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## Synthesis and structure of an acyclic dialkylstannylene

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## Abstract

The reaction between  $i\text{Pr}_2\text{P}\text{Cl}$  and one equivalent of  $\text{MeMgBr}$ , followed by one equivalent of  $\text{BH}_3\cdot\text{SMe}_2$  gives the phosphine-borane  $i\text{Pr}_2\text{P}(\text{BH}_3)\text{Me}$  (**4**). Treatment of **4** with  $n\text{BuLi}$ , followed by  $\text{Me}_3\text{SiCl}$  gives the sterically demanding phosphine-borane  $\{i\text{Pr}_2\text{P}(\text{BH}_3)\}(\text{Me}_3\text{Si})\text{CH}_2$  (**5**) in good yield. Metalation of **5** with  $n\text{BuLi}$  yields  $\{i\text{Pr}_2\text{P}(\text{BH}_3)\}(\text{Me}_3\text{Si})\text{CHLi}$  (**6**), which was crystallised as the TMEDA adduct  $[\{i\text{Pr}_2\text{P}(\text{BH}_3)\}(\text{Me}_3\text{Si})\text{CH}]\text{Li}(\text{TMEDA})$  (**6a**) and characterised by X-ray crystallography. The reaction between two equivalents of *in situ*-generated **6** and  $\text{Cp}_2\text{Sn}$  in toluene gives the dialkylstannylene  $[\{i\text{Pr}_2\text{P}(\text{BH}_3)\}(\text{Me}_3\text{Si})\text{CH}]_2\text{Sn}$  (**7**), which was crystallised from methylcyclohexane/THF as the *rac* diastereomer. X-ray crystallography reveals that stabilisation of the Sn centre in **7** is afforded by two agostic-type B-H...Sn interactions, one from each  $\text{BH}_3$  group.

## Introduction

There is continuing interest in the chemistry of low oxidation state compounds of the heavier group 14 elements, formal analogues of carbenes, alkenes and alkynes, due to their unusual structures and exceptional reactivities (For reviews see: Barrau and Rima, 1998; Tokitoh and Okazaki 2000; Kira, 2004; Weidenbruch, 1999; Klinkhammer, 2002; Hill and West, 2004; Gehrhus and Lappert, 2001; Kühn, 2004; Zabala and Hahn 2008; Mizuhata et al, 2009). In the vast majority of cases, heavier group 14 carbene analogues  $R_2E$  ( $E = Si, Ge, Sn, Pb$ ) are stabilised either by  $\pi$ -donation from the lone pair on an adjacent heteroatom into the vacant p-orbital at the tetrel centre (e.g. diamidotetrylenes  $(R_2N)_2E$ ), or by the use of bulky substituents  $R$ , which sterically occlude the electron-deficient tetrel centre.

Over the last few years we have developed a new approach to the stabilisation of heavier group 14 carbene analogues through agostic-type B-H...E contacts, which mitigate the electron deficiency of the tetrel centre, and have isolated a number of compounds of this type (**1-3**) (Izod et al 2006a; Izod et al 2008; Izod et al 2009a; Izod et al 2009b; Izod et al 2013). We are continuing to explore the limits of this approach, particularly with respect to the steric properties of the substituents in these systems and the effect that the substituents at phosphorus have on the B-H...E contacts. In this contribution we describe the synthesis of a new phosphine-borane, its deprotonation to give the corresponding phosphine-borane-stabilised carbanion, and the use of this latter species for the synthesis of an agostically-stabilised dialkylstannylene.

