Synthesis of Stannaindenyl Anions and a Dianion

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Reduction of 1,1-diphenylstannaindene with excess lithium gave the intermediary 1-phenyl-1-stannaindenyl anion, which was further reduced to provide the 1-stannaindenyl dianion. The remarkable upfield ^{7}Li NMR resonance in the dianion and the theoretical calculation suggest that the 1-stannaindenyl dianion has considerable aromatic character, as was observed in the sila- and germaindenyl dianions. Reaction of the 1-stannaindenyl dianion with *tert*-butyl chloride gave the 1-*tert*-butyl-1-stannaindenyl anion, as evidenced by NMR detection as well as a trapping experiment.

Introduction

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] After considerable work on anions and dianions of group 14 metalloles,[1−3] attention was next focused on the effect of benzannulation of metallole anions and dianions on aromaticity. The five-membered ring in the silaindenyl anion has a diene character with C−C bond alternation, and hence, the silole ring is essentially nonaromatic.[5] The six-membered rings in both silaindenyl and germaindenyl dianions have a diene property, while the five-membered ring of each has considerable aromatic character with no C−C bond alternation.[6,7] In contrast to the well-investigated mono- and 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.[8,9] In the course of our studies on tin-containing aromatic compounds, we report herein the synthesis of 1-stannaindenyl anions and a dianion and their structural analysis by NMR spectra and theoretical calculations.

Results and Discussion

(a) Synthesis of 1,1-Diphenylstannaindene 1. Reductive cleavage of phenyl groups on the tin in the reduction of a stannole[8b,c] prompted us to choose 1,1-diphenylstannaindene **1** as a precursor of 1-stannaindenyl dianion **2**. The dilithium intermediate **3** prepared by the reaction of diphenylacetylene with butyllithium reacted with dichlorodiphenylstannane to give 1,1-diphenylstannaindene **1** (57%).[10]

(b) Reduction of 1,1-Diphenylstannaindene 1. Reaction of **1** with 2.5 equiv of lithium in ether at room temperature gave a deep red solution, suggesting the formation of an anionic species. Treatment of the reaction mixture with methyl iodide afforded 1-methyl-1-phenylstannaindene **4** (45%) as well as 1,1-dimethylstannaindene **5** (15%),[11] implying the formation of intermediary 1-stannaindenyl anion **6** and dianion **2**, respectively. When an ether solution of **1** in the presence of excess lithium was refluxed[12] and then the reaction mixture was treated

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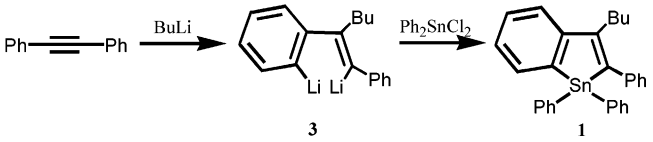
[10] The general synthetic route to metallaindenes was developed by Rausch and Klemann, see: Rausch, M. D.; Klemann, L. P. *J. Am. Chem. Soc.* **1967**, *89*, 5732.

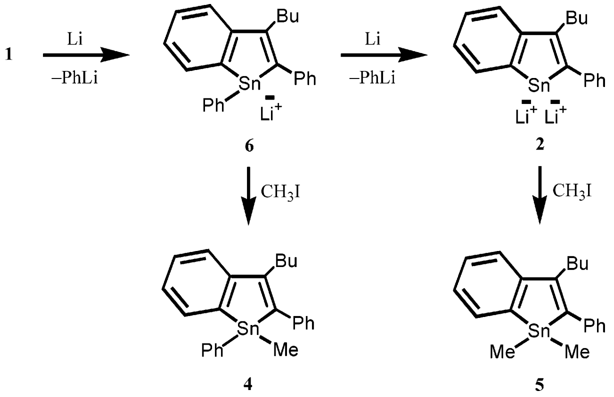
[11] Compound **5** was first reported by Rausch and co-workers, see: Rausch, M. D.; Klemann, L. P.; Boon, W. H. *Synth. React. Inorg. Met.−Org. Chem.* **1985**, *15*, 923. Although compound **5** could not be isolated in the literature, a ^{1}H signal due to Sn−Me protons was observed at 0.40 ppm in CD_2Cl_2. However, neither other spectral data nor elemental analysis was provided. We carried out independently the characterization of compound **5** (see, Experimental Section). We observed a ^{1}H signal due to Sn−Me protons at 0.46 ppm in CD_2Cl_2, suggesting that our compound **5** should be probably identical to Rausch's compound.

