Electronic Supporting Information for

Synthesis, Structure and Reactions of a Trianion Equivalent, Trilithiostannane

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Experimental

General Procedure. All reactions were carried out under an argon atmosphere. THF, diethyl ether and THF-d_8 used in the synthesis or NMR analyses were distilled from sodium benzophenone ketyl under an argon atmosphere followed by redistillation from potassium mirror using trap-to-trap technique. ^{1}H (400 MHz), ^{13}C (101 MHz), ^{7}Li (156 MHz) and ^{119}Sn (149 MHz) spectra were recorded on a Bruker DPX-400 or a DRX-400 spectrometer. ^{1}H and ^{13}C NMR chemical shifts were recorded in ppm relative to tetramethylsilane (0 ppm) and were referenced internally with respect to the residual proton impurity ($CDCl_3$: 7.25 ppm, C_6D_6: 7.15 ppm THF-d_8: 1.73 ppm) and the ^{13}C resonance of the solvent ($CDCl_3$: 77.0 ppm, C_6D_6: 128.0 ppm THF-d_8: 67.4 ppm), respectively. The multiplicities of signals in ^{13}C NMR are given in parentheses. ^{7}Li NMR chemical shifts were referenced with lithium chloride (δ = 0 ppm) as an external

standard. ^{119}Sn NMR chemical shifts were referenced with tetramethylstannane (δ = 0 ppm) as an external standard. The ^{n}J(C,Sn) couplings were observed in the ^{13}C NMR spectra as satellite signals. Preparative gel permeation chromatography (GPC) was carried out on an LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H column. Wet column chromatography (WCC) was carried out with Kanto Silica gel 60N (SiO_2). Preparative thin layer chromatography (PTLC) was carried out with Merck Kieselgel 60 (SiO_2). Melting point was determined on a Mitamura Riken Kogyo MEL-TEMP apparatus and was uncorrected. IR spectra were measured at room temperature on a JASCO FT/IR-460 plus. Elemental analysis was carried out at the Microanalytical Laboratory of Molecular Analysis and Life Science Center, Saitama University.

Preparation of ArSn(SiHMe$_2$)$_3$ 2. A THF (12 mL) solution of 1,2-dibromoethane (0.58 mL, 6.71 mmol) was heated under reflux in the presence of Mg powder (385 mg, 15.8 mmol) for 30 min. To the mixture was added of Me_2SiHCl (1.5 mL, 13.5 mmol) and the resulting mixture was heated under reflux for 30 min. The resulting mixture was treated with a THF (10 mL) solution of $ArSnCl_3$[S1] (700 mg, 0.99 mmol) and heated under reflux for 24 h. After the removal of volatile substances, materials insoluble in dichloromethane were removed by filtration. After concentration of the filtrate, the residue was subjected to WCC (hexane : ethyl acetate = 20 : 1) followed by GPC to afford $ArSn(SiHMe_2)_3$ **2** (180 mg, 23%) and ArH (136 mg, 28%). **2**: mp 154-156 ˚C(dichloromethane+ethanol). ^{1}H NMR (400 MHz, $CDCl_3$): δ –0.02 (d, J_{HH} = 5 Hz, J_{SnH} = 13, 23 Hz, 18H), 0.96 (d, J_{HH} = 7 Hz, 12H), 1.28 (d, J_{HH} = 7 Hz, 24H), 2.75 (sept, J_{HH} = 7 Hz, 4H), 2.91 (sept, J_{HH} = 7 Hz, 2H), 3.47 (sept, J_{HH} = 7 Hz, J_{SnH} = 80 Hz, 3H), 6.94 (d, J_{HH} = 8 Hz, 2H), 7.02 (s, 4H), 7.20 (t, J_{HH} = 8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ –1.41 (q, J_{SnC} = 33, 43 Hz), 23.62 (d), 24.11 (q), 25.69 (q), 30.55 (d), 34.42 (d), 121.34 (d, J_{SnC} = 56 Hz), 125.26 (d), 130.43 (d, J_{SnC} =34 Hz), 140.54 (s), 141.75 (s), 146.10 (s), 147.88 (s), 148.89 (s, J_{SnC} =31 Hz); ^{119}Sn NMR (150 MHz, $CDCl_3$): δ –434.8. Anal. Calcd for $C_{42}H_{70}Si_3Sn$: C, 64.84; H, 9.07. Found: C, 64.62; H, 9.17.

