Synthesis, structure and reactions of a trianion equivalent, trilithiostannane†

Tomoyuki Tajima,[a] **Masatoshi Ikeda,**[a] **Masaichi Saito,***[a] **Kazuya Ishimura**[b] **and Shigeru Nagase**[b]

Transmetallation reaction of trisilylstannane ArSn(SiHMe₂)₃ (Ar = 2,6-bis(2,4,6-triisopropylphenyl)phenyl), bearing a bulky substituent on the tin atom, with methyllithium in THF at room temperature gave the first trianion equivalent, trilithiostannane ArSnLi₃, the generation of which was confirmed by trapping experiments with some electrophiles as well as by ^{119}Sn and ^{7}Li NMR spectroscopy.

Since the first report of the synthesis of alkyl- and aryllithiums in 1917,[1] the organolithium compounds have been one of the most important classes of organometallic compounds and are now recognized as very powerful synthetic tools in organic chemistry.[2] The chemistry of lithium compounds of heavier group 14 elements has also bloomed in the last few decades.[3] Very recently, attention has been paid to the synthesis and reactions of stable geminal dilithio species of group 14 elements as novel difunctional building blocks, leading to the synthesis of novel compounds having double bonds and unique structures of considerable interest. The geminal trilithio species, one of the most exotic species in this field, can be regarded as a trianion equivalent. However, no stable trilithio derivatives of group 14 elements have appeared, although the generation of a trilithiomethane by the reaction of trichlorophenylmethane with t-butyllithium at $-110\ ^\circ$C in THF has been suggested by NMR analysis.[4] On the other hand, the compounds having a tin–alkali metal bond are usually prepared by the reactions of R_3SnX (X = halogen), R_3SnH[5] and R_3SnSnR$_3$[6] with bases and reductants, respectively. Transmetallation reactions are known to occur in the reaction of tetrakis(trimethylsilyl)stannane with methyllithium to give the corresponding lithiostannane.[7] We became interested in the transmetallation reactions of trisilylstannanes having a bulky m-terphenyl ligand on the tin atom with alkyl metal reagents. We report herein the first synthesis of a trilithiostannane, stable in solution at ambient temperature, and its NMR analysis and reactivity. Theoretical calculations are also performed to discuss structures of the newly obtained trilithiostannane.

A THF solution of ArSnCl₃ **1** (Ar = 2,6-bis(2,4,6-triisopropylphenyl)phenyl) and excess of Me₂SiHCl in the presence of Mg–MgBr₂ was heated under reflux to give ArSn(SiHMe₂)₃ **2** and ArH in 23% and 28% yields, respectively. The yield of **2** was improved to 51% when the reaction was carried out in the presence of triethylamine (Scheme 1).

First, the transmetallation reaction of ArSn(SiHMe₂)₃ **2** was carried out. Treatment of **2** with excess methyllithium in THF gave a deep orange solution. After the reaction was quenched with H₂O, ArSnH₃ **3a**[8] was obtained in 90% yield (Scheme 2). The ^{1}H NMR spectrum of **3a** in C₆D₆ showed a signal at 4.28 ppm assignable to SnH₃ protons with a characteristic couple of satellites of $^1J(^{117}$Sn–H) (1847 Hz) and $^1J(^{119}$Sn–H) (1933 Hz), respectively.[9] Addition of D₂O to the reaction mixture instead of H₂O at room temperature resulted in the formation of ArSnD₃ **3b** in 72% yield (D content: 99%) (Scheme 2). The ^{119}Sn NMR spectrum of **3b** in C₆D₆ showed a septet signal at -389 ppm with a $^1J($Sn–D) coupling constant of 200 Hz.[10] In the IR spectrum, a unique absorption was observed at 1315 cm^{-1}, which could be assigned to a stretching vibration of Sn–D moieties in **3b**.[11] The formation of **3a** and **3b** in high yields in the trapping experiments can be interpreted in terms of the almost quantitative generation of trilithiostannane **4a**, stable in THF at room temperature. The formation of trilithiostannane **4a** was also confirmed by trapping experiments with other electrophiles. When trilithiostannane **4a** was treated with iodomethane, the corresponding trimethyl derivative, ArSnMe₃ **5**, was obtained in 92% yield (Scheme 2).‡[12] The reaction of **4a** with bromoethane afforded the corresponding triethyl derivative **6** in 89% yield (Scheme 2). In this reaction, ArSnMe₃ **5** was not obtained. Thus, the trilithiostannane **4a** did not undergo halophilic reaction to afford ArSnI₃ and ArSnMe₃ **5** was not derived from the reaction of ArSnI₃ with the remaining MeLi. Futhermore, ArSn(SiHMe₂)₃ **2** did not react with iodomethane. Thus, trilithiostannane **4a** can function as a trianion equivalent.

