Supplementary Material (ESI) for Chemical Communications

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Synthesis and Properties of a Stable 6-Stannapentafulvene

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Expreimental Section

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. Solvents used for the reactions were purified by The Ultimate Solvent System (GlassContour Company).[1] ^{1}H NMR (300 MHz), ^{13}C NMR (76 MHz), and ^{119}Sn NMR (111 MHz) spectra were measured in $CDCl_3$ or C_6D_6 with a JEOL JNM-AL300 spectrometer. In ^{1}H NMR, signals due to $CHCl_3$ (7.25 ppm) and C_6D_5H (7.15 ppm) were used as references, and those due to $CDCl_3$ (77 ppm) and C_6D_6 (128 ppm) were used in ^{13}C NMR. ^{119}Sn NMR was measured with NNE technique using $SnMe_4$ as an external standard. Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT technique. High-resolution mass spectral data were obtained on a JEOL JMS-SX102GC/MS spectrometer. WCC (wet column chromatography) was performed on Wakogel C-200. PTLC (preparative thin-layer chromatography) was performed with Merck Kieselgel 60 PF254 (Art. No. 7747). GPLC (gel permeation liquid chromatography) was performed on an LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL 1H and 2H columns (eluent: chloroform or toluene). All melting points were determined on a Yanaco micro melting point apparatus and were uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. Tbt(Mes)$SnCl_2$ was prepared according to the reported procedures.[2]

Preparation of 6. To a THF (4 mL) solution of fluorene (102 mg, 0.614 mmol) was added *n*-butyllithium (1.5 M in hexane, 0.340 mL, 0.510 mmol) at –78 ˚C. After stirring at the same temperature for 1 h, THF (4 mL) solution of Tbt(Mes)$SnCl_2$ (353 mg, 0.410 mmol) was added to the mixture. After stirring for 3 h at –78 ˚C, the reaction mixture was warmed to room temperature and stirred for 12 h at the same temperature. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed. The residue was separated by GPLC ($CHCl_3$) to afford **6** (304 mg, 0.307 mmol, 75%). **6**: colorless crystals, m.p. 223-224 ˚C (dec.); ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 0.02 (s, 9H), 0.17 (s, 18H), 0.21 (s, 9H), 0.24 (s, 18H), 1.56 (s, 1H), 1.86 (s, 3H), 2.00 (s, 6H), 2.48 (s, 1H), 2.91 (s, 1H), 5.21 (s, 1H), 6.46 (s, 2H), 6.69 (br s, 1H), 6.84 (br s, 1H), 7.03-7.22 (m, 5H), 7.66-7.70 (m, 2H), 8.64 (d, ^{3}J= 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 0.90 (q), 1.15 (q), 1.76 (q), 2.16 (q), 20.86 (q), 26.18 (q), 29.52 (d), 30.50

(d), 30.73 (d), 48.18 (d), 119.36 (d), 119.45 (d), 123.74 (d), 125.18 (d), 125.80 (d), 126.02 (d), 126.22 (d), 126.32 (d), 126.58 (d), 128.56 (d), 128.65 (d), 137.21 (s), 139.82 (s), 140.89 (s), 141.16 (s), 142.43 (s), 142.76 (s), 143.09 (s), 144.90 (s), 145.59 (s), 152.24 (s), 152.64 (s); ^{119}Sn NMR (111 MHz, $CDCl_3$, 25 °C): δ –35.2; Anal. Calcd for $C_{49}H_{79}ClSi_6Sn$: C, 59.40; H, 8.04. Found: C, 59.16; H, 8.06.