10.1021/om050879x CCC: $33.50

Scheme 1



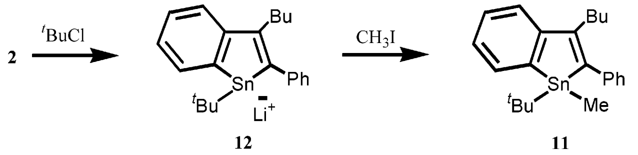
Scheme 2



with methyl iodide at room temperature, 1,1-dimethylstannaindene **5** was isolated in 40% yield,[13] suggesting the exclusive formation of 1-stannaindenyl dianion **2**.

(c) Monitoring the Reduction of 1,1-Diphenylstannaindene 1 by NMR. The reaction of **1** with excess lithium in ether$-$$C_6D_6$ was monitored by NMR. Compound **1** (78 mg, 0.154 mmol) and lithium (11 mg, 1.51 mmol) in ether were placed in an NMR tube with C_6D_6 for NMR lock. The color of the solution changed to dark red. The ^{119}Sn NMR spectrum showed two major signals at -14.2 and -104.8 ppm, assigned to 1-stannaindenyl dianion **2** and 1-stannaindenyl anion **6**, respectively. The ^{119}Sn signal attributable to **2** (-14.2 ppm) appeared at lower field than that for **1** (-99.2 ppm in $CDCl_3$), as was observed in the stannole dianion.[8a,b,9] On the contrary, the tin atom of **6** (-104.8 ppm) resonated at higher field than that of **1**, as was observed in the formation of the silaindenyl anion (δ(^{29}Si): -23.06) from the corresponding chloride (δ(^{29}Si): 14.90).[5] After standing at room temperature for several hours, the ^{1}H and ^{13}C NMR spectra of the reaction mixture showed the signals due to dianion **2** and phenyllithium. The intermediary 1-stannaindenyl anion **6** was easily reduced to provide 1-stannaindenyl dianion **2** even at room temperature. After refluxing the reaction solution overnight, phenyllithium completely decomposed and we could assign NMR signals due to **2**.[12] In the ^{13}C NMR spectrum, the signals assignable to the α-carbons were observed at 176.16 and 193.24 ppm with large ^{1}J(Sn$-$C)s of about 350 MHz. The remarkable downfield resonance of the α-carbon in the stannole dianion was also reported.[8a] Although detailed assignment of ^{13}C NMR chemical shifts of sila- and germaindenyl dianions was not reported in the literature,[6,7] the two most downfielded resonances (146.99 and 158.07 ppm for the silaindenyl dianion;[6] 167.94 and 174.87 ppm for the germaindenyl dianion)[7] in the metallaindenyl dianions shift to downfield as the atomic number of the group 14 elements increases.[14] The ^{7}Li signal assignable to **2** was observed at -5.8 ppm.[15] This appreciable upfield resonance is evidently caused by the strong shielding effect of the diatropic ring current resulting from the 6π-electron system, and hence 1-stannaindenyl dianion **2** is concluded to have considerable aromatic character, as was suggested in the sila- and germaindenyl dianions.[6,7,16]

Scheme 3



(d) Synthesis of Stannaindenyl Anion from the Dianion. To synthesize a 1-stannaindenyl anion from the dianion **2**, the alkylation of **2** was studied. Since the reaction of **2** with methyl iodide gave dimethylated compound **5**, *tert*-butyl chloride was chosen as a bulkier alkylating reagent than methyl iodide. When *tert*-butyl chloride was added to an ether solution of **2** at room temperature, the color of the solution turned from deep red to bright red. By treatment of the reaction mixture with methyl iodide, 1-*tert*-butyl-1-methylstannaindene **11** was obtained in 40% yield, suggesting the formation of 1-stannaindenyl anion **12** by alkylation of **2** (Scheme 3). The formation of **12** from **2** was reasonably explained in terms of an electron transfer mechanism, as was proposed in the reaction of a stannole dianion with *tert*-butyl chloride.[8b]

Monitoring the reaction of **2** with *tert*-butyl chloride by NMR was also carried out. In ^{119}Sn NMR there appeared a signal for 1-stannaindenyl anion **12** at -30.3 ppm. In ^{7}Li NMR a single resonance was observed at 1.04 ppm, suggesting the rapid intermolecular exchange of lithium cations between **12** and lithium chloride.