Second, NMR characterization of trilithiostannane **4a** was carried out. The ^{119}Sn NMR spectrum of **4a** in THF at room temperature showed only one signal at -443 ppm, in a field

[a] Department of Chemistry, Graduate School of Science and Engineering, Saitama University, Shimo-okubo, Sakura-ku, Saitama-city, Saitama 338-8570, Japan. E-mail: masaichi@chem.saitama-u.ac.jp; Fax: +81 48 858 3698; Tel: +81 48 858 9029
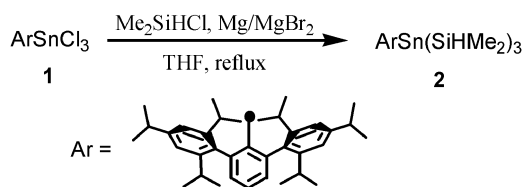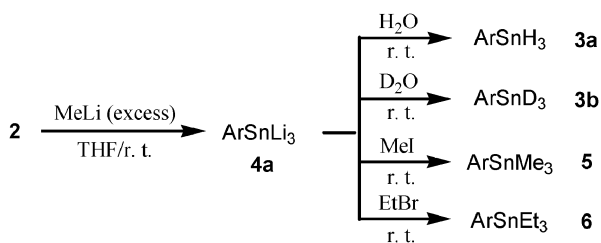*[b] Department of Theoretical and Computational Molecular Science, Institute for Molecular Science, Myodaiji, Okazaki, Aichi 444-8585, Japan*

† Electronic supplementary information (ESI) available: Experimental details and Cartesian coordinates of optimized geometries of ArSnLi₃ **4a**. See DOI: 10.1039/b815371j

$$ \text{ArSnCl}_3 \xrightarrow[\text{THF, reflux}]{\text{Me}_2\text{SiHCl, Mg/MgBr}_2} \text{ArSn(SiHMe}_2)_3 $$
1   **2**

Scheme 1 Preparation of ArSn(SiHMe₂)₃.

Scheme 2 Synthesis and reactions of trilithiostannane 4a.

	A	B
relative energy (kcal/mol)	0	−6.4

Fig. 1 Optimized geometries of trilithiostannane 4a and their relative energy.

much higher than those of the lithio- and dilithio-stannanes.[13] In the ^{7}Li NMR, only one signal was observed at 1.08 ppm, suggesting the rapid exchange of lithium cations between 4a and the remaining MeLi. The coupling constant between ^{119}Sn and ^{7}Li nuclei was not observed even at −80 °C in THF-d_8.[14] After the NMR sample was kept at room temperature for a few days, the signals did not change, and hence, trilithiostannane 4a was quite stable in solution at ambient temperature.

We next examined the synthesis of tripotassiostannane 4b by transmetallation reaction of ArSn(SiHMe$_2$)$_3$ 2 with ^{t}BuOK. Treatment of 2 with ^{t}BuOK in THF at room temperature gave tripotassiostannane 4b, the formation of which was confirmed by a trapping experiment with iodomethane to afford ArSnMe$_3$ 5 in 92% yield (Scheme 3). The ^{119}Sn NMR spectrum of 4b in THF at room temperature revealed only one signal at −473 ppm, in a region similar to that of trilithiostannane 4a.