Preparation of 7. A CH_2Cl_2 (18 mL) solution of **6** (203 mg, 0.204 mmol) and $AgBF_4$ (ca. 150 mg, 0.77 mmol) was stirred for 1 h at room temperature. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed. The residue was separated by WCC ($CHCl_3$) to afford **7** (183 mg, 0.188 mmol, 92%). **7**: colorless crystals, m.p. 264-266 ˚C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ –0.02 (s, 18H), –0.01 (s, 9H), 0.03 (s, 9H), 0.09 (s, 18H), 1.39 (s, 1H), 1.73 (s, 6H), 1.88 (br s, 1H), 1.97 (br s, 1H), 2.08 (s, 3H), 4.90 (s, 1H), 6.45 (br s, 1H), 6.49 (s, 2H), 6.57 (br s, 1H), 7.13 (dd, ^3J= 7.5 Hz, ^3J= 7.5 Hz 1H), 7.22-7.32 (m, 3H), 7.49 (d, ^3J= 7.5 Hz, 1H), 7.71-7.73 (m, 2H), 7.94 (d, ^3J= 6.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 0.76 (q), 0.84 (q), 1.02 (q), 1.13 (q), 1.51 (q), 20.85 (q), 25.23 (q), 25.29 (q), 30.65 (d), 31.11 (d), 31.49 (d), 49.74 (d, $^2J_{CF}$ = 9.3 Hz), 119.42 (d), 119.72 (d), 122.62 (d), 124.95 (d), 125.60 (d), 125.74 (d), 125.85 (d), 125.95 (d), 126.37 (d), 127.48 (d), 128.10 (d), 138.93 (s, $^2J_{CF}$ = 54 Hz), 139.21 (s), 139.95 (s), 140.72 (s), 143.32 (s), 143.47 (s, $^2J_{CF}$ = 33 Hz), 143.64 (s), 144.27 (s), 145.68 (s), 151.49 (s), 152.02 (s); ^{19}F NMR (283 MHz, $CDCl_3$, 25 °C): δ –177.1 ($^1J_{SnF}$ = 2340 Hz (^{117}Sn), 2450 Hz (^{119}Sn); ^{119}Sn NMR (111 MHz, $CDCl_3$, 25 °C): δ –50.5 ($^1J_{SnF}$ = 2450 Hz); Anal. Calcd for $C_{49}H_{79}FSi_6Sn$: C, 60.40; H, 8.17. Found: C, 60.51; H, 8.17.

Synthesis of 1a. To a solution of **7** (36.0 mg, 0.0369 mmol) in dry Et_2O (6 mL) placed in a glovebox filled with argon was added *t*-butyllithium (1.0 M hexane solution, 0.060 mL, 0.060 mmol) at –40 ˚C. The reaction mixture was stirred for 0.5 h at the same temperature and for 1 h while being warmed up to room temperature. After removal of the solvents, dry hexane was added to the residue and the mixture was filtered with Celite®. The filtrate was evaporated to afford **1a** in a pure form as purple crystalline solids (35.2 mg, 0.0369 mmol, quant.).

Reaction of 1a with water. To a THF (1 mL) solution of **1a** (16.6 mg, 0.0174 mmol) was added H_2O (0.3 mL) at room temperature. After addition of an aqueous solution (sat.) of NH_4Cl, the mixture was extracted with Et_2O. After removal of the solvent, the residue was separated by PTLC ($CHCl_3$/hexane = 1/5) to afford **9** (12.9 mg, 0.0133 mmol, 76%). **9**: colorless crystals, m.p. 246-248 ˚C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ –0.09 (s, 9H), –0.06 (s, 9H), 0.07 (s, 18H), 0.09 (s, 18H), 0.59 (s, 1H, O<u>H</u>), 1.39 (s, 1H), 1.67 (s, 6H), 2.06 (s, 3H+2H), 4.90 (s, 1H), 6.39 (s, 2H), 6.43 (br s, 1H), 6.55 (br s, 1H), 7.06 (dd, ^3J= 7.2 Hz, ^3J= 7.2 Hz, 1H), 7.13 (dd, ^3J= 7.2 Hz, ^3J= 7.2 Hz, 1H), 7.27-7.32 (m, 2H), 7.48 (d, ^3J= 7.5 Hz, 1H), 7.57 (d, ^3J= 7.5 Hz, 1H), 7.73 (dd, ^3J= 4.4 Hz, ^3J= 4.4 Hz, 1H), 7.85 (dd, ^3J= 4.2 Hz, ^3J= 4.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 0.78 (q), 0.86 (q), 0.90 (q), 1.11 (q), 1.52 (q), 1.81 (q), 20.83 (q), 25.73 (q), 30.48 (d), 31.37 (d), 31.66 (d), 50.13 (d), 119.54 (d), 120.01 (d), 122.57 (d), 124.01 (d), 124.78 (d), 125.06 (d), 125.30 (d), 125.52 (d), 125.97 (d), 127.40 (d), 127.74 (d), 138.25 (s), 138.48 (s), 139.79 (s), 140.04 (s), 140.34 (s), 143.72 (s), 144.39

(s), 144.72 (s), 144.75 (s), 150.69 (s), 151.18 (s); ^{119}Sn NMR (111 MHz, $CDCl_3$, 25 °C): δ –87.5; High resolution FAB-MS *m/z* calcd for $C_{49}H_{80}OSi_6{}^{120}Sn$: 972.3847, found: 972.3842. Anal. Calcd for $C_{49}H_{80}OSi_6Sn•1.5H_2O$: C, 58.89; H, 8.37. Found: C, 58.95; H, 8.29.

