Synthesis and Characterization of Dimetallostannafluorenes

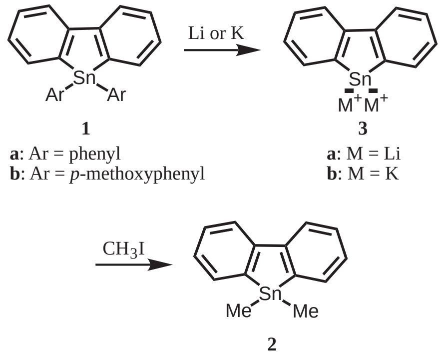
Masaichi Saito,*[1] Masakazu Shimosawa,[1] Michikazu Yoshioka,[1] Kazuya Ishimura,[2] and Shigeru Nagase[2]
[1]*Department of Chemistry, Graduate School of Science and Engineering, Saitama University,*
Shimo-okubo, Sakura-ku, Saitama 338-8570
[2]*Department of Theoretical Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki 444-8585*

(Received June 5, 2006; CL-060640; E-mail: masaichi@chem.saitama-u.ac.jp)

The reaction of 9,9-bis(*p*-methoxyphenyl)-9-stannafluorene with lithium or potassium gave the corresponding dimetallostannafluorene, as evidenced by NMR spectral analysis and a trapping experiment.

For a decade there has been considerable interest in the chemistry of anions and dianions of group 14 metalloles as heavier congeners of the cyclopentadienyl anion.[1] Silole and germole dianions are believed to have considerable aromatic character, based on the X-ray crystal structures which indicated no C–C bond alternation in each five-membered ring,[2] and theoretical calculations.[3] After considerable work on dianions of group 14 metalloles,[1–3] attention was next paid to the effect of benzannulation of metallole anions and dianions on aromaticity. The six-membered rings in both silaindenyl and germaindenyl dianions have a diene property, while each five-membered ring has considerable aromatic character with no C–C bond alternation.[4,5] Both silafluorenyl and germafluorenyl dianions have also considerable aromatic character as evidenced by the X-ray structures and theoretical calculations.[6–8] In contrast to the well-investigated dianions of siloles and germoles, neither mono- nor dianions of stannole had been reported before the start of our project to investigate stannole mono- and dianions. Very recently, we have reported the first synthesis and characterization of mono- and dianions of stannoles, the latter of which is the first stannaaromatic compound.[9] In the course of our studies on the effect of benzannulation of stannole dianions on aromaticity,[10] we report herein the first synthesis of 9-stannafluorenyl dianions.

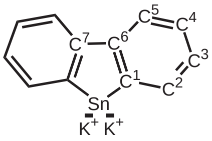
Reductive cleavage of the phenyl groups on the tin in the reduction of stannoles[9a,9c,9d,10] prompted us to first choose 9,9-diphenyl-9-stannafluorene (**1a**)[11] as a precursor of 9-stannafluorenyl dianions. The reduction of **1a** with lithium, however, became rather complicated although the treatment of the resulting reaction mixture with methyl iodide gave 9,9-dimethylstannafluorene (**2**) (31%),[11,12] suggesting the formation of the first 9,9-dilithiostannafluorene (**3a**) (Scheme 1). Next was chosen 9,9-bis(*p*-methoxyphenyl)-9-stannafluorene (**1b**)[11] as another precursor of 1-stannafluorenyl dianions. Reduction of **1b** with lithium also gave 9,9-dilithiostannafluorene (**3a**), as evidenced by the formation of **2** (46%)[11] after the treatment of the reaction mixture with methyl iodide. The reduction of **1b** with potassium became cleaner than that with lithium. The yield of **2** was improved to be 54%,[11] suggesting high efficiency of the generation of 9,9-dipotassiostannafluorene (**3b**) (Scheme 1). The best method for the synthesis of 9-stannafluorenyl dianion was concluded to be the reduction of 9,9-bis(*p*-methoxyphenyl)-9-stannafluorene (**1b**) with potassium.



Scheme 1.