(e) Theoretical Calculations. To aid in understanding the structure of **2**, the geometry of unsolvated **2** was optimized with the hybrid density functional theory at the B3LYP[17] level using Huzinaga's (433321/43321/421) (DZP) basis set and a polarization d-function ($\xi = 0.183$) for Sn[18] and 6-31G(d) for C,[19,20] H,[21] and Li.[20,22,23] Six different dilithio complexes (**2a**$-$**f**) were found to be minima (Figure 1). The most stable complex (**2a**) has two lithium atoms η^5-coordinated to the planar stannole ring. The complex **2f**, having an η^1- and an η^5-coordinated lithium atom, is less stable than **2a** by 16.3 kcal/mol, as was observed in the calculation of the stannole dianion.[9] To estimate the effect

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[12] The 1-stannaindenyl dianion **2** was formed without refluxing. Thus, the reflux conditions are necessary only for the decomposition of phenyllithium.

[13] Although the ^{1}H NMR spectrum of the crude product revealed the formation of **5** as a main product, the isolated yield of **5** became low because **5** gradually decomposed in solution during purification to give a complex mixture.

[14] The two most downfield resonances in the sila- and germaindenyl dianions can be probably assigned to the α-carbon atoms of each dianion.

[15] In the ^{7}Li NMR spectrum, signals besides that for the dianion **2** were observed at 0.66 and 0.95 ppm due to products resulting from the decomposition of phenyllithium. The assignment of these two signals was evidenced by separate experiments. After an ether$-$$C_6D_6$ solution of phenyllithium was refluxed, the ^{7}Li NMR spectrum of the resulting mixture showed signals at 0.56 and 0.91 ppm.

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

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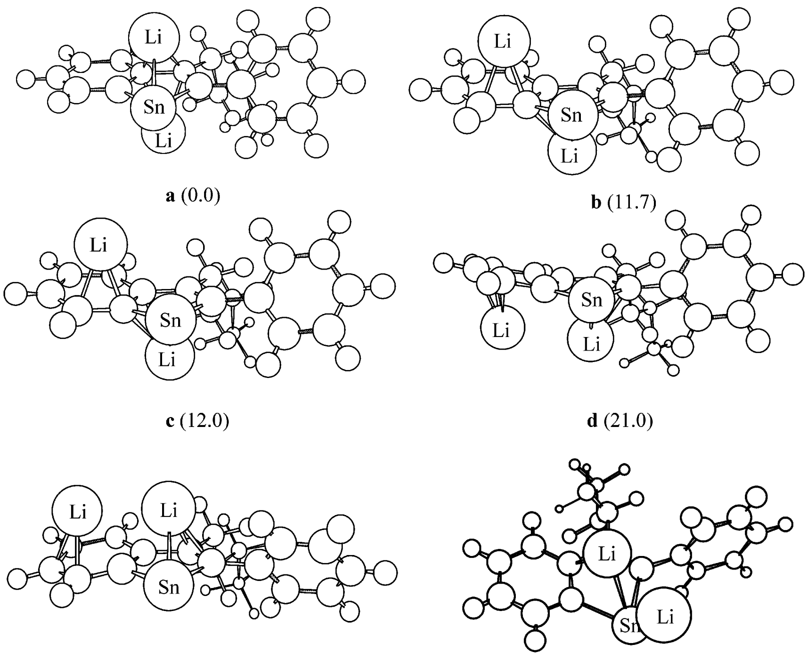
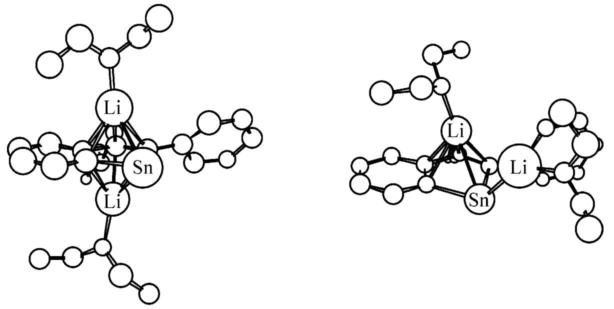


a (0.0) **b** (11.7) **c** (12.0) **d** (21.0) **e** (21.4) **f** (16.3)

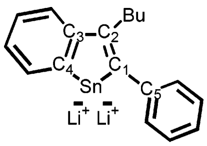
Figure 1. Optimized geometry and relative energy (kcal/mol) of unsolvated **2**.



g (0.0) **h** (15.5)

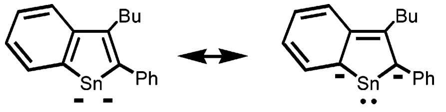
Figure 2. Optimized geometry and relative energy (kcal/mol) of solvated **2**. Hydrogen atoms are omitted for clarity.