To aid in understanding the structure of trilithiostannane 4a, the geometry of 4a was optimized with hybrid density functional theory at the B3LYP[15] level using the Gaussian 03 program.[16] The LANL2DZ basis set augmented by d polarization functions (d exponent 0.186) and p diffuse functions (p exponent 0.0174) was used for Sn[17] and 6-31 + G(d) for C, H, and Li.[18] Two different structures of 4a were found to be minima (Fig. 1). One of these (geometry A) has three lithium atoms located asymmetrically to the central phenyl plane. One lithium atom is on a flanking phenyl ring. The other structure (geometry B) is more stable than the first by 6.4 kcal mol^{-1}. In geometry B, three lithium atoms are located symmetrically to the perpendicular to the central phenyl plane. Two lithium atoms are located on each of the flanking phenyl rings, suggesting that there are some interactions between the benzene rings and the lithium atoms, probably leading to unusual stability of the trilithiostannane. Similar interactions were found in anionic species having terphenyl ligands, where the counter cations were coordinated with the flanking phenyl ligands.[19]

In summary, we have succeeded in the first synthesis of a trilithiostannane, a trianion equivalent, by the transmetallation reaction of an aryltrisilylstannane with methyllithium, the formation of which was evidenced by trapping experiments and NMR spectroscopy. A tripotassiostannane was also synthesized using ^{t}BuOK. Both trimetallostannanes were remarkably stable in solution at ambient temperature. Theoretical calculations revealed that trilithiostannane corresponds
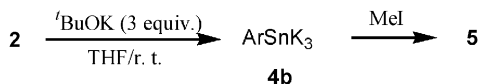
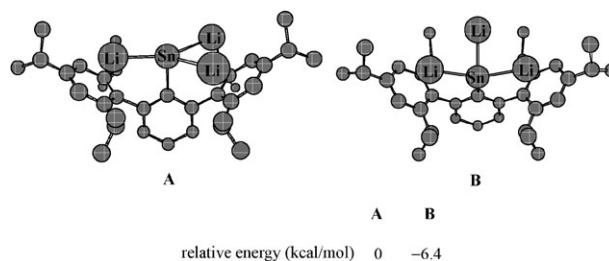
Scheme 3 Synthesis and reaction of tripotassiostannane 4b.

to a stable energy minimum, and the most stable structure has interactions between the lithium atoms and the flanking phenyl groups. The present trimetallostannanes would be useful building blocks for the synthesis of compounds having novel bonding modes and further investigation on their application is currently in progress.

This paper is dedicated to Professor Renji Okazaki on the occasion of his nomination as an honorary member of the Chemical Society of Japan. This work was partially supported by Grants-in-Aid for Scientific Research (No. 20038010 for M.S. and No. 18066017 for S.N.) in Priority Areas "Molecular Theory for Real Systems" and the Nanotechnology Support Project from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