<1-3>

## Results and Discussion

The phosphine-borane adduct  $iPr_2P(BH_3)Me$  (**4**) is readily prepared by the treatment of  $iPr_2PCl$  with one equivalent of  $MeMgBr$ , followed by one equivalent of  $BH_3 \cdot SMe_2$  (Scheme 1). Treatment of **4** with one equivalent of  $nBuLi$  in THF, followed by one equivalent of

Me<sub>3</sub>SiCl yields {*i*Pr<sub>2</sub>P(BH<sub>3</sub>)}(Me<sub>3</sub>Si)CH<sub>2</sub> (**5**). Compounds **4** and **5** were isolated as air stable, colourless oils and their composition was confirmed by multinuclear (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H}) magnetic resonance spectroscopy. Treatment of **5** with one equivalent of *n*BuLi in THF gives the lithium salt {*i*Pr<sub>2</sub>P(BH<sub>3</sub>)}(Me<sub>3</sub>Si)CHLi (**6**) in good yield. We were unable to obtain crystals of this lithium salt, but isolated the corresponding TMEDA adduct [{*i*Pr<sub>2</sub>P(BH<sub>3</sub>)}(Me<sub>3</sub>Si)CH]Li(TMEDA) (**6a**) as colourless blocks from cold (−30 °C) diethyl ether. The <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>11</sup>B{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H} and <sup>7</sup>Li{<sup>1</sup>H} NMR spectra of **6a** are typical of such species: the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum consists of a broad quartet at 33.4 ppm, while the <sup>11</sup>B{<sup>1</sup>H} NMR spectrum consists of a broad doublet at −39.6 ppm. We have previously noted that α-metalation of phosphine-borane adducts results in a significant increase in the <sup>11</sup>B-<sup>31</sup>P coupling constant; consistent with this, the <sup>11</sup>B-<sup>31</sup>P coupling constants of **5** and **6a** are 59 and 90 Hz, respectively (Izod et al 2014; Izod et al 2010; Izod et al 2007; Izod et al 2006b; Izod et al 2006c; Izod et al 2004).

<Scheme 1>

X-ray crystallography reveals that **6a** adopts a monomeric structure in the solid state (Figure 1). The lithium ion is bound by the carbanion centre and one of the hydrogen atoms of the BH<sub>3</sub> group to give a pseudo-four-membered chelate ring and the coordination of Li is completed by two nitrogen atoms from a molecule of TMEDA, affording a pseudo-tetrahedral geometry about the lithium ion. The Li-C(1) distance [2.213(3) Å] is similar to the corresponding distances in previously reported lithium complexes of phosphine-borane-stabilised carbanions (Izod et al 2014; Izod et al 2010; Izod et al 2007; Izod et al 2006c; Izod et al 2004), while the Li...H(1B) distance [2.02(2) Å] lies in the normal range for η<sup>1</sup>-BH<sub>*n*</sub>...Li contacts (Kimblin et al 2000; Franz et al 2011), although we note that such contacts are rare in comparison to η<sup>2</sup>- and η<sup>3</sup>-BH<sub>*n*</sub>...Li interactions. The carbanion centre adopts a pyramidal geometry [sum of angles in the CHSiP framework = 350.7°].

<Figure 1>

The reaction between freshly sublimed Cp<sub>2</sub>Sn (Fischer and Grubert 1956) and two equivalents of *in situ*-generated **6** in toluene gives the dialkylstannylene [*i*Pr<sub>2</sub>P(BH<sub>3</sub>)}(Me<sub>3</sub>Si)CH]<sub>2</sub>Sn (**7**), along with the insoluble CpLi by-product, the latter of which was removed by filtration. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the crude reaction mixture exhibits a single, broad quartet at 38.5 ppm (*J*<sub>PB</sub> = 76 Hz) due to the *rac* diastereomer, as confirmed by X-ray crystallography, with no evidence for the corresponding *meso* isomer; a similar absence of the *meso* diastereomer was observed in the synthesis of **3** (Izod et al 2009a). The <sup>119</sup>Sn chemical shift of 403 ppm observed for **7** is comparable to those observed for **3a** and **3b** (377 and 375 ppm, respectively), suggesting significant stabilisation of the electron-deficient tin centre by agostic-type B-H...Sn contacts; no evidence for <sup>31</sup>P-<sup>119</sup>Sn coupling was observed in either spectrum. The broadness of the <sup>119</sup>Sn signal for **7** (FWHM = 380 Hz) appears to be a recurring feature of stannylenes with phosphine-borane-substituted alkyl substituents; while we do not have a conclusive explanation for this line-broadening, it appears not to be associated with chemical exchange or quadrupolar broadening, but may be due to significant <sup>119</sup>Sn chemical shift anisotropy and/or the population of a low-lying triplet excited state (Izod et al, 2008).