Table 1. Natural Population Analysis for 2a and 2g



	2a	**2g**
C1	−0.68	−0.67
C2	−0.27	−0.25
C3	−0.28	−0.25
C4	−0.68	−0.67

Chart 1



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of solvation on the relative stability of the dianion, the geometry of solvated **2**, whose lithium atoms each are coordinated to an ether molecule, was optimized. The complex (**2g**) having two lithium atoms η^5-coordinated to the stannole ring is more stable than that (**2h**) having an η^1- and an η^5-coordinated lithium atom by 15.5 kcal/mol (Figure 2). Thus, the solvation does not remarkably affect the relative stability of the complexes **2**. The following discussion about the structure and NMR analysis of the dianion is concentrated on the complexes **2a** and **2g**. The calculated C−C distances within the ring of **2a** are nearly equal (1.428, 1.461, and 1.468 Å), suggesting the considerable aromatic delocalization of the negative charges in **2a**. The trend is quite similar to that of **2g** (1.427, 1.459, and 1.461 Å). According to the natural population analysis (Table 1), the α-carbons are considerably negatively charged (−0.68 for **2a** and −0.67 for **2g**), suggesting the large contribution of a resonance form with stannylene character (Chart 1).[24] The calculated ^{13}C chemical shifts[25] of the quaternary carbons are in good agreement with the measured values (Table 2).[26] The low-field resonance due to the α-carbon could be explained by paramagnetic contribution of a tin−carbon bond, as was observed in the stannole dianion.[8a,9] The nucleus-independent-chemical-shifts (NICS) values calculated at 1.0 Å above each

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[23] All calculations were performed using *Gaussian98*, revision A. 11.1: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian98*, revision A. 11.1; Gaussian, Inc.: Pittsburgh, PA, 2001.

[24] The low-field shift of the ^{119}Sn nuclei of the dianion **2** compared to that of **1** is reflected in the strong contribution of a stannylene character, although the chemical shift itself is in a higher region than those of cyclic diaminostannylenes isoelectronic to the resonance form **A**.[29]

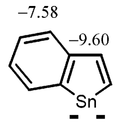
[25] The theoretical calculations were carried out at GIAO-B3LYP/(4333111/433111/421) and two polarization d-functions ($\xi = 0.253, 0.078$) (TZDP) for Sn[18] and 6-311G(d) for C and H, and Li//B3LYP/DZP for Sn and 6-31G(d) for C, H, and Li.

[26] The assignment of CH carbons could not be achieved by the aid of theoretical calculations because all of the CH carbons resonated closely in the range of error of the theoretical calculation.

Table 2. Observed (2) and Calculated (2a and 2g) ^{13}C Chemical Shifts

	2	2a	2g
C1	193.24	213.02	209.74
C2	123.57	126.34	123.76
C3	135.62	136.91	137.70
C4	176.16	187.89	188.78
C5	152.29	157.13	158.74

Table 3. NICS(1) Calculation in 7−10



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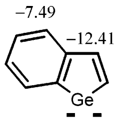

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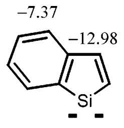

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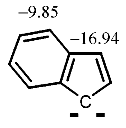

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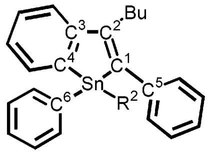
Table 4. Observed (1, 4, 5, and 11) and Calculated (4) ^{13}C Chemical Shifts



	1	4	5	11	4
C1	142.80	143.75	144.82	145.07	155.48
C2	153.18	152.34	150.90	151.90	162.70
C3	150.35	150.25	149.71	150.49	158.06
C4	137.61	139.14	140.69	140.82	145.53
C5	144.48	144.80	145.08	145.78	153.28
C6	138.36	139.49			146.63

ring[27] (nonweighted mean of the heavy atom coordinate) of non-lithium-coordinated **7**−**10** are shown in Table 3. The five-membered rings of all the dianions **7**−**10** have more negative NICS values than the six-membered rings, suggesting greater aromatic character for the five-membered ring, as was calculated in the sila- and germafluorenyl dianions[28] and the parent fluorenyl dianion (Table 3). The negative NICS(1) value of the five-membered ring of **7** also suggests that the 1-stannaindenyl dianion **2** should have an aromatic nature, although the degree of aromaticity of **2** is smaller than those of the germanium and silicon analogues, judging from the NICS(1) values of **8** and **9**. The ^{13}C signal of all the aromatic quaternary carbons of 1,1-disubstituted stannindenes, **1**, **4**, **5**, and **11**, could be assigned by the aid of theoretical calculations and J(Sn−C) values (Table 4).[26]