Preparation of $ArSn(SiHMe_2)_3$ 2 in the presence of triethylamine. A THF (5.0 mL) solution of 1,2-dibromoethane (0.40 mL, 4.68 mmol) was heated under reflux in the presence of Mg powder (250 mg, 10.7 mmol) for 30 min. To the mixture was added a THF solution (50 mL) of Me_2SiHCl (1.1 mL, 9.03 mmol) and the resulting mixture was heated under reflux for 30 min. The resulting mixture was treated with a THF (10 mL) solution of $ArSnCl_3$[S1] (760 mg, 1.08 mmol) in the presence of triethylamine (1.0 mL) at room temperature. After the solution was stirred for 14 h under reflux, the reaction mixture was cooled to room temperature. After the removal of volatile substances, materials insoluble in hexane were removed by filtration. After concentration of the filtrate, the residue was subjected to GPLC to afford $ArSn(SiHMe_2)_3$ **2** (429 mg, 51%).

Generation of $ArSnLi_3$ 4a, quenched by H_2O. Methyllithium (0.92 N solution in diethyl ether, 0.30 mL, 0.28 mmol) was added to a THF solution (3.5 mL) of $ArSn(SiHMe_2)_3$ **2** (36 mg, 0.046 mmol) at room temperature. After the reaction mixture was kept at the same temperature, H_2O (0.1 mL) was added to the reaction mixture. After the removal of volatile substances, materials insoluble in dichloromethane were removed by filtration. After concentration of the filtrate, the residue was recrystallized from dichloromethane and ethanol to give $ArSnH_3$[S1] **3a** (25 mg, 90%).

Generation of $ArSnLi_3$ 4a, quenched by D_2O. Methyllithium (1.14 N solution in diethyl ether, 0.42 mL, 0.48 mmol) was added to a THF solution (3.0 mL) of $ArSn(SiHMe_2)_3$ **2** (62 mg, 0.080 mmol). After the reaction mixture was stirred for 2 h, D_2O (0.3 mL) was added to the reaction mixture at room temperature. After the removal of volatile substances, materials insoluble in hexane were removed by filtration. After the filtrate was dried over anhydrous $MgSO_4$, the filtrate was concentrated. The resulting residue was subjected to PTLC to give $ArSnD_3$ **3b** (35 mg, 72%) (D content: 99%). **3b**: mp 154.8 ˚C(dec.). ^{119}Sn NMR (150 MHz, C_6D_6): δ –389.1 (sept, $^1J_{SnD}$ = 297 Hz); IR (KBr) 1315.2 cm^{-1} (Sn–D).

Generation of $ArSnLi_3$ 4a, quenched by iodomethane. Methyllithium (0.92 N 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, materials insoluble in dichloromethane were 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.

