

## Disproportionation of $\text{Sn(II)}\{\text{CH}(\text{SiMe}_3)_2\}_2$ to $\cdot\text{Sn(III)}\{\text{CH}(\text{SiMe}_3)_2\}_3$ and $\cdot\text{Sn(I)}\{\text{CH}(\text{SiMe}_3)_2\}$ : Characterization of the Sn(I) product

### Supporting Information

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## General Procedures

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitrogen. A Vacuum Atmospheres OMNI-Lab glovebox was employed, operating at <0.1 ppm O<sub>2</sub> and <0.1 ppm H<sub>2</sub>O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried in an oven overnight at 120 °C prior to use. C<sub>6</sub>D<sub>6</sub> was dried over 3 Å molecular sieves and was freeze-pump thaw degassed thrice prior to use. All chemicals were procured from either Sigma or Oakwood Chemicals and was used without further purification. Lappert's alkyl stannylene (complex **1**) and Jones' magnesium dimer were synthesized according to the literature.<sup>1-3</sup> NMR spectra were recorded on a 400 MHz Bruker Nanobay AVIIIHD (<sup>1</sup>H, <sup>13</sup>C and <sup>119</sup>Sn) or a 500 MHz Bruker Avance DRX spectrometer and values were recorded in ppm. Data were processed using MestReNova software. UV-vis spectra were recorded as dilute toluene solutions in 3.5 mL quartz cuvettes using an Olis 17 modernized Cary 14 UV-vis-near IR spectrophotometer. Melting points were determined on a Meltemp II apparatus using flame-sealed glass capillaries and are uncorrected.

## Synthetic Methods

### Procedure 1: Synthesis of Sn<sub>6</sub>{CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>6</sub>, cluster **2**

In an argon filled glovebox, 110.0 mg (0.126 mmol) of Lappert's alkyl stannylene (distannene as a solid [Sn(CH(SiMe<sub>3</sub>)<sub>2</sub>)<sub>2</sub>]<sub>2</sub>, complex **1**) was added to a Schlenk flask containing a Teflon stir bar. To the same flask was added 111.3 mg (0.126 mmol) of Jones' magnesium reagent [MgBDI<sup>Dip</sup>]<sub>2</sub> (BDI = (DipNCMe)<sub>2</sub>CH, Dip = 2,6-diisopropylphenyl). The flask was removed from the box and attached to a Schlenk line. Toluene (10 mL) was added to the solid mixture with stirring. An intense pink/red solution resulted after stirring for 5 mins, and after 1 hour, some colorless precipitate had formed. The resulting dark red solution was separated by filtration through a glass fibre tipped canula and concentrated slightly (to ca. 5 mL). Storage of this solution at -30 °C overnight resulted in red-orange crystals with a needle/rod-like morphology (Fig S1). Yield = 78.7 mg (40%).

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, δ in ppm): 0.4, 0.21 (s, 18H, CHSiMe<sub>3</sub>), 0.35 (s, 1H, CHSiMe<sub>3</sub>).

<sup>13</sup>C{<sup>1</sup>H} NMR: 4.01 & 3.91 (CHSiMe<sub>3</sub>), 1.43 (CHSiMe<sub>3</sub>). <sup>119</sup>Sn NMR: +225.9 ppm (slight <sup>1</sup>J<sup>119</sup>Sn-<sup>117</sup>Sn coupling, 210 Hz). <sup>29</sup>Si NMR: -2.10 ppm (s, 4 Si, CHSiMe<sub>3</sub>), -6.19 ppm (8 Si, CHSiMe<sub>3</sub>, <sup>2</sup>J<sup>29</sup>Si-<sup>1</sup>H coupling, 5.5 Hz). M.p.: Sweats at 103 °C, melts at 128-129 °C. UV-Vis analysis: λ/nm (ε/L mol<sup>-1</sup> cm<sup>-1</sup>): 353 (48,000), 496 (broad, 36,363).