Both the isopropyl groups in **7** and the methyl groups within them are diastereotopic, by virtue of the chiral carbanion centre and the prochiral phosphorus atom, and so the <sup>1</sup>H NMR spectrum of **7** exhibits four doublets of doublets for these methyl groups, with this splitting pattern arising from coupling of the protons in each methyl group both to the methine proton of the same isopropyl group and to the phosphorus centre. The isopropyl methine protons are also diastereotopic and give rise to complex multiplets in the <sup>1</sup>H NMR spectrum at 1.87 and 2.14 ppm.

Compound **7** was crystallised from cold ( $-30\text{ }^{\circ}\text{C}$ ) methylcyclohexane containing a few drops of THF as yellow blocks suitable for X-ray crystallography. Compound **7** crystallises as a discrete molecular species; the shortest Sn...Sn distance is  $6.934\text{ \AA}$  [*cf.* Sn...Sn distances of  $6.685$  and  $4.401\text{ \AA}$  in **3a** and **3b**, respectively] (Izod et al 2009a). The Sn-C distances of  $2.306(2)$  and  $2.293(2)\text{ \AA}$  are similar to the corresponding distances in **3a** and **3b**, which range from  $2.2864(16)$  to  $2.3149(16)\text{ \AA}$ ; the C-Sn-C angle [ $100.43(7)^{\circ}$ ] is also similar to those of **3a** and **3b** [ $98.26(6)^{\circ}$  and  $99.60(17)^{\circ}$ , respectively].

The solid-state structure of **7** exhibits short contacts between one hydrogen of each borane group and the tin atom [B-H...Sn =  $2.32(2)$  and  $2.36(2)\text{ \AA}$ ]; these distances compare with the corresponding distances in **3a** and **3b** of  $2.38(2)/2.29(2)$  and  $2.41(8)/2.35(6)$ , respectively. The short B-H...Sn contacts cause the stannylene to adopt a *syn, syn*-configuration, as the alkyl substituents are essentially locked into place.

<Figure 2>

Although **7** has very approximate  $C_2$  symmetry, the two B-H...Sn contacts lock the alkyl substituents into differing conformations in the solid state. This places one of the methyl groups of an isopropyl substituent in close proximity to the tin centre: the Sn...C(6) distance [ $3.652(2)\text{ \AA}$ ] is substantially shorter than the remaining Sn...Me(Pr) distances, which are all in excess of  $4.7\text{ \AA}$ , and is significantly less than the sum of the van der Waals radii of tin and carbon ( $3.87\text{ \AA}$ ). This structural feature appears to be preserved in solution: three of the four magnetically inequivalent isopropyl methyl groups have very similar  $^1\text{H}$  chemical shifts ( $1.06$ ,  $1.07$  and  $1.08\text{ ppm}$ ), while a fourth is shifted slightly downfield and is observed at  $1.26\text{ ppm}$ , which we attribute to its proximity to the tin centre. A similar effect is seen in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **7**: three of the isopropyl methyl groups give rise to signals between  $17.34$  and  $18.01\text{ ppm}$ , while the fourth is shifted downfield to  $19.13\text{ ppm}$ .

## Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen or in a nitrogen-filled glove-box. Toluene, THF, methylcyclohexane and diethyl ether were distilled under nitrogen from sodium, potassium or sodium/potassium alloy, and were stored over either a potassium film or activated 4 Å molecular sieves.

