

Synthesis of **1**: A solution of  $\text{Is}_2\text{SnF}_2$  (1.58 g, 2.81 mmol) in 10 ml mesitylene is allowed to react with  $\text{Si}(\text{PH}_2)_4$  (0.43 g, 2.69 mmol) at  $-30^\circ\text{C}$  in a teflon-vessel. After the reaction mixture has reached room temperature (2h), the volatile components have been removed in vacuo ( $10^{-3}$  torr) leading to the desired product in the form of a colourless powder in quantitative yield.  $^1\text{H}$  NMR (300K,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.10$  (s, 4H, arom. H), 3.35 (sept.,  $^3\text{J}(\text{H}, \text{H}) = 6.6$  Hz, 4 H,  $\text{Me}_2\text{CH}$ ), 2.72 (sept.,  $^3\text{J}(\text{H}, \text{H}) = 6.9$  Hz, 2H,  $\text{Me}_2\text{CH}$ ), 2.41 (dd,  $^1\text{J}(\text{H}, \text{P}) = 121$  Hz,  $^3\text{J}(\text{H}, \text{F}) = 12$  Hz, 2H,  $\text{PH}_2$ ), 1.23 (d,  $^3\text{J}(\text{H}, \text{H}) = 6.9$  Hz, 12H,  $\text{Me}_2\text{CH}$ ), 1.27 (d,  $^3\text{J}(\text{H}, \text{H}) = 6.6$  Hz), 24H,  $\text{Me}_2\text{CH}$ ). Selected MS(EI, 70 eV) data:  $m/z(\%) = 559$  ( $[\text{M-F}]^+$ , 5), 203 ( $\text{Is}^+$ , 100).

$\text{C}_{30}\text{H}_{48}\text{FPSn}$  (577.3): calc. C (62.41%), H (8.38%); obs. C (62.03%), H (8.32%).

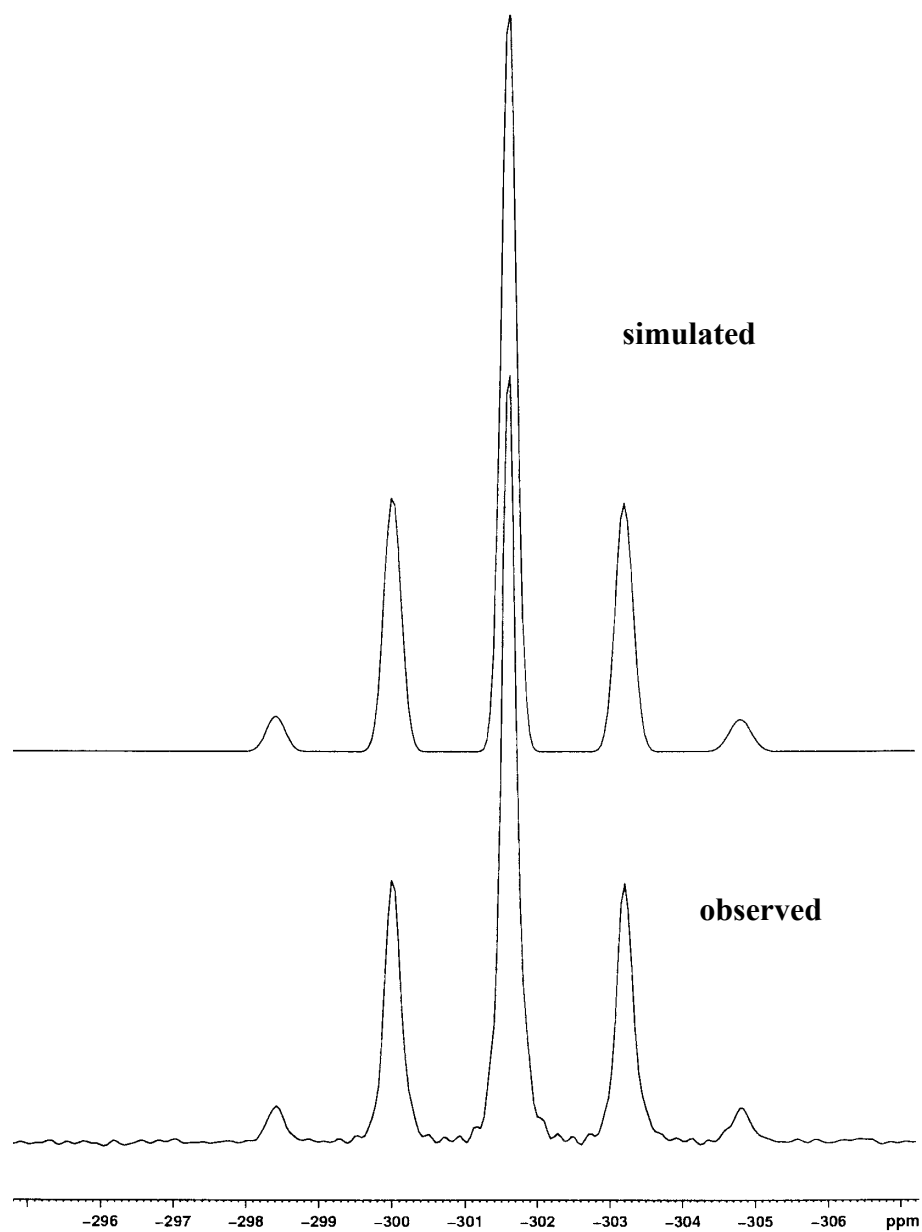
Synthesis of **2**: A solution of **1** (2.22 mmol) in 5 ml THF is stirred for 3 d in a sealed glass tube. The desired product crystallises during the reaction time in the form of large colourless cubes.  $\text{SiF}_4$  escapes after opening the tube and the solvent is removed in vacuo. Recrystallisation of the solid residue in hot THF furnishes analytically pure **2** in quantitative yield.  $^1\text{H}$  NMR (300 K,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.22$  (s, 8H, arom. H), 4.38 (md,  $^1\text{J}(\text{H}, \text{P}) = 121$  Hz, 2H,  $\text{PH}$ ), 3.76 (br.s, 8H,  $\text{Me}_2\text{CH}$ ), 2.82 (sept.,  $^3\text{J}(\text{H}, \text{H}) = 7.1$  Hz, 4H,  $\text{Me}_2\text{CH}$ ), 1.29 (d,  $^3\text{J}(\text{H}, \text{H}) = 7.0$  Hz, 48 H,  $\text{Me}_2\text{CH}$ ), 1.25 (d,  $^3\text{J}(\text{H}, \text{H}) = 7.0$  Hz, 48H,  $\text{Me}_2\text{CH}$ ). Selected MS (EI, 70 eV) data:  $m/z(\%) = 558$  ( $\text{M}/2^+$ , 17), 545 ( $[\text{M}/2\text{-CH}_2]^+$ , 23), 43 ( $i\text{Pr}^+$ , 100).