Generation of $ArSnLi_3$ 4a, quenched by bromoethane. Methyllithium (1.09 N solution in diethyl ether, 0.70 mL, 0.76 mmol) was added to a THF solution (3.0 mL) of $ArSn(SiHMe_2)_3$ **2** (62 mg, 0.080 mmol) at room temperature. After the reaction mixture was kept at the same temperature for 1 h, bromoethane (0.4 mL, 5.36 mmol) was added to the reaction mixture. After the removal of volatile substances, materials insoluble in hexane were removed by filtration and concentration of the filtrate gave $ArSnEt_3$ **6** (49 mg, 89%) was obtained. **6**: mp 143.0-143.5 °C(hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.09 (q, J_{HH} = 8 Hz, 6H), 0.69 (t, J_{HH} = 8 Hz, J_{SnH} = 28 Hz, 9H), 0.95 (d, J_{HH} = 7 Hz, 12H), 1.12 (d, J_{HH} = 7 Hz, 12H), 1.21 (d, J_{HH} = 7 Hz, 12H), 2.61 (sept, J_{HH} = 7 Hz, 4H), 2.86 (sept, J_{HH} = 7 Hz, 2H), 6.95 (s, 4H), 7.01 (d, J_{HH} = 8 Hz, 2H), 7.17 (t, J_{HH} = 8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 3.92 (t), 11.41 (q, J_{SnC} = 33 Hz), 22.91 (q), 24.23 (q), 25.85 (q), 31.59 (d), 34.50 (d), 120.47 (d), 125.98 (d), 129.37 (d, J_{SnC} = 36, 42 Hz), 139.88 (s), 144.85 (s), 146.49 (s), 147.93 (s), 148.21 (s); ^{119}Sn NMR (150 MHz, $CDCl_3$):δ –56.6. Anal. Calcd for $C_{42}H_{64}Sn$: C, 73.36; H, 9.38. Found: C, 73.44; H, 9.46.

NMR Measurement of $ArSnLi_3$ 4a. In a glovebox, THF-d_8 was added to a mixture of MeLi-Et_2O 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.

Generation of $ArSnK_3$ 4b, quenched by iodomethane. Potassium *t*-butoxide (0.157 N solution in THF, 4 mL, 0.63 mmol) was added to a THF solution (2.0 mL) of $ArSn(SiHMe_2)_3$ **2** (49 mg, 0.063 mmol) at room temperature. After the reaction mixture was kept at the same temperature for 1 h, iodomethane (0.5 mL, 8.03 mmol) was added to the reaction mixture. After the removal of volatile substances, materials insoluble in dichloromethane were removed by filtration. After concentration of the filtrate, the residue was recrystallized from dichloromethane and methanol to give $ArSnMe_3$ **5** (38 mg, 92%).

NMR Measurement of $ArSnK_3$ 4b. THF (1 mL) and C_6D_6 (0.2 mL) were added to a mixture of potassium *t*-butoxide (49 mg, 0.44 mmol) and $ArSn(SiHMe_2)_3$ **2** (55 mg, 0.069 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-C_6D_6):δ –473.

References

[S1] M. Saito, H. Hashimoto, T. Tajima and M. Ikeda, *J. Organomet. Chem.*, 2007, **692**, 2729.

Theoretically optimized coordinates of $ArSnLi_3$ (cartesian coordinate in angstrom) at the B3LYP/LanL2DZPD(Sn),6-31+G(d) (C, H, Li) level.

Geometry **A**

C 0 1.246300 0.450314 2.256852

C 0	0.036807	0.578737	2.943415
C 0	-1.153854	0.445288	2.227884
C 0	-1.143316	0.192974	0.848494
C 0	0.069746	0.062130	0.105577
C 0	1.259332	0.196909	0.879823
Sn 0	0.091620	-0.321098	-2.167669
C 0	-2.467366	0.052678	0.149342
C 0	-3.109666	1.189120	-0.409598
C 0	-3.071927	-1.227637	0.008793
C 0	-4.311399	1.017146	-1.122889
C 0	-4.272376	-1.346639	-0.712819
C 0	-4.908215	-0.239310	-1.298204
C 0	-2.537057	2.593551	-0.229501
C 0	-2.557380	3.437994	-1.515625
C 0	-3.269130	3.319158	0.918939
C 0	-6.214596	-0.383489	-2.069848
C 0	-6.066985	-1.294427	-3.303548
C 0	-7.356314	-0.870871	-1.156693
C 0	-2.454384	-2.468117	0.651142
C 0	-3.157806	-2.777091	1.989505
C 0	-2.452161	-3.703171	-0.266300
C 0	2.568241	0.044327	0.165048
C 0	3.226174	1.180497	-0.380122
C 0	3.162068	-1.243518	0.038909
C 0	4.371352	0.980152	-1.188709
C 0	4.313371	-1.391317	-0.769581
C 0	4.897869	-0.298222	-1.435375
C 0	2.771457	2.603289	-0.043681
C 0	2.796227	3.579178	-1.236700
C 0	3.620663	3.169447	1.116010
C 0	2.637207	-2.438826	0.839264
C 0	3.453695	-2.600494	2.140844
C 0	2.620031	-3.769360	0.062031
C 0	6.157490	-0.459513	-2.278474
C 0	6.027733	-1.554129	-3.352567
C 0	7.389877	-0.709596	-1.384228
Li 0	2.354864	-1.799545	-2.051553
Li 0	-2.580988	-0.358211	-2.187858
Li 0	2.387229	1.040717	-2.522208
H 0	2.186776	0.545203	2.797786
H 0	0.022950	0.775504	4.011909
H 0	-2.106641	0.537619	2.747545