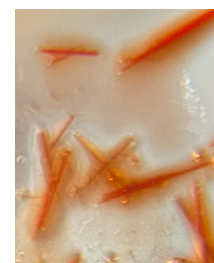


Fig. S1: Crystals of complex **2**.

### Procedure 2: Generation of [BDI<sup>Dip</sup>Mg(CH(SiMe<sub>3</sub>)<sub>2</sub>)], complex **3**

**Direct synthesis:** 126.4 mg (0.29 mmol) of Li(BDI<sup>Dip</sup>) was combined in toluene (20 mL) with 100.2 mg (0.15 mmol) of [(OEt<sub>2</sub>)BrMgCH(SiMe<sub>3</sub>)<sub>2</sub>]<sub>2</sub> and heated to reflux for 2 hr. On cooling, hexane was added, and the mixture was filtered to remove the LiBr side product. Volatiles were removed yielding the product colorless flakes. Yield = 83.5 mg, 93%. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, δ in ppm): -1.59 (s, 1H, CHSiMe<sub>3</sub>), 0.00 (s, 18H, CHSiMe<sub>3</sub>), 1.15 (d, <sup>3</sup>J(<sup>1</sup>H-<sup>1</sup>H) = 6.7 Hz, 12H, Dip-CH<sub>3</sub>), 1.36 (d, <sup>3</sup>J(<sup>1</sup>H-<sup>1</sup>H) = 6.8 Hz, 12H, Dip-CH<sub>3</sub>), 1.62 (s, 6H, BDI-CH<sub>3</sub>), 3.16 (sept, <sup>3</sup>J(<sup>1</sup>H-<sup>1</sup>H) = 6.8 Hz, 4H, Dip-CH), 4.83 (s, 1H, BDI-CH), 7.12 (br s, 6H, Dip-ArH). <sup>13</sup>C{<sup>1</sup>H} NMR: 170.34 (HC{C(CH<sub>3</sub>)NAr}<sub>2</sub>), 144.7 (C<sub>ipso</sub>), 142.1 (C<sub>ortho</sub>), 126.1 (C<sub>para</sub>), 124.3 (C<sub>meta</sub>), 96.0 (HC{C(CH<sub>3</sub>)NAr}<sub>2</sub>), 29.2 (ArCH(CH<sub>3</sub>)<sub>2</sub>), 25.1 (ArCH(CH<sub>3</sub>)<sub>2</sub>), 24.6 (ArCH(CH<sub>3</sub>)<sub>2</sub>), 24.5 (HC{C(CH<sub>3</sub>)NAr}<sub>2</sub>), 5.3 (MgCH{SiMe<sub>3</sub>})<sub>2</sub>, -0.5 (MgCH{SiMe<sub>3</sub>})<sub>2</sub>. M.p.: 209-211 °C, decomposes to red-brown powder at 248 °C.