Notes and references

‡ Representative experimental procedure: (a) generation of ArSnLi$_3$ 4a, quenched by iodomethane. Methyllithium (0.92 M solution in diethyl ether, 0.50 mL, 0.47 mmol) was added to a THF solution (4.0 mL) of ArSn(SiHMe$_2$)$_3$ 2 (61 mg, 0.078 mmol) at room temperature. After the reaction mixture was kept at the same temperature, iodomethane (0.5 mL, 8.03 mmol) was added to the reaction mixture. After the removal of volatile substances, material insoluble in dichloromethane was removed by filtration. After concentration of the filtrate, the residue was recrystallized from dichloromethane and methanol to give ArSnMe$_3$ 5 (46 mg, 92%). 5: mp 123–126 °C (dichloromethane + methanol). ^{1}H NMR (400 MHz, CDCl$_3$): δ −0.63 (s, J_{SnH} = 52, 55 Hz, 9H), 1.04 (d, J_{HH} = 7 Hz, 12H), 1.19 (d, J_{HH} = 7 Hz, 12H), 1.28 (d, J_{HH} = 7 Hz, 12H), 2.67 (sept, J_{HH} = 7 Hz, 4H), 2.92 (sept, J_{HH} = 7 Hz, 2H), 7.02 (s, 4H), 7.10 (d, J_{HH} = 8 Hz, 2H), 7.28 (t, J_{HH} = 8 Hz, 1H); ^{13}C NMR (101 MHz, CDCl$_3$): δ −6.66 (q, J_{SnC} = 327, 343 Hz), 22.84 (q), 24.26 (q), 25.75 (q), 30.36 (d), 34.42 (d), 120.56 (d), 126.48 (d, J_{SnC} = 9 Hz), 129.12 (d, J_{SnC} = 39 Hz), 139.29 (s, J_{SnC} = 19 Hz), 143.05 (s), 146.52 (s), 148.01 (s), 148.16 (s); ^{119}Sn NMR (150 MHz, CDCl$_3$): δ −55.1. Anal. Calcd for C$_{39}$H$_{58}$Sn: C, 72.56; H, 9.06. Found: C, 72.59; H, 9.36%. (b) NMR measurement of ArSnLi$_3$ 4a. In a glovebox, THF-d_8 was added to a mixture of MeLi–Et$_2$O powder (186 mg, 1.94 mmol) and ArSn(SiHMe$_2$)$_3$ 2 (125 mg, 0.16 mmol) in a 5 mm glass NMR tube. After the mixture was degassed by freeze–pump–thaw cycles and sealed, the reaction was monitored by NMR spectroscopy. 4a: ^{119}Sn NMR (150 MHz, THF-d_8): δ −443; ^{7}Li NMR (156 MHz, THF-d_8): δ 1.08.

1 W. Schlenk and J. Holtz, *Ber. Dtsch. Chem. Ges.*, 1917, **50**, 272.
2 J. Clayden, in *Organolithiums: Selectivity for Synthesis*, ed. J. E. Baldwin and R. M. Williams, Pergamon, Elsevier Science Ltd, Amsterdam, 2002.
3 For recent reviews, see: (a) P. D. Lickiss and C. M. Smith, *Coord. Chem. Rev.*, 1995, **145**, 75; (b) K. Tamao and A. Kawachi, *Adv. Organomet. Chem.*, 1995, **38**, 1; (c) J. Belzner and U. Dehnert, in *The Chemistry of Organic Silicon Compounds*, ed. Z. Rappoport and Y. Apeloig, Wiley, Chichester, 1998, vol. 2, p. 779; (d) A. Sekiguchi, V. Y. Lee and M. Nanjo, *Coord. Chem. Rev.*, 2000, **210**, 11.
4 J. R. Baran and R. J. Lagow, *J. Am. Chem. Soc.*, 1990, **112**, 9415.

5 (a) M. Newcomb and M. G. Smith, J. Organomet. Chem., 1982, **228**, 61; (b) A. Mordini, M. Taddei and G. Seconi, Gazz. Chim. Ital., 1986, **116**, 239; (c) U. Hermann, G. Reeske, M. Schurmann and F. Uhlig, Z. Anorg. Allg. Chem., 2001, **627**, 453; (d) U. Hermann, I. Prass and F. Uhlig, Phosphorus, Sulfur Silicon Relat. Elem., 2001, **168**, 145; (e) T. Schollmeier, U. Englich, R. Fischer, I. Prass, K. Ruhlandt, M. Schuermann and F. Uhlig, Z. Naturforsch., B: Chem. Sci., 2004, **59**, 1462.

6 (a) M. S. Alnajjar and H. G. Kuivila, J. Am. Chem. Soc., 1985, **107**, 416; (b) J. S. Sawyer, A. Kucerovy, T. L. Macdonald and G. J. McGarvey, J. Am. Chem. Soc., 1988, **110**, 842; (c) M. Saito, R. Haga and M. Yoshioka, Chem. Commun., 2002, 1002; (d) R. Haga, M. Saito and M. Yoshioka, J. Am. Chem. Soc., 2006, **128**, 4934.