The reaction of **1b** with excess potassium was monitored by NMR. Compound **1b** (92 mg, 0.19 mmol) and potassium (131 mg, 3.36 mmol) were mixed in THF (2 mL) in a glovebox. The color of the solution changed to dark red. An aliquot of the reaction solution was placed in an NMR tube with C_6D_6 for NMR lock.[13] The ^{119}Sn NMR spectrum showed only one signal at −21.8 ppm, assignable to 9,9-dipotassiostannafluorene (**3b**). The ^{119}Sn signal attributable to **3b** appeared in lower field than that for the starting **1b** (−95.3 ppm in $CDCl_3$), as was observed in the stannole dianions.[9,10] Similar downfield shifting was observed in the silafluorenyl dianion.[7] The ^{29}Si chemical shift is strongly correlated with the aromaticity of silole dianions. The downfield shifting of the ^{29}Si nuclei in silole dianions is consistent with delocalization of the negative charges into the silole ring, resulting in their aromatic nature. Hence, the downfield resonance of the ^{119}Sn nuclei suggests that the 9,9-dipotassiostannafluorene (**3b**) also should have a considerable aromatic character. The ^{1}H and ^{13}C NMR spectra were rather complicated. Some major signals were assignable to those of anisyl potassium, which can be prepared from the reaction of *p*-bromoanisole with potassium, as evidenced by a separate experiment. The ^{1}H and ^{13}C NMR signals due to **3b** could be finally assigned by subtracting these signals from those for the reaction mixture as well as by the comparison to those of the silicon and germanium derivatives.[7,8] The α-carbon atom resonated at 189 ppm with a large $J(^{119}\text{Sn}–^{13}\text{C})$ coupling constant of 308 Hz, similar to those of the stannole dianions.[9d,10] The β-carbon in the five-membered ring resonated at 138 ppm, slightly downfield-shifted compared to those of the stannaindenyl dianion (136 ppm)[10] and the stannole dianion (133 ppm).[9d] The assignment is consistent with the calculated values (206.2 and 141.9 ppm for α- and β-carbon atoms, respectively; vide infra).[14,15] The resonances of the α- and β-carbon atoms shift downfield, as the atomic number of the group 14 elements goes down, as were observed in the non-benzannulated systems.[2,9] The complete assignment of other ^{13}C NMR signals could not be achieved even by the aid of theoretical calculations because of intervention of the signals

Table 1. Theoretical calculations of **3b**



3b

C–C bond lengths/Å		$\delta(^{13}C)^a$	
C^1–C^2	1.418	C^1	206.2
C^2–C^3	1.388	C^2	148.9
C^3–C^4	1.413	C^3	120.0
C^4–C^5	1.387	C^4	123.7
C^5–C^6	1.422	C^5	125.9
C^6–C^1	1.444	C^6	141.9
C^6–C^7	1.470		

[a] Ref. 15.

due to unidentifiable decomposition products from **3b**.[13] After the solution was stored at room temperature for a few days, no ^{119}Sn NMR signal was observed and a black precipitate was formed. The 1,1-dipotassiostannafluorene (**3b**) was unstable in solution and gradually decomposed probably to metallic tin.

To aid in understanding the structure of dipotassiostannafluorene, the geometry of **3b** was optimized with the hybrid density functional theory at the B3LYP[16] level using Huzinaga's (433321/43321/421) (DZP) basis set and a polarization d-function ($\xi = 0.183$) for Sn[17] and 6-31G(d) for C,[18,19] H,[20] and K[21] (Table 1). The most stable complex has two potassium atoms η^5-coordinated to the planar stannole ring. The calculated C–C distances within the stannole ring of **3b** are nearly equal (1.444 and 1.470 Å), suggesting the considerable aromatic delocalization of the negative charges in **3b**. On the contrary, the six-membered ring has a slight alternation of the C–C bonds (1.387–1.422 Å), as was observed in sila- and germafluorenyl dianions.[7,8] The more negative NICS(1) value (-8.59) of the five-membered ring of the free stannafluorenyl dianion than that (-7.82) of the six-membered rings also suggests the considerable aromatic character of the five-membered ring.[15]

In summary, the first synthesis of dimetallostannafluorenes was reported. The downfield ^{119}Sn resonance and theoretical calculations suggest the dipotassiostannafluorene **3b** should have a considerable aromatic character, as do sila- and germafluorenyl dianions.[7,8]

This work was partially supported by Grant-in-Aid for Encouragement of Young Scientists (B), No. 17750032 (M. Saito) and the Nanotechnology Support Project from the Ministry of Education, Culture, Sports, Science and Technology, Japan. M. Saito acknowledges a research grant from Toray Science Foundation.