Conclusion

Reduction of 1,1-diphenylstannaindene with lithium gave the 1-phenyl-1-stannaindenyl anion, which is further reduced to provide the 1-stannaindenyl dianion **2**. The strong upfield resonance due to the diatropic ring current by the 6π-electron system was observed in the ^{7}Li NMR of **2**. Theoretical calculations revealed the planar structure of **2** with no C−C bond alternation within the ring, suggesting the considerable aromatic delocalization of the negative charges. Thus, the 1-stannaindenyl dianion **2** is considerably aromatic. The alkylation of the 1-stannaindenyl dianion **2** by *tert*-butyl chloride gave the 1-stannaindenyl anion **12**.

Experimental Section

General Procedure. All reactions were carried out under argon. THF and diethyl ether used in the synthesis were distilled from sodium benzophenone ketyl under argon atmosphere before use. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AM-400 or an ARX-400 spectrometer with tetramethylsilane as an internal standard. Although ^nJ(Sn−^{13}C) couplings were observed in the ^{13}C NMR spectra as satellite signals, most of the ^nJ(^{119}Sn−^{13}C)s and ^nJ(^{117}Sn−^{13}C)s could not be separately estimated because of broadening. The multiplicities of signals in the ^{13}C NMR given in parentheses were deduced from DEPT spectra. ^{119}Sn (149 MHz) and ^{7}Li NMR (156 MHz) spectra were recorded on a Bruker DRX-400 spectrometer with tetramethylstannane and lithium chloride as external standards, respectively. Wet column chromatography (WCC) was carried out with Merck Kieselgel 60 (SiO_2). Preparative gel permeation chromatography (GPC) was carried out on LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns. All melting points were determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and are uncorrected. High-resolution mass spectra were measured on a JEOL JMX700-AM. Elemental analyses were carried out at the Microanalytical Laboratory of Chemical Analytical Center, Saitama University.

Preparation of 3-Butyl-1,1,2-triphenyl-1-stannaindene (1). To a hexane (8 mL) solution of diphenylacetylene (1.004 g, 5.63 mmol) and TMEDA (1.8 mL, 12 mmol) was added butyllithium (1.58 M in hexane; 8.0 mL, 12.6 mmol) at room temperature. After being stirred for 3 h, to the resulting mixture was added a THF (8 mL) solution of dichlorodiphenylstannane (4.610 g, 13.1 mmol). After the mixture was heated under reflux overnight, volatile substances were evaporated. The residue was subjected to WCC (SiO_2, hexane−ethyl acetate, 20:1) followed by GPC to afford 3-butyl-1,1,2-triphenyl-1-stannaindene (**1**) (1.605 g, 57%). **1**: mp 98−99 °C (recrystallized from hexane); ^{1}H NMR ($CDCl_3$) δ 0.84 (t, J = 7 Hz, 3H), 1.29−1.38 (m, 2H), 1.57−1.65 (m, 2H), 2.64−2.68 (m, 2H), 7.10−7.14 (m, 3H), 7.23−7.35 (m, 9H), 7.40−7.43 (m, 1H), 7.52−7.60 (m, 5H), 7.63−7.73 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.86 ($-\mathrm{CH_2CH_2CH_2}CH_3$), 22.96 ($-\mathrm{CH_2CH_2}CH_2\mathrm{CH_3}$), 28.87 ($-CH_2\mathrm{CH_2CH_2CH_3CH_2}$, J(Sn−C) = 54 Hz), 32.22 ($-\mathrm{CH_2}CH_2\mathrm{CH_2CH_3CH_2}$), 124.94 (CH), 125.15 (CH), 127.35 (CH), 127.43 (CH), 128.29 (CH), 128.77 (CH, J(Sn−C) = 55 Hz), 129.33 (CH, J(Sn−C) = 12 Hz), 135.77 (CH, J(Sn−C) = 44 Hz), 137.08 (CH, J(Sn−C) = 41 Hz), 137.61 (C^4), 138.36 (C^6), 142.80 (C^1, J(Sn−C) = 427, 447 Hz), 144.48 (C^5, J(Sn−C) = 44 Hz), 150.35 (C^3, J(Sn−C) = 95 Hz), 153.18 (C^2, J(Sn−C) = 61 Hz); ^{119}Sn NMR ($CDCl_3$) δ −99.2. Anal. Calcd for $C_{30}H_{28}Sn$: C, 71.03; H, 5.56. Found: C, 71.19; H, 5.63.