## NMR Spectra

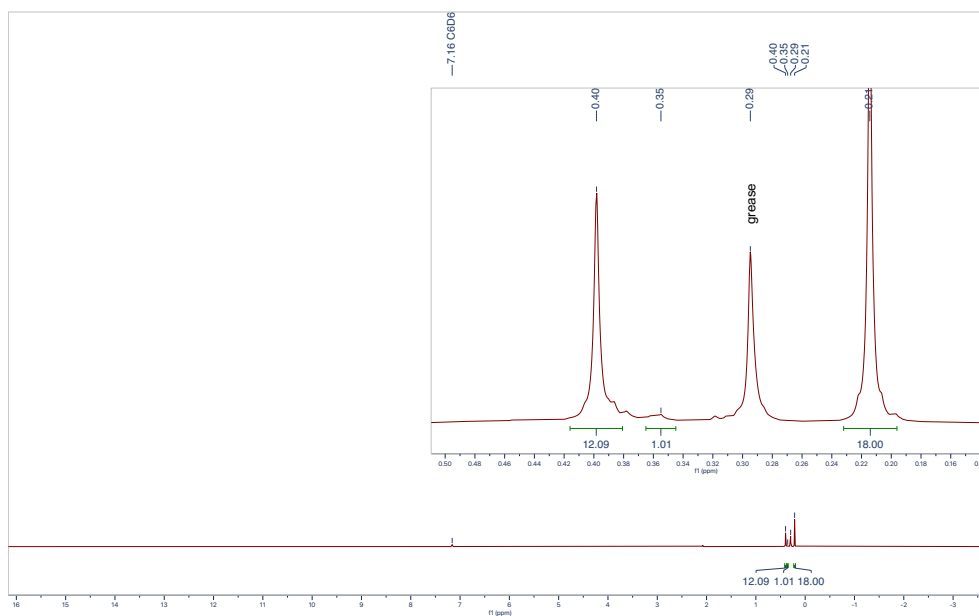


Fig. S2:  $^1\text{H}$  NMR spectrum of complex **2** in  $\text{C}_6\text{D}_6$  at 298 K.