$\text{C}_{60}\text{H}_{94}\text{P}_2\text{Sn}_2$  (1114.6): calc. C (64.73%), H (8.51%); obs. C (64.36%), H (8.40%).

Synthesis of **3**: A solution of **1** (2.81 mmol) in 10 ml benzene is allowed to react with  $\text{Si}(\text{PH}_2)_4$  (5.62 mmol) at room temperature. After stirring for 16 h, the volatile components of the reaction mixture have been removed in vacuo and the solid residue has been recrystallised in 5 ml hexane. The product can be isolated in the form of large colourless crystals in quantitative yield. M.p. =  $50^\circ\text{C}$ , decomp.  $>180^\circ\text{C}$ .  $^1\text{H}$  NMR (300K,  $\text{C}_6\text{D}_6$ ):  $\delta = 7.17$  (s, 4H, arom. H), 3.45 (sept.,  $^3\text{J}(\text{H}, \text{H}) = 6.6$  Hz, 4 H,  $\text{Me}_2\text{CH}$ ), 2.86 (sept.,  $^3\text{J}(\text{H}, \text{H}) = 6.9$  Hz, 2H,  $\text{Me}_2\text{CH}$ ), 2.21 (md,  $^1\text{J}(\text{H}, \text{P}) = 172.8$  Hz, 4H,  $\text{PH}_2$ ), 1.30 (d,  $^3\text{J}(\text{H}, \text{H}) = 6.9$  Hz, 12H,  $\text{Me}_2\text{CH}$ ), 1.29 (d,  $^3\text{J}(\text{H}, \text{H}) = 6.6$  Hz), 24H,  $\text{Me}_2\text{CH}$ ). Selected MS(EI, 70 eV) data:  $m/z(\%) = 559$  ( $[\text{M-PH}_2]^+$ , 100), 527 ( $\text{Is}_2\text{Sn}^+$ , 11).

$\text{C}_{30}\text{H}_{50}\text{P}_2\text{Sn}$  (591.3): calc. C (60.90%), H (8.50%); obs. C (60.90%), H (8.39%).

Synthesis of **4**: A solution of **3** (1.45 g, 2.45 mmol) in 10 ml THF is allowed to react with Me<sub>3</sub>SnF (0.56 g, 3.07 mmol) in a glass-tube at room temperature. All of the insoluble Me<sub>3</sub>SnF has been consumed after 4 h, leading to a clear solution. The sparingly soluble product precipitates quantitatively after 12 h. Re-crystallisation of the latter solid in hot THF furnishes large crystals. Alternatively, **4** is also suitable in quantitative yield by the reaction of a solution of P(SnMe<sub>3</sub>)<sub>3</sub> (1.83 g, 3.50 mmol) with Me<sub>3</sub>SnF (0.64 g, 3.50 mmol) in an atmosphere of SiF<sub>4</sub> at -20°C in 10 ml THF. Yield: 3.30 g (3.5 mmol). Decomp.>40°C. <sup>1</sup>H NMR (310 K, C<sub>4</sub>D<sub>8</sub>O): δ = 0.43 (s, w<sub>1/2</sub> = 4 Hz); <sup>13</sup>C {<sup>1</sup>H} NMR: δ = -3.5 (s, w<sub>1/2</sub> = 24 Hz). C<sub>12</sub>H<sub>36</sub>F<sub>5</sub>PSiSn<sub>4</sub> (809.24): calc. C (17.81%), H (4.48%) Sn (58.66%); obs. C (17.21%), H (4.32%), Sn (58.39%).



CP/MAS  $^{31}\text{P}$  NMR of **4**

$\delta (^{31}\text{P}) = -301.55$

$J_{\text{PSn}} = 512 \text{ Hz}$