Reduction of 3-Butyl-1,1,2-triphenyl-1-stannaindene (1) with Lithium (2.5 equiv). To a mixture of **1** (259 mg, 0.51 mmol) and lithium (9 mg, 1.27 mmol) was added ether (6 mL) at room temperature, and then the reaction mixture was stirred for 4 h. After addition of methyl iodide (0.1 mL, 1.61 mmol) to the reaction mixture, insoluble materials were filtered off. After removal of volatile substances, the residue was subjected to GPC to afford recovered **1** (45 mg, 18%), 3-butyl-1-methyl-1,2-diphenyl-1-stannaindene (**4**) (83 mg, conv 45%), and 3-butyl-1,1-dimethyl-2-phenyl-1-stannaindene (**5**) (24 mg, conv 15%). **4**: pale yellow oil; ^{1}H NMR($CDCl_3$) δ 0.69 (s, J(Sn−H) = 57, 59 Hz, 3H), 0.84 (t, J = 7 Hz, 3H), 1.27−1.37 (m, 2H), 1.54−1.62 (m, 2H), 2.58−2.62 (m, 2H), 7.10−7.14 (m, 3H), 7.23−7.35 (m, 9H), 7.40−7.43 (m, 1H), 7.52−7.60 (m, 5H), 7.63−7.73 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −10.23 ($\mathrm{Sn-CH_3}$, ^1J(Sn−C) = 352, 368 Hz), 13.86 ($-\mathrm{CH_2CH_2CH_2}CH_3$), 22.96 ($-\mathrm{CH_2CH_2}CH_2\mathrm{CH_3}$), 28.78 ($-CH_2\mathrm{CH_2CH_2CH_3CH_2}$, J(Sn−C) = 50 Hz), 32.17 ($-\mathrm{CH_2}CH_2\mathrm{CH_2CH_3CH_2}$), 124.66 (CH, J(Sn−C) = 43 Hz), 124.99 (CH), 127.07 (CH), 127.21 (CH,

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J(Sn−C) = 18 Hz), 128.23 (CH), 128.54 (CH), 129.03 (CH), 129.09 (CH), 135.58 (CH, J(Sn−C) = 45 Hz), 136.43 (CH, J(Sn−C) = 41 Hz), 139.14 (C^4), 139.49 (C^6), 143.75 (C^1, ^1J(Sn−C) = 432, 452 Hz), 144.80 (C^5, J(Sn−C) = 44 Hz), 150.25 (C^3, J(Sn−C) = 89, 93 Hz), 152.34 (C^2, J(Sn−C) = 59 Hz); ^{119}Sn NMR (CDCl$_3$) δ −53.4; HRMS [M], calcd for $\mathrm{C_{25}H_{26}{}^{120}Sn}$ 446.1057, found 446.1057. Anal. Calcd for $\mathrm{C_{25}H_{26}Sn}$: C, 67.45; H, 5.89. Found: C, 66.64; H, 5.79. **5**: colorless oil; ^{1}H NMR (CDCl$_3$) δ 0.45 (s, J(Sn−H) = 56, 59 Hz, 6H), 0.83 (t, J = 7 Hz, 3H), 1.25−1.34 (m, 2H), 1.49−1.55 (m, 2H), 2.51−2.55 (m, 2H), 7.07−7.09 (m, 2H), 7.15−7.21 (m, 1H), 7.22−7.40 (m, 4H), 7.46−7.51 (m, 1H), 7.58−7.65 (m, 1H); ^{13}C NMR (CDCl$_3$) δ −8.93 (Sn−CH$_3$, J(Sn−C) = 332, 348 Hz), 13.63 ($\mathrm{-CH_2CH_2CH_2}\mathit{CH_3}$), 22.73 ($\mathrm{-CH_2CH_2}\mathit{CH_2}\mathrm{CH_3}$), 28.45 ($-\mathit{CH_2}\mathrm{CH_2CH_2CH_3CH_2}$, J (Sn−C) = 48 Hz), 31.84 ($\mathrm{-CH_2}\mathit{CH_2}\mathrm{CH_2CH_3CH_2}$), 124.20 (CH, J(Sn−C) = 41 Hz), 124.58 (CH), 126.46 (CH, J(Sn−C) = 41 Hz), 126.71 (CH, J(Sn−C) = 18 Hz), 127.99 (CH), 128.55 (CH), 135.08 (CH, J(Sn−C) = 45 Hz), 140.69 (C^4, J(Sn−C) = 430, 450 Hz), 144.82 (C^1, J(Sn−C) = 413, 432 Hz), 145.08 (C^5), 149.71 (C^3, J(Sn−C) = 85, 89 Hz), 150.90 (C^2, J(Sn−C) = 55 Hz); ^{119}Sn NMR (CDCl$_3$) δ −17.3; HRMS [M], calcd for $\mathrm{C_{20}H_{24}{}^{120}Sn}$ 384.0900, found 384.0902. Anal. Calcd for $\mathrm{C_{20}H_{24}Sn}$: C, 62.70; H, 6.31. Found: C, 62.14; H, 6.18.