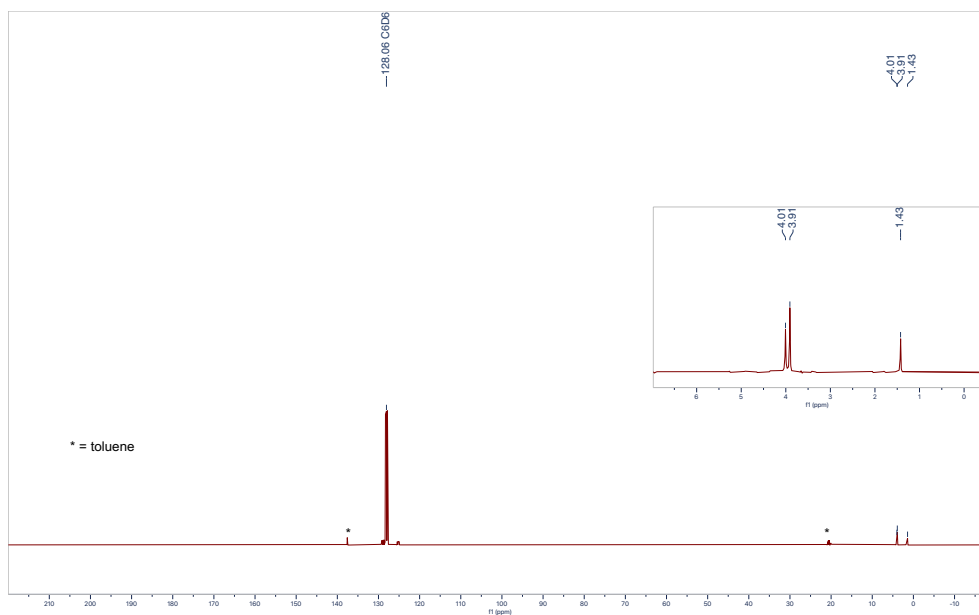
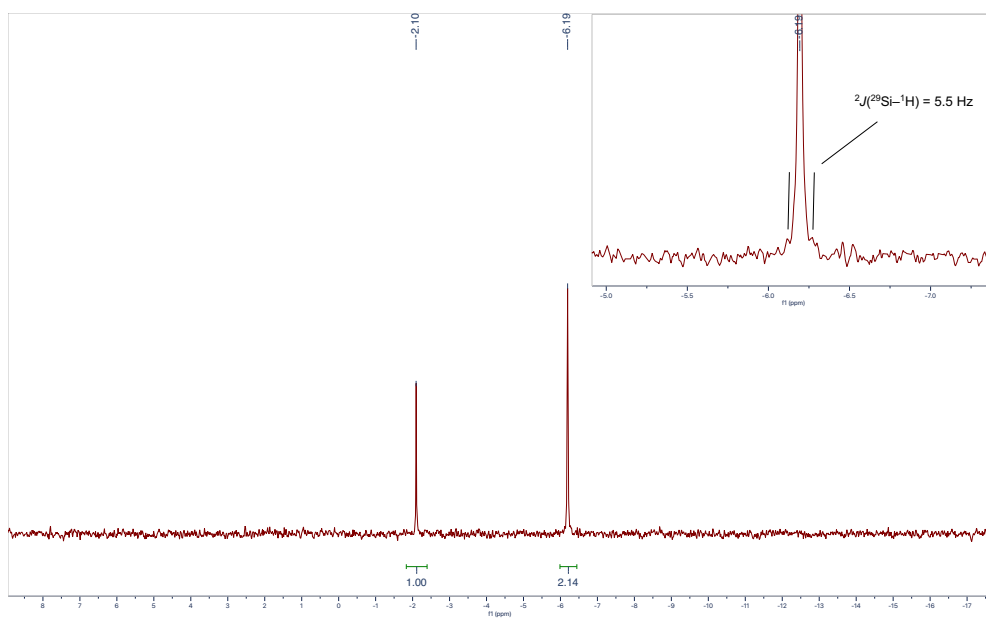
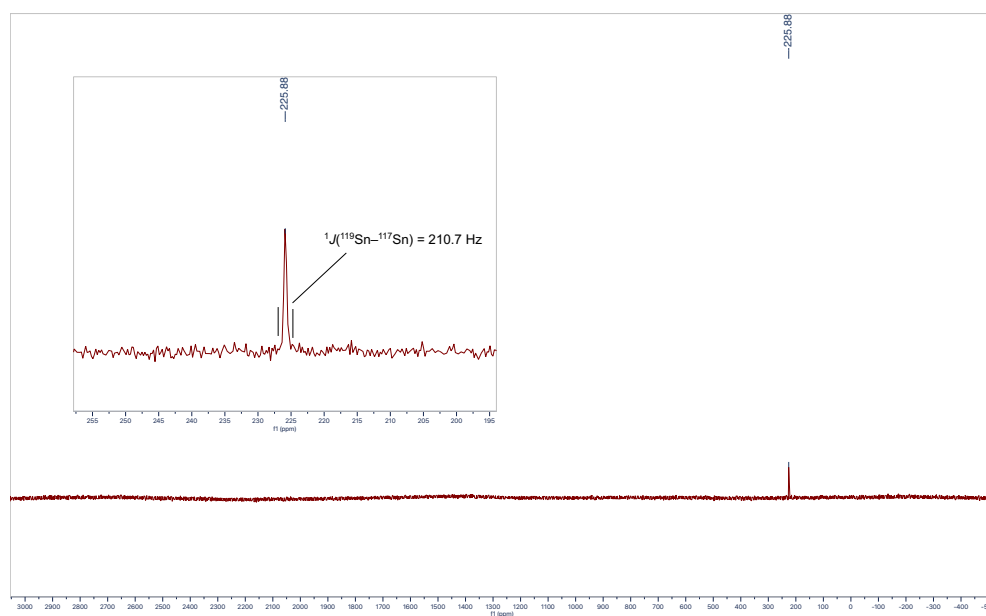