Deuterated toluene was distilled under nitrogen from potassium and was deoxygenated by three freeze-pump-thaw cycles and was stored over activated 4 Å molecular sieves.  $\text{Cp}_2\text{Sn}$  was prepared by a previously published procedure (Fischer and Grubert 1956),  $n\text{BuLi}$  was purchased as a 2.5 M solution in hexanes but was standardised prior to each use,  $\text{MeMgBr}$  was purchased as a 3.0 M solution in diethyl ether and  $\text{BH}_3\cdot\text{SMe}_2$  as a 2.0 M solution in THF; all other chemicals were used as supplied with the exception of TMEDA which was distilled from  $\text{CaH}_2$  and stored over activated 4 Å molecular sieves.

$^1\text{H}$ ,  $^7\text{Li}\{^1\text{H}\}$ ,  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{119}\text{Sn}\{^1\text{H}\}$  NMR spectra were recorded on a JEOL Eclipse500 Spectrometer operating at 500.16, 194.38, 160.35, 125.65, 202.35, and 186.50 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane ( $^1\text{H}$  and  $^{13}\text{C}$ ), aqueous  $\text{LiCl}$  (1M) ( $^7\text{Li}$ ), external  $\text{BF}_3(\text{OEt}_2)$  ( $^{11}\text{B}$ ), external 85%  $\text{H}_3\text{PO}_4$  ( $^{31}\text{P}$ ), and external  $\text{Me}_4\text{Sn}$  ( $^{119}\text{Sn}$ ), as appropriate. The positions of the  $\text{BH}_3$  signals in the  $^1\text{H}$  NMR spectra and  $J_{\text{PH}}$  for these signals were determined using selective  $^1\text{H}\{^{11}\text{B}\}$  experiments. Selective proton decoupling and  $^1\text{H}\{^{31}\text{P}\}$  NMR experiments were used to determine the coupling constants for the *iPr* groups in **7**. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

***iPr*<sub>2</sub>P(BH<sub>3</sub>)Me (4):** To a cold (−78 °C) solution of *iPr*<sub>2</sub>PCl (5 mL, 31.4 mmol) in diethyl ether (60 mL) was added  $\text{MeMgBr}$  (10.5 mL, 31.4 mmol). The resulting solution was allowed to warm to room temperature, was stirred for 3 h, and then  $\text{BH}_3\cdot\text{SMe}_2$  (15.7 mL, 31.4 mmol) was added. After 2 h stirring, water (40 mL) was added, and the organic layer

was extracted into diethyl ether (2 x 30 mL). The combined organic extracts were dried over MgSO<sub>4</sub>. The solution was filtered and the solvent was removed *in vacuo* to yield *i*Pr<sub>2</sub>P(BH<sub>3</sub>)Me as a colourless oil. Isolated yield 3.64 g, 79%. <sup>1</sup>H{<sup>11</sup>B} NMR (CDCl<sub>3</sub>, 25 °C): δ 0.23 (d, *J*<sub>PH</sub> = 15.1 Hz, 3H, BH<sub>3</sub>), 1.06 (m, 15H, CHMe<sub>2</sub> + PMe), 1.88 (m, 2H, CHMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 25 °C): δ 3.11 (d, *J*<sub>PC</sub> = 33.6 Hz, CHMeMe), 16.42 (CHMeMe), 16.71 (CHMeMe), 21.69 (d, *J*<sub>PC</sub> = 34.5 Hz, PMe). <sup>11</sup>B{<sup>1</sup>H} (CDCl<sub>3</sub>, 25 °C): δ -44.1 (d, *J*<sub>PB</sub> = 60 Hz). <sup>31</sup>P{<sup>1</sup>H} (CDCl<sub>3</sub>, 25 °C): δ 28.1 (q, *J*<sub>PB</sub> = 60 Hz).