References and Notes

1 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*, ed. by Z. Rappoport, Y. Apeloig, John Wiley and Sons, Chichester, **1998**, pp. 1961. c) M. Saito, M. Yoshioka, *Coord. Chem. Rev.* **2005**, *249*, 765.
2 a) R. West, H. Sohn, U. Bankwitz, J. Calabrese, Y. Apeloig, T. Mueller, *J. Am. Chem. Soc.* **1995**, *117*, 11608. b) W. P. Freeman, T. D. Tilley, G. P. A. Yap, A. L. Rheingold, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 882. c) W. P. Freeman, T. D. Tilley, L. M. Liable-Sands, A. L. Rheingold, *J. Am. Chem. Soc.* **1996**, *118*, 10457. d) R. West, H. Sohn, D. R. Powell, T. Müller, Y. Apeloig, *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1002.
3 a) B. Goldfuss, P. v. R. Schleyer, F. Hampel, *Organometallics* **1996**, *15*, 1755. b) B. Goldfuss, P. v. R. Schleyer, *Organometallics* **1997**, *16*, 1543.
4 S.-B. Choi, P. Boudjouk, P. Wei, *J. Am. Chem. Soc.* **1998**, *120*, 5814.
5 S.-B. Choi, P. Boudjouk, K. Qin, *Organometallics* **2000**, *19*, 1806.
6 The first NMR characterization of a silafluorenyl dianion, see: S.-B. Choi, P. Boudjouk, *Tetrahedron Lett.* **2000**, *41*, 6685.
7 Y. Liu, T. C. Stringfellow, D. Ballweg, I. A. Guzei, R. West, *J. Am. Chem. Soc.* **2002**, *124*, 49.
8 Y. Liu, D. Ballweg, T. Müller, I. A. Guzei, R. W. Clark, R. West, *J. Am. Chem. Soc.* **2002**, *124*, 12174.
9 a) M. Saito, R. Haga, M. Yoshioka, *Chem. Commun.* **2002**, 1002. b) M. Saito, R. Haga, M. Yoshioka, *Chem. Lett.* **2003**, *32*, 912. c) M. Saito, R. Haga, M. Yoshioka, *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 703. d) M. Saito, R. Haga, M. Yoshioka, K. Ishimura, S. Nagase, *Angew. Chem., Int. Ed.* **2005**, *44*, 6553. e) R. Haga, M. Saito, M. Yoshioka, *J. Am. Chem. Soc.* **2006**, *128*, 4934.
10 For the first synthesis of a 9-stannaindenyl dianion and its aromaticity, see: M. Saito, M. Shimosawa, M. Yoshioka, K. Ishimura, S. Nagase, *Organometallics* **2006**, *25*, 2967.
11 Experimental procedure, see Supporting Information.
12 J. P. M. Van Klink, H. J. R. de Boer, G. Schat, O. S. Akkerman, F. Bickelhaupt, A. L. Speak, *Organometallics* **2002**, *21*, 2119.
13 **3b**: ^{1}H NMR (THF–C_6D_6, 400 MHz) δ 6.18 (dd, $J = 8$, 8 Hz, 2H), 6.54 (dd, $J = 8$, 8 Hz, 2H), 8.03 (d, $J = 8$ Hz, 2H), 8.71 (d, $J = 8$ Hz, 2H); ^{13}C NMR (THF–C_6D_6, 101 MHz) δ 138.25 (s, C_β), 189.35 (s, J(Sn–C) = 308 Hz, C_α), We tentatively assigned other signals by the aid of theoretical calculations: 113.48 (d), 118.96 (d), 123.57 (d), 167.19 (d); ^{119}Sn NMR (THF–C_6D_6, 149 MHz) δ -21.8.
14 All calculations were performed using Gaussian98, 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, O. 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, *Gaussian98, Revision A*, Gaussian, Inc., Pittsburgh PA, **2001**.
15 The theoretical calculations of the ^{13}C NMR chemical shifts were carried out at GIAO-B3LYP/(4333111/433111/421) and two polarization d-functions ($\xi = 0.253$, 0.078) (TZDP) for Sn[17] and 6-311G(d) for C, H, and K. For the optimized structure, see Table1.
16 a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648. b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
17 S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, **1984**.
18 W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, *56*, 2257.
19 P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.
20 R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys.* **1971**, *54*, 724.
21 V. Rassolov, J. A. Pople, M. Ratner, T. L. Windus, *J. Chem. Phys.* **1998**, *109*, 1223.