Fig. S3:  $^{13}\text{C}$  NMR spectrum of complex **2** in  $\text{C}_6\text{D}_6$  at 298 K.



**Fig. S4:**  $^{29}\text{Si}$  NMR spectrum of complex **2** in  $\text{C}_6\text{D}_6$  at 298 K.



**Fig. S5:**  $^{119}\text{Sn}$  NMR spectrum of complex **2** in  $\text{C}_6\text{D}_6$  at 298 K.

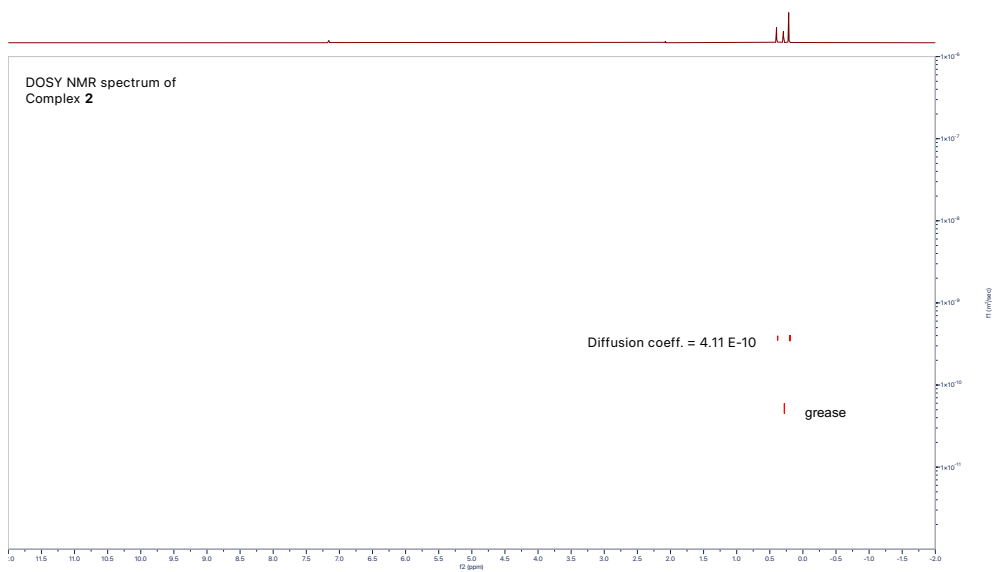


Fig. S6:  $^1\text{H}$  DOSY NMR spectrum of complex **2** in  $\text{C}_6\text{D}_6$  at 298 K.