Reaction of 1a with 2,3-dimethyl-1,3-butadiene. To a THF (2 mL) solution of **1a** (75.4 mg, 0.0790 mmol) was added 2,3-dimethyl-1,3-butadiene (0.4 mL) at room temperature. After removal of the solvent, hexane was added to the residue. The resulting suspension was filtered through Celite®, and the solvent was removed. The residue was separated by PTLC (hexane) to afford **10** (41.9 mg, 0.0404 mmol, 51%). **10**: colorless crystals, m.p. 180-183 ˚C (dec.); ^{1}H NMR (300 MHz, C_6D_6, 50 °C): δ –0.06 (s, 18H), 0.12 (s, 18H), 0.15 (s, 9H), 0.21 (s, 9H), 1.36 (s, 3H), 1.41 (s, 1H), 1.77 (s, 3H), 2.00 [(s, 3H+1H) + (d, 1H, ^2J = 18.3 Hz)], 2.15 (s, 3H+1H), 2.54 (d, 1H, ^2J = 17.6 Hz), 2.71 [(s, 3H) + (d, 1H, ^2J = 17.6 Hz)], 3.16 (d, 1H, ^2J = 18.3 Hz), 6.52 (br s, 1H), 6.63 (br s, 1H), 6.71 (br s, 1H), 6.90 (br s, 1H), 6.83-7.28 (m, 5H), 7.74-7.81 (m, 2H), 7.90 (m, 1H), ^{13}C NMR (75 MHz, C_6D_6, 50 °C): δ 1.06 (q), 1.27 (q), 1.58 (q), 1.92 (q), 2.37 (q), 2.56 (q), 20.99 (q), 23.51 (q), 24.88 (q), 27.23 (q), 28.55 (t), 29.49 (d), 30.67 (q), 32.33 (d), 33.24 (d), 46.45 (t), 53.53 (s), 120.64 (d), 120.95 (d), 123.17 (d), 124.64 (d), 125.65 (d), 126.25 (d), 126.47 (d), 126.92 (d), 128.58 (d), 128.75 (d), 128.84 (d), 129.14 (s×2), 129.55 (d), 130.11 (s), 138.91 (s), 139.44 (s), 140.57 (s), 140.89 (s), 141.85 (s), 143.19 (s), 145.61 (s), 146.99 (s), 151.28 (s×2), 152.14 (s); ^{119}Sn NMR (111 MHz, C_6D_6, 50 °C): δ –113.1; High resolution FAB-MS *m/z* calcd for $C_{55}H_{88}Si_6{}^{120}Sn$: 1036.4524, found: 1036.4559. Anal. Calcd for $C_{55}H_{88}Si_6Sn•0.5C_6H_6$: C, 64.77; H, 8.53. Found: C, 64.47; H, 8.52.

References

1 A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, and F. J. Timmers, *Organometallics*, **15**, 1518 (1996).

2 Y. Matsuhashi, N. Tokitoh, R. Okazaki, M. Goto, and S. Nagase, *Organometallics*, **12**, 1351 (1993).

Coordinates of the optimized structure for 1c

atom	x	y	z
C	-4.275355	2.962161	-0.524845
C	-2.944778	3.398298	-0.613047
C	-1.886872	2.504525	-0.455713
C	-2.153697	1.153193	-0.194088
C	-3.508428	0.715191	-0.120274
C	-4.560281	1.618269	-0.283516
H	-5.086734	3.673649	-0.653103
H	-2.73431	4.445699	-0.813801
H	-0.864704	2.862397	-0.549408
H	-5.592122	1.279158	-0.227594
C	-2.150857	-1.156848	0.194586
C	-1.880548	-2.507594	0.455642
C	-2.936201	-3.403715	0.614688
C	-4.267891	-2.970485	0.528945
C	-4.556227	-1.627197	0.288319
C	-3.506652	-0.721824	0.123066
H	-0.857418	-2.8632	0.547513
H	-2.723087	-4.450683	0.8149
H	-5.077471	-3.683769	0.658633
H	-5.588915	-1.290338	0.234433
C	-1.27278	-0.000749	0.000312
Sn	0.724969	0.000736	-0.005956
C	1.939717	1.741054	0.107004
C	3.196751	1.757454	-0.5238
C	1.545543	2.87315	0.842844
C	4.028839	2.874713	-0.430642
H	3.535837	0.895856	-1.094298
C	2.37851	3.989336	0.936134
H	0.583591	2.891546	1.348914
C	3.620773	3.992726	0.298671
H	4.994432	2.871936	-0.929859
H	2.057689	4.854805	1.510095
H	4.268351	4.862437	0.371383
C	1.943619	-1.737483	-0.109251
C	3.198679	-1.748769	0.525602
C	1.554384	-2.873041	-0.842364
C	4.033395	-2.864623	0.439364
H	3.534063	-0.884341	1.094005
C	2.389967	-3.987828	-0.92873
H	0.594172	-2.895308	-1.351603
C	3.630098	-3.986212	-0.287105
H	4.997319	-2.857962	0.941745
H	2.072877	-4.856097	-1.500519
H	4.279746	-4.854815	-0.354425