**{*i*Pr<sub>2</sub>P(BH<sub>3</sub>)}(Me<sub>3</sub>Si)CH<sub>2</sub> (5):** To a solution of *i*Pr<sub>2</sub>P(BH<sub>3</sub>)Me **4** (3.03 g, 20.8 mmol) in THF (20 mL) was added *n*BuLi (8.3 mL of a 2.5 M solution, 20.8 mmol). The resulting solution was stirred for 2 h then added to a cold (-78 °C) solution of Me<sub>3</sub>SiCl (3.2 mL, 25.2 mmol) in THF (10 mL). The resulting solution was allowed to warm to room temperature and was stirred for 16 h. The solvent was removed *in vacuo*, water (40 mL) was added, and the organic layer was extracted into diethyl ether (2 x 30 mL). The combined organic extracts were dried over MgSO<sub>4</sub>. The solution was filtered and the solvent was removed *in vacuo* to yield {*i*Pr<sub>2</sub>P(BH<sub>3</sub>)}(Me<sub>3</sub>Si)CH<sub>2</sub> (**5**) as a colourless oil. Isolated yield 3.44 g, 76%. <sup>1</sup>H{<sup>11</sup>B} NMR (*d*<sub>8</sub>-toluene, 25 °C): δ 0.18 (s, 9H, SiMe<sub>3</sub>), 0.43 (d, *J*<sub>PH</sub> = 14.2 Hz, 2H, CH<sub>2</sub>), 0.92 (dd, *J*<sub>PH</sub> = 13.7 Hz, *J*<sub>HH</sub> = 7.1 Hz, 6H, CHMeMe), 0.96 (dd, *J*<sub>PH</sub> = 14.1 Hz, *J*<sub>HH</sub> = 7.1 Hz, 6H, CHMeMe), 0.96 (d, *J*<sub>PH</sub> = 13.9 Hz, 3H, BH<sub>3</sub>), 1.58 (m, 2H, CHMeMe). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene, 25 °C): δ 0.75 (SiMe<sub>3</sub>), 5.08 (d, *J*<sub>PC</sub> = 17.7 Hz, CH<sub>2</sub>), 16.58 (CHMeMe), 16.72 (CHMeMe), 23.96 (d, *J*<sub>PC</sub> = 32.3 Hz, CHMeMe). <sup>11</sup>B{<sup>1</sup>H} (*d*<sub>8</sub>-toluene, 25 °C): δ -41.9 (d, *J*<sub>PB</sub> = 59 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene, 25 °C): δ 32.1 (q, *J*<sub>PB</sub> = 59 Hz).

**[{*i*Pr<sub>2</sub>P(BH<sub>3</sub>)}(Me<sub>3</sub>Si)CH]Li(TMEDA) (6a):** To a solution of **5** (0.73 g, 3.35 mmol) in THF (30 mL) was added *n*BuLi (1.45 mL of a 2.3 M solution, 3.35 mmol). The resulting solution was stirred for 30 min and TMEDA (0.39 g, 3.35 mmol) was then added. After 3 h

stirring the solvent was removed *in vacuo* and the resulting oily solid was dissolved in diethyl ether (20 mL). This solution was cooled to  $-30\text{ }^{\circ}\text{C}$  for 48 hours to obtain colourless block crystals of **6a** suitable for X-ray crystallography. Isolated yield: 0.64 g, 56%. Anal. Calcd. for  $\text{C}_{16}\text{H}_{42}\text{BLiN}_2\text{PSi}$ : C 56.63, H 12.48, N 8.26. Found: C 56.48, H 12.38, N 8.16.  $^1\text{H}\{^{11}\text{B}\}$  NMR ( $d_8$ -toluene,  $21\text{ }^{\circ}\text{C}$ ):  $\delta$ -1.70 (d,  $J_{\text{PH}} = 6.6\text{ Hz}$ , 1H,  $\text{CHLi}$ ), 0.25 (s, 9H,  $\text{SiMe}_3$ ), 0.53 (d,  $J_{\text{PH}} = 10.4\text{ Hz}$ , 3H,  $\text{BH}_3$ ), 1.23 (dd,  $J_{\text{PH}} = 14.2\text{ Hz}$ ,  $J_{\text{HH}} = 7.0\text{ Hz}$ , 6H,  $\text{CHMeMe}$ ), 1.26 (dd,  $J_{\text{PH}} = 14.2\text{ Hz}$ ,  $J_{\text{HH}} = 7.0\text{ Hz}$ , 6H,  $\text{CHMeMe}$ ), 1.79 (br, 4H,  $\text{NCH}_2$ ), 1.98 (s, 12H,  $\text{NMe}_2$ ), 2.01 (m, 2H,  $\text{CHMeMe}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_8$ -toluene,  $21\text{ }^{\circ}\text{C}$ ):  $\delta$ -7.74 (br,  $\text{CHLi}$ ), 5.71 (d,  $J_{\text{PC}} = 3.3\text{ Hz}$ ,  $\text{SiMe}_3$ ), 17.49 ( $\text{CHMeMe}$ ), 17.64 ( $\text{CHMeMe}$ ), 23.94 (d,  $J_{\text{PC}} = 32.6\text{ Hz}$ ,  $\text{CHMeMe}$ ), 45.89 ( $\text{NMe}_2$ ), 56.52 ( $\text{NCH}_2$ ).  $^7\text{Li}\{^1\text{H}\}$  NMR ( $d_8$ -toluene,  $21\text{ }^{\circ}\text{C}$ ):  $\delta$ 0.6.  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $d_8$ -toluene,  $21\text{ }^{\circ}\text{C}$ ):  $\delta$ -39.6 (d,  $J_{\text{PB}} = 90\text{ Hz}$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_8$ -toluene,  $21\text{ }^{\circ}\text{C}$ ):  $\delta$ 33.4 (q,  $J_{\text{PB}} = 90\text{ Hz}$ ).