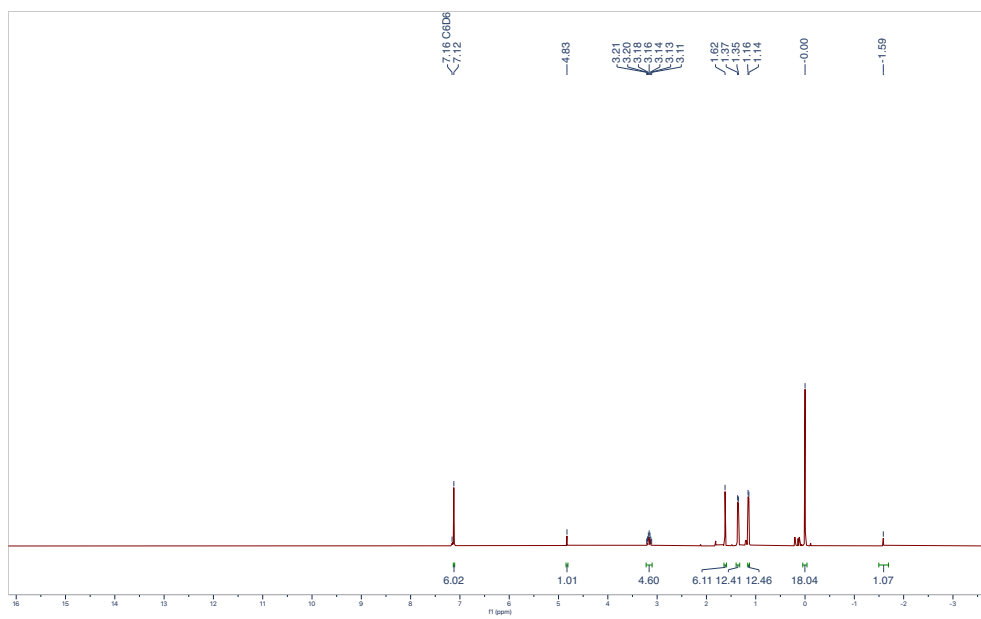
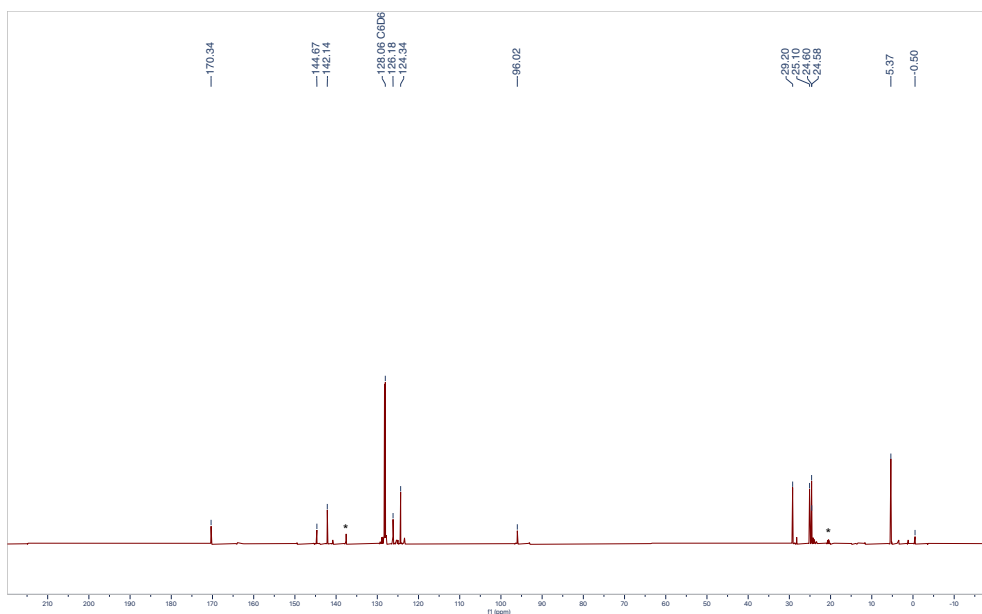
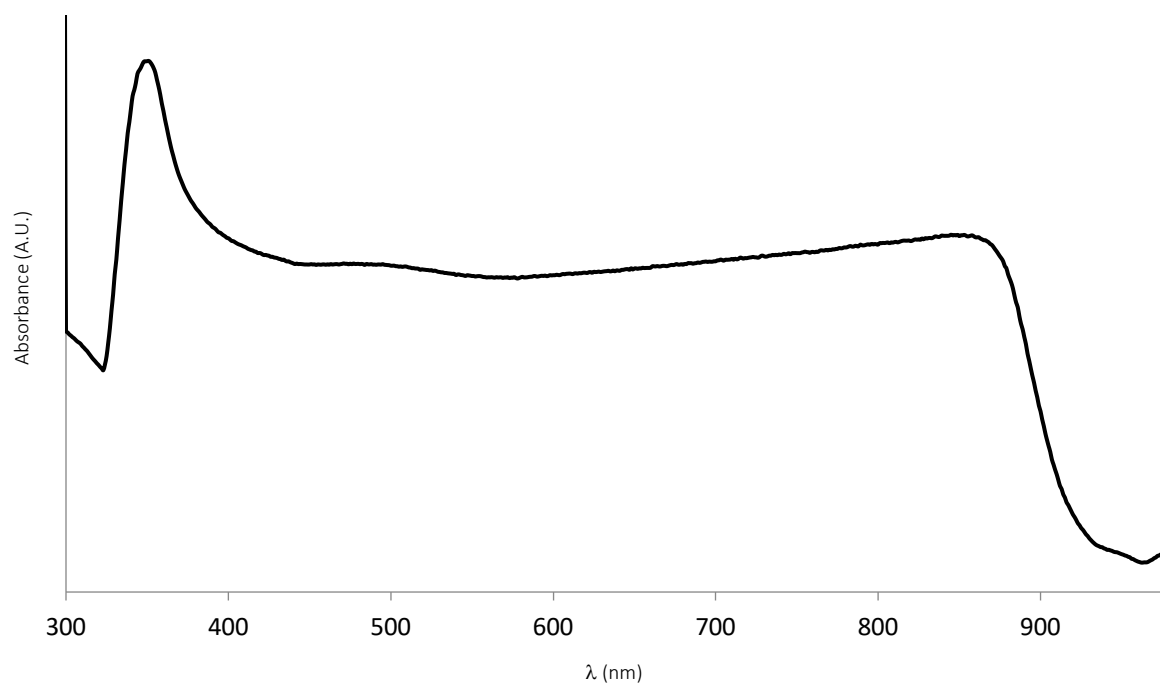


Fig. S7:  $^1\text{H}$  NMR spectrum of complex **3** in  $\text{C}_6\text{D}_6$  at 298 K.



