Haga, M. Yoshioka, *Chem. Commun.* **2002**, 1002.

[7] M. Saito, R. Haga, M. Yoshioka, *Chem. Lett.* **2003**, 912.

[8] The high-field ^{6}Li/^{7}Li chemical shift is diagnostic of aromatic ring currents. For examples, see: a) R. H. Cox, H. W. Terry, Jr., L. W. Harrison, *J. Am. Chem. Soc.* **1971**, *93*, 3297; b) R. H. Cox, H. W. Terry, Jr., *J. Magn. Reson.* **1974**, *14*, 317; c) L. A. Paquette, W. Bauer, M. R. Sivik, M. Bühl, M. Feigel, P. von R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 8776; d) A. Sekiguchi, Y. Sugai, K. Ebata, C. Kabuto, H. Sakurai, *J. Am. Chem. Soc.* **1993**, *115*, 1144.

[9] a) W. Z. Rhee, J. J. Zuckerman, *J. Am. Chem. Soc.* **1975**, *97*, 2291; b) J. Ferman, J. P. Kakareka, W. T. Klooster, J. L. Mullin, J. Quattrucci, J. S. Ricci, H. J. Tracy, W. J. Vining, S. Wallace, *Inorg. Chem.* **1999**, *38*, 2464.

[10] A new singlet was observed in the ^{1}H NMR spectrum in ether/C_6D_6 at $\delta = 5.23$ ppm. In a separate experiment, a solution of phenyllithium was refluxed in ether/C_6D_6 for 14 h. The ^{1}H NMR spectrum of the resulting mixture showed a singlet at $\delta = 5.23$ ppm with the complete disappearance of the signals for phenyllithium. The ^{13}C NMR spectrum showed signals at $\delta = 122.79$ and 128.53 ppm, the latter being assignable to benzene. The signals at $\delta = 5.23$ ppm in the ^{1}H NMR spectrum and $\delta = 122.79$ ppm in the ^{13}C NMR spectrum probably arise from ethylene.

[11] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[12] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, **1984**.

[13] W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.

[14] P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.

[15] R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724.

[16] J. D. Dill, J. A. Pople, *J. Chem. Phys.* **1975**, *62*, 2921.

[17] All calculations were performed with Gaussian 98, Revision A.11.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2001**.

[18] T. Gans-Eichler, D. Gudat, M. Nieger, *Angew. Chem.* **2002**, *114*, 1966; *Angew. Chem. Int. Ed.* **2002**, *41*, 1888.

[19] The calculations were carried out at GIAO-B3LYP/(4333111/433111/421) with two polarization d functions ($\xi = 0.253$, 0.078; TZDP) for Sn,[12] GIAO-B3LYP/(433111/43111/211) with two polarization d functions ($\xi = 0.382$, 0.108; TZDP) for Ge,[12] GIAO-B3LYP/(53111/5111) with two polarization d functions ($\xi = 0.424$, 0.118; TZDP) for Si,[12] and 6-31G(d) for C and H. The geometry optimization for **3**, **4**, and **5** was carried out at B3LYP/DZP for Sn,[12] Ge,[12] and Si[12] and at 6-31G(d) for C and H.

[20] The strong high-frequency resonance of the α carbon atoms was predicted by calculations in reference [4b].

[21] NICS values are effective probes for dia- and paratropic ring currents associated with aromaticity and antiaromaticity, respectively, see: P. von R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. van Eikema Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317.

[22] The contribution of the resonance form with allyl anion character is small because the bond order of the Sn–C_α bond of $C_4H_4Sn^{2-}$ is calculated to be 1.171, which is nearly the same as that of $C_4H_4SnH_2$ (0.986).

[23] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343.

[24] G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, Universität Göttingen, Göttingen, Germany, **1997**.