Reduction of 3-Butyl-1,1,2-triphenyl-1-stannaindene (1) with Lithium (Excess). To a mixture of **1** (247 mg, 0.49 mmol) and lithium (26 mg, 3.72 mmol) was added ether (5 mL) at room temperature, and the reaction mixture was stirred for 3 h. After being refluxed for 14 h, the resulting mixture was treated with methyl iodide (0.15 mL, 2.41 mmol). After removal of volatile substances, the residue was subjected to GPC to afford 3-butyl-1,1-dimethyl-2-phenyl-1-stannaindene (**5**) (75 mg, 40%).

Monitoring the Reduction of 3-Butyl-1,1,2-triphenyl-1-stannaindene (1) with Lithium by NMR. Compound **1** (78 mg, 0.154 mmol) and lithium (11 mg, 1.51 mmol) in ether were placed in an NMR tube with C$_6$D$_6$ for NMR lock. The tube was degassed by freeze−pump−thaw cycles and sealed, and the reaction was monitored by NMR spectroscopy. After an ether solution was refluxed overnight, we could assign NMR signals due to 1-stannaindenyl dianion **2**. **2**: ^{13}C NMR (Et$_2$O−C$_6$D$_6$) δ 14.06 ($\mathrm{-CH_2CH_2CH_2}\mathit{CH_3}$), 23.67 ($\mathrm{-CH_2CH_2}\mathit{CH_2}\mathrm{CH_3}$), 30.27 ($-\mathit{CH_2}\mathrm{CH_2CH_2CH_3CH_2}$), 35.08 ($\mathrm{-CH_2}\mathit{CH_2}\mathrm{CH_2CH_3CH_2}$), 112.50 (CH), 121.04 (CH), 122.26 (CH), 123.57 (C^2), 127.01 (CH), 128.72 (CH, J(Sn−C) = 14 Hz), 135.62 (C^3), 143.66 (CH, J(Sn−C) = 40 Hz), 152.59 (C^5, J(Sn−C) = 37 Hz), 176.16 (C^4, J(Sn−C) = 357, 372 Hz), 193.24 (C^1, J(Sn−C) = 360 Hz); ^{119}Sn NMR (Et$_2$O−C$_6$D$_6$) δ −9.2; ^{7}Li NMR (Et$_2$O−C$_6$D$_6$) δ −5.8. The ^{1}H signals of **2** could not be assigned because of overlapping of signals due to **2** and a solvent. The ^{13}C NMR signal due to **6** could be assigned by subtracting the signals for **2** from those for the reaction mixture. **6**: ^{13}C NMR (Et$_2$O−C$_6$D$_6$) δ 14.10 ($\mathrm{-CH_2CH_2CH_2}\mathit{CH_3}$), 23.50 ($\mathrm{-CH_2CH_2}\mathit{CH_2}\mathrm{CH_3}$), 29.76 ($-\mathit{CH_2}\mathrm{CH_2CH_2CH_3CH_2}$), 33.17 ($\mathrm{-CH_2}\mathit{CH_2}\mathrm{CH_2CH}$), 122.55 (CH), 123.76 (CH), 123.86 (CH), 125.05 (CH), 125.13 (CH), 126.97 (CH), 127.02 (CH), 127.46 (CH), 136.14 (CH), 138.33 (CH), 147.31 (C), 151.81 (C), 154.98 (C), 157.53 (C), 164.44 (C), 168.51 (C); ^{119}Sn NMR (Et$_2$O−C$_6$D$_6$) δ −104.8. The ^nJ(Sn−C)s could not be estimated because of low S/N ratios. The ^{1}H signals due to **6** could not be assigned because of overlapping of signals due to **6**, **2**, and a solvent.