7 (a) F. Preuss, T. Wieland, J. Perner and G. Heckmann, Z. Naturforsch., B: Chem. Sci., 1992, **47**, 1355; (b) R. Fischer, J. Baumgarter, C. Marschner and F. Uhlig, Inorg. Chim. Acta, 2005, **358**, 3174; (c) G. Becker, M. Gekeler, H.-M. Hartmann, O. Mundt and M. Westerhausen, in Synthetic Methods in Organometallic and Inorganic Chemistry, ser. ed. W. A. Herrmann, vol. ed. N. Auner and U. Klingebiel, Thieme, Stuttgart, 1996, vol. 2, p. 186.

8 M. Saito, H. Hashimoto, T. Tajima and M. Ikeda, J. Organomet. Chem., 2007, **692**, 2729.

9 M. L. Maddox, N. Flitcroft and H. D. Kaesz, J. Organomet. Chem., 1965, **4**, 50.

10 J.-P. Quintard, M. Degueil-Castaing, G. Dumartin, B. Barbe and M. Petraud, J. Organomet. Chem., 1982, **234**, 27.

11 The Sn–H stretching frequency of ArSnH$_3$ **3a** was observed at 1845 cm^{-1}, in a region similar to that of Sn–H stretching frequencies of previous reports, see: (a) A. K. Sawyer, J. E. Brown and E. L. Hanson, J. Organomet. Chem., 1965, **3**, 464; (b) R. Gupta and B. Majee, J. Organomet. Chem., 1972, **36**, 71.

12 A reviewer suggested the possibility of involvement of radical species or a stannylene intermediate, where only one lithium atom would be associated with the tin atom. However, if the corresponding lithiostannylene had been involved in the reaction, ArSnMe$_2$I would have been formed together with or instead of **5**. Thus, the involvement of the lithiostannylene can be ruled out. When the reaction of ArSn(SiHMe$_2$)$_3$ **2** and excess methyllithium was monitored by ESR spectroscopy, the reaction mixture was ESR-silent, and hence the involvement of radical species can be ruled out.

13 For ^{119}Sn NMR spectra of dilithiostannanes, see: (a) P. A. Chugunov, N. A. Troitskii, K. S. Nosov, M. P. Egorov and O. M. Nefedov, Russ. Chem. Bull., 2004, **53**, 2327; (b) T. Tajima, N. Takeda, T. Sasamori and N. Tokitoh, Eur. J. Inorg. Chem., 2005, 4291.

14 A half width maximum of the signal observed at −80 °C was 90 Hz, while Sn–Li coupling constants of trimethylstannyl- and tributylstannyl-lithium were observed, see: H. J. Reich, J. P. Borst and R. R. Dykstra, Organometallics, 1994, **13**, 1.

15 (a) A. D. Becke, J. Chem. Phys., 1993, **98**, 5648; (b) C. Lee, W. Yang and R. G. Parr, Phys. Rev. B: Condens. Matter Mater. Phys., 1988, **37**, 785.

16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, 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, C. Gonzalez and J. A. Pople, GAUSSIAN 03 (Revision D. 01), Gaussian, Inc., Wallingford, CT, 2004.

17 (a) W. R. Wadt and P. J. Hay, J. Chem. Phys., 1985, **82**, 284; (b) C. E. Check, T. O. Faust, J. M. Bailey, B. J. Wright, T. M. Gilbert and L. S. Sunderlin, J. Phys. Chem. A, 2001, **105**, 8111.

18 (a) W. J. Hehre, R. Ditchfield and J. A. Pople, J. Chem. Phys., 1972, **56**, 2257; (b) P. C. Hariharan and J. A. Pople, Theor. Chim. Acta, 1973, **28**, 213; (c) R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys., 1971, **54**, 724; (d) T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, J. Comput. Chem., 1983, **4**, 294.

19 (a) R. Pietschnig, R. West and D. R. Powell, Organometallics, 2000, **19**, 2724; (b) B. E. Eichler and P. P. Power, Inorg. Chem., 2000, **39**, 5444; (c) B. E. Eichler, A. D. Phillips and P. P. Power, Organometallics, 2003, **22**, 5423; (d) S. Hino, M. M. Olmstead, J. C. Fettinger and P. P. Power, J. Organomet. Chem., 2005, **690**, 1638.