

## ELECTRONIC Supplementary Information

### The hexamethylpentalene dianion and other reagents for organometallic pentalene chemistry

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#### Experimental details

All operations were carried out under a N<sub>2</sub> atmosphere using Schlenk line and glove-box techniques. Solvents were dried using standard methods and distilled under N<sub>2</sub>. The following instrumentation was used: Varian Unity Plus 500 MHz for <sup>1</sup>H, <sup>13</sup>C, <sup>119</sup>Sn (reference SnMe<sub>4</sub>, 112 MHz) NMR spectroscopy; an Enraf-Nonius FR590 KappaCCD diffractometer for X-ray diffraction. Pn\*<sup>-</sup> was prepared according to the procedure described in ref. 18. **1**, **2a** and **2b** proved too oxygen and moisture-sensitive for elemental microanalysis.

**Synthesis of [LiPn\*H, **1**].** To Pn\*<sup>-</sup> (9.50 g, 51.0 mmol) in Et<sub>2</sub>O (200 ml) was added LS-Selectride (1M in THF, 51.0 ml, 51.0 mmol, Aldrich) at room temperature and after stirring for 2 hr a fine precipitate had formed. Reaction continued for a further 72 hr after which the suspension was filtered on a frit, washed with Et<sub>2</sub>O (3 x 50 ml) and the beige pyrophoric solid dried in vacuo. Yield 9.11 g (92 %, 46.9 mol). <sup>1</sup>H NMR (C<sub>5</sub>D<sub>5</sub>N): δ = 1.45 (d, <sup>3</sup>J(H,H) = 6.6 Hz, 3H; Me), 2.00 (s, 3H; Me), 2.20 (s, 3H, Me), 2.31 (s, 3H; Me), 2.37 (s, 3H; Me), 2.47 (s, 3H; Me), 3.14 (br, m, 1H; CH) ppm; <sup>13</sup>C NMR {<sup>1</sup>H} (C<sub>5</sub>D<sub>5</sub>N): δ = 11.5, 12.1, 12.3, 12.6, 13.2, 18.2 (Me), 42.4 (CH), 99.0, 103.9, 109.8, 125.9, 130.4, 131.3 (quaternary C, one unresolved from solvent resonance) ppm; selected IR data (KBr): 1616 cm<sup>-1</sup> (m; ν(C=C)).

**Synthesis of [Li<sub>2</sub>Pn\*(TMEDA)<sub>x</sub>, 2a].** To a stirred suspension of **1** (10.28 g, 52.9 mmol) in hexane (125 ml) was added *n*BuLi (2.5M in hexanes, 31.7 ml, 79.3 mmol) and TMEDA (8 ml, 52.9 mmol), and then brought to reflux for 84 hr. The mixture was then cooled and filtered on a frit, and the solid washed with hexane until the washings were colourless. The highly pyrophoric brown solid was then dried in vacuo (10<sup>-2</sup> mbar). Yield 11.55 g (98%, mmol, *x* = 0.19). *x* is found to vary between 0.1-0.3 and is determined on the NMR scale by conversion to **3** using excess Me<sub>3</sub>SnCl in C<sub>6</sub>D<sub>6</sub>, followed by addition of C<sub>5</sub>D<sub>5</sub>N to solubilise LiCl, and comparative integration of TMEDA resonances with those of the Me groups in **3**. <sup>1</sup>H NMR ([D<sub>8</sub>]THF): δ = 1.98 (s, 6H; Me), 2.04 (s, 12H; TMEDA), 2.19 (s, 4H, TMEDA), 2.35 (s, 12H; Me) ppm; <sup>13</sup>C NMR {<sup>1</sup>H} ([D<sub>8</sub>]THF): δ = 11.2, 13.0 (Me), 46.1 (TMEDA), 58.6 (TMEDA), 84.1, 114.1, 119.02 (quaternary C) ppm.

**Synthesis of [Li<sub>2</sub>Pn\*(TMEDA)<sub>2</sub>, 2b].** **3** (0.30 g, 0.58 mmol) was dissolved in TMEDA (10 ml) to give a pale yellow solution. Halide-free LiMe (1.6 M in Et<sub>2</sub>O, 0.76 ml, 1.20 mmol) was then added rapidly at RT. The colour changed to orange and then dark red over 1 min, and a microcrystalline solid began to precipitate. Warming led to redissolution of this material and slow cooling to -35°C over 24 hr provided dark orange prisms which were suitable for X-ray analysis. Decantation of the supernatant followed by washing with Et<sub>2</sub>O (10 ml) and drying under a flush of N<sub>2</sub> gave an orange solid, yield 78 % (0.195 g, 0.45 mmol) as an extremely air-sensitive powder which readily loses coordinated TMEDA. Characterising data as for **2a**.

**Synthesis of [cis/trans-(SnMe<sub>3</sub>)<sub>2</sub>Pn\*, 3].** To a stirred suspension of **2a** (*x* = 0.19, 1.00 g, 4.5 mmol) in Et<sub>2</sub>O (30 ml) was added a solution of Me<sub>3</sub>SnCl (1.84 g, 9.2 mmol) in Et<sub>2</sub>O (20 ml) at -78°C, followed by warming to RT. The solution immediately turned pale yellow and a fine precipitate of LiCl formed. Volatiles were removed in vacuo and the residue was extracted with pentane (2 x 30 ml) and filtered. The solvent was then stripped to provide *cis/trans*-**3** (2.27 g, 4.4 mmol, 98%) as a pale yellow crystalline solid. Elemental analysis (%) calcd for C<sub>20</sub>H<sub>36</sub>Sn<sub>2</sub>: C 46.74, H 7.06; found C 46.81, H 7.15; <sup>1</sup>H NMR (C<sub>7</sub>D<sub>8</sub>, 173 K): δ = 0.00 (s, <sup>3</sup>J(Sn,H) = 50 Hz, 18H; SnMe<sub>3</sub>, *trans*), 0.09 (s,

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$^3J(\text{Sn,H}) = 50 \text{ Hz}$ , 18H; SnMe<sub>3</sub>, *cis*), 1.64 (s, 6H, Me, *cis*), 1.73 (s, 6H; Me, *trans*), 1.97 (s, 6H; Me, *trans*), 1.99 (s, 6H; Me, *cis*), 2.21 (s, 6H; Me, *cis*), 2.25 (s, 6H; Me, *trans*) ppm;  $^{13}\text{C}$  NMR { $^1\text{H}$ } (C<sub>7</sub>D<sub>8</sub>, 173 K):  $\delta = -9.1$  ( $^1J(^{119}\text{Sn,H}) = 308 \text{ Hz}$ ; SnMe<sub>3</sub>, *trans*),  $-9.0$  ( $^1J(^{119}\text{Sn,H}) = 272 \text{ Hz}$ ; SnMe<sub>3</sub>, *cis*), 11.5 (Me, *cis*), 11.7 (Me, *trans*), 12.3, 14.7 (Me, both *cis* and *trans*), 50.0 (SnC, *cis*), 51.4 (SnC, *trans*), 124.3, 137.1, 147.8 (quaternary-C, *trans*), 126.2, 138.2, 150.8 (quaternary-C, *cis*) ppm;  $^{119}\text{Sn}$  { $^1\text{H}$ } NMR (C<sub>7</sub>D<sub>8</sub>, 173 K):  $\delta = 39.4$  (*trans*), 41.4 (*cis*) ppm. MS (EI): m/z (%): 516.0852 (2) [M<sup>+</sup>], 351 (57) [M<sup>+</sup>-SnMe<sub>3</sub>], 186 (100) [Pn\*<sup>+</sup>].