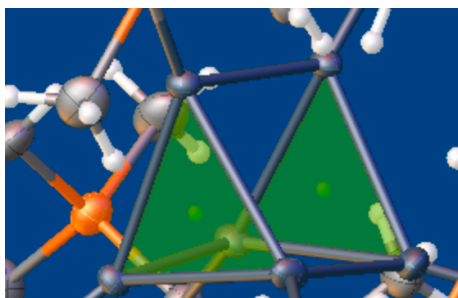
**Fig. S8:**  $^{13}\text{C}$  NMR spectrum of complex **3** in  $\text{C}_6\text{D}_6$  at 298 K. \* denotes toluene.

## UV-Vis Spectrum

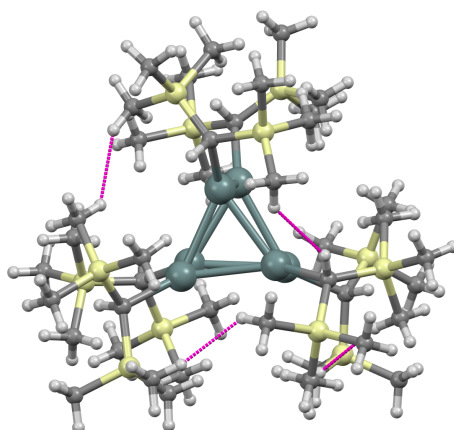


**Fig. S9:** UV-Vis spectrum of complex **2** (27.5  $\mu\text{M}$  in toluene).

## Other Details



**Fig. S10:** Plane centroids used to calculate distance between the triangular faces of complex **2** (Software: Olex2).



**Fig. S11:** H–H close contacts (pink dashed lines) between the SiMe<sub>3</sub> groups of the cluster complex **2**.

## DOSY Calculation

The hydrodynamic radius of **2** in benzene was calculated using the following equation:

$$r = \frac{kT}{6\pi\eta D}$$

Where  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\eta$  is the viscosity of benzene at 300 K and  $D$  is the diffusion coefficient. Following the calculation,  $r = 7.67$  Å. Comparing this with the approximated spherical radius using the volume ( $r_v$ ) from the crystal structure of **2**, we find that  $r_v = 7.69$  Å. These values are in good agreement, suggesting that the species observed at 298 K is indeed the cluster **2**.

## Crystallographic Details of cluster 2

Empirical formula	C <sub>42</sub> H <sub>114</sub> Si <sub>12</sub> Sn <sub>6</sub>
Formula weight	1668.55
Temperature/K	90
Crystal system	triclinic
Space group	P-1
a/Å	13.2745(4)
b/Å	13.7262(3)
c/Å	22.6390(6)
α/°	86.4949(14)
β/°	76.8746(14)
γ/°	72.0005(13)
Volume/Å <sup>3</sup>	3820.46(18)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.450
μ/mm <sup>-1</sup>	2.143
F(000)	1668.0
Crystal size/mm <sup>3</sup>	0.418 × 0.16 × 0.096
Reflections collected	30190
Independent reflections	17603 [R <sub>int</sub> = 0.0209, R <sub>sigma</sub> = 0.0340]
Goodness-of-fit on F <sup>2</sup>	1.034
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0314, wR <sub>2</sub> = 0.0697
Final R indexes [all data]	R <sub>1</sub> = 0.0411, wR <sub>2</sub> = 0.0739
CCDC Number	2252108

## References

- 1 B. J. Peter Davidson and M. F. Lappert, *J. Chem. Soc. Chem. Comm.*, 1973, 317a–317a.
- 2 P. J. Davidson, D. H. Harris and M. F. Lappert, *J. Chem. Soc. Dalton Trans.*, 1976, 2268–2274.
- 3 S. P. Green, C. Jones and A. Stasch, *Science (1979)*, 2007, **318**, 1754–1757.