H 0	-4.794323	1.886631	-1.560475
H 0	-4.718698	-2.330144	-0.824397
H 0	-1.490896	2.476239	0.064415
H 0	-2.053778	4.395097	-1.335157
H 0	-2.028591	2.925121	-2.326488
H 0	-3.576712	3.669588	-1.849922
H 0	-3.190185	2.759915	1.857199
H 0	-2.835448	4.313426	1.079983
H 0	-4.334502	3.450281	0.690820
H 0	-6.485335	0.618042	-2.430406
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H 0	-5.795190	-2.317263	-3.016894
H 0	-7.484727	-0.208200	-0.293985
H 0	-8.302969	-0.900799	-1.708722
H 0	-7.159415	-1.880574	-0.777605
H 0	-1.411798	-2.225089	0.870550
H 0	-3.089686	-1.930578	2.680881
H 0	-4.220256	-3.004784	1.835990
H 0	-2.694517	-3.646240	2.471751
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H 0	-1.951281	-3.482409	-1.215373
H 0	-1.909524	-4.522088	0.220877
H 0	4.894440	1.840415	-1.603265
H 0	4.787392	-2.367198	-0.846589
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H 0	3.271006	4.170413	1.396566
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H 0	3.058247	-3.427199	2.743385
H 0	4.507560	-2.813848	1.923656
H 0	3.410579	-1.689869	2.746239
H 0	1.986005	-3.707905	-0.836901
H 0	3.623300	-4.105411	-0.228698
H 0	2.186250	-4.559458	0.685519
H 0	6.318742	0.494555	-2.799041
H 0	6.931172	-1.592721	-3.972230
H 0	5.897947	-2.546463	-2.903550

H 0	5.172094	-1.365329	-4.011909
H 0	8.302969	-0.755768	-1.989497
H 0	7.510529	0.088619	-0.643858
H 0	7.297526	-1.658016	-0.841942

Geometry **B**

C 0	2.201000	0.156000	1.200000
C 0	2.913000	0.193000	0.000000
C 0	0.031000	0.087000	0.000000
C 0	0.799000	0.099000	1.204000
Sn 0	-2.264000	0.397000	0.000000
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C 0	0.047000	2.602000	2.645000
C 0	-1.099000	3.622000	2.769000
C 0	1.329000	3.147000	3.312000
C 0	0.357000	-2.529000	2.524000
C 0	1.711000	-2.940000	3.144000
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C 0	-2.011000	-0.170000	6.364000
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C 0	-1.097000	-0.713000	7.482000
Li 0	-3.414000	-1.999000	0.000000
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C 0	-0.140000	-1.228000	-3.154000
C 0	-0.982000	1.123000	-4.429000
C 0	-0.835000	-1.272000	-4.377000
C 0	-1.277000	-0.110000	-5.029000
C 0	0.047000	2.602000	-2.645000
C 0	-1.099000	3.622000	-2.769000
C 0	1.329000	3.147000	-3.312000
C 0	0.357000	-2.529000	-2.524000

C 0	1.711000	-2.940000	-3.144000
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