Synthesis of 1-*tert*-Butylstannaindenyl Anion 12 by the Reaction of 1-Stannaindenyl Dianion 2 with *tert*-Butyl Chloride. To a mixture of **1** (251 mg, 0.49 mmol) and lithium (32 mg, 4.65 mmol) was added ether (5 mL), and the mixture was stirred for 21 h at room temperature. To the resulting solution of **2** was added *tert*-butyl chloride (0.08 mL, 0.72 mmol) at room temperature. After being stirred for 20 min, the resulting solution of **12** was treated with methyl iodide (0.1 mL, 1.65 mmol). After removal of volatile substances, the residue was subjected to GPC to afford 3-butyl-1-*tert*-butyl-1-methyl-2-diphenyl-1-stannaindene (**11**) (83 mg, 40%). **11**: colorless oil; ^{1}H NMR (CDCl$_3$) δ 0.45 (s, J(Sn−H) = 51, 54 Hz, 3H), 0.82 (t, J = 7 Hz, 3H), 1.17 (J(Sn−H) = 72, 75 Hz, 9H), 1.28−1.34 (m, 2H), 1.46−1.59 (m, 2H), 2.51−2.58 (m, 2H), 7.07−7.09 (m, 2H), 7.13−7.16 (m, 1H), 7.22−7.27 (m, 1H), 7.29−7.37 (m, 4H), 7.46−7.50 (m, 1H), 7.52−7.62 (m, 1H); ^{13}C NMR (CDCl$_3$) δ −11.64 (Sn−CH$_3$, ^1J(Sn−C) = 274, 287 Hz), 13.87 ($\mathrm{-CH_2CH_2CH_2}\mathit{CH_3}$), 22.93 ($\mathrm{-CH_2CH_2}\mathit{CH_2}\mathrm{CH_3}$), 28.45 ($\mathit{C}\mathrm{(CH_3)_3}$), 28.74 ($-\mathit{CH_2}\mathrm{CH_2CH_2CH_3CH_2}$, J(Sn−C) = 44 Hz), 30.56 ($\mathrm{C(}\mathit{CH_3}\mathrm{)_3}$), 32.20 ($\mathrm{-CH_2}\mathit{CH_2}\mathrm{CH_2CH}$), 124.46 (CH, J(Sn−C) = 37 Hz), 124.67 (CH), 126.52 (CH, J(Sn−C) = 38 Hz), 127.04 (CH, J(Sn−C) = 16 Hz), 128.21 (CH), 128.62 (CH), 135.51 (CH, J(Sn−C) = 43 Hz), 140.82 (C^4), 145.07 (C^1), 145.78 (C^5, J(Sn−C) = 43 Hz), 150.49 (C^3, J(Sn−C) = 75, 78 Hz), 151.90 (C^2, J(Sn−C) = 47 Hz); ^{119}Sn NMR (CDCl$_3$) δ −15.6; HRMS [M], calcd for $\mathrm{C_{23}H_{30}{}^{120}Sn}$ 426.1369, found 426.1368. Anal. Calcd for $\mathrm{C_{23}H_{30}Sn}$: C, 64.97; H, 7.11. Found: C, 65.19; H, 7.04.

Monitoring the Reaction of 1-Stannaindenyl Dianion 2 with *tert*-Butyl Chloride by NMR. To a mixture of **1** (404 mg, 0.80 mmol) and lithium (54 mg, 7.77 mmol) was added ether (4 mL), and the mixture was heated under reflux for 12 h. To the resulting solution of **2** was added *tert*-butyl chloride (0.09 mL, 0.82 mmol) at room temperature. After being stirred for 2 h, an aliquot of the solution was placed in an NMR tube with C$_6$D$_6$ (0.2 mL) for NMR lock. The tube was degassed by freeze−pump−thaw cycles and sealed, and the reaction was monitored by NMR spectroscopy. **12**: ^{119}Sn NMR(Et$_2$O−C$_6$D$_6$) δ −30.3.

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