**[*i*Pr<sub>2</sub>P(BH<sub>3</sub>)](Me<sub>3</sub>Si)CH]<sub>2</sub>Sn (7):** To a solution of **5** (1.25 g, 5.73 mmol) in THF (30 mL) was added *n*BuLi (2.73 mL of a 2.1 M solution, 5.73 mmol). This mixture was stirred for 1 h, and then the solvent was removed *in vacuo*. The resulting colourless oil was dissolved in toluene (20 mL) and added to a solution of freshly sublimed  $\text{Cp}_2\text{Sn}$  (0.71 g, 2.86 mmol). This solution was stirred for 30 min and then filtered. The solvent was removed *in vacuo* from the filtrate to yield a yellow solid, which was dissolved in methylcyclohexane (20 mL) containing a few drops of THF and cooled to  $-30\text{ }^{\circ}\text{C}$  for 16 h to yield **7** as yellow blocks. Isolated yield: 0.92 g, 58%. Anal. Calcd. for  $\text{C}_{20}\text{H}_{54}\text{B}_2\text{P}_2\text{Si}_2\text{Sn}$ : C 43.43, H 9.84. Found: C 43.53, H 9.90.  $^1\text{H}\{^{11}\text{B}\}$  NMR ( $d_8$ -toluene,  $25\text{ }^{\circ}\text{C}$ ):  $\delta$ 0.33 (s, 9H,  $\text{SiMe}_3$ ), 0.79 (d,  $J_{\text{PH}} = 8.8\text{ Hz}$ , 3H,  $\text{BH}_3$ ), 1.06 (dd,  $J_{\text{PH}} = 13.6\text{ Hz}$ ,  $J_{\text{HH}} = 7.1\text{ Hz}$ , 3H,  $\text{CHMeMe}$ ), 1.07 (dd,  $J_{\text{PH}} = 14.8\text{ Hz}$ ,  $J_{\text{HH}} = 7.0\text{ Hz}$ , 3H,  $\text{CHMeMe}$ ), 1.08 (dd,  $J_{\text{PH}} = 14.5\text{ Hz}$ ,  $J_{\text{HH}} = 7.2\text{ Hz}$ , 3H,  $\text{CHMeMe}$ ), 1.22 (d,  $J_{\text{PH}} = 13.5\text{ Hz}$ , 1H,  $\text{SnCH}$ ), 1.26 (dd,  $J_{\text{PH}} = 15.1\text{ Hz}$ ,  $J_{\text{HH}} = 7.3\text{ Hz}$ ,  $\text{CHMeMe}$ ), 1.87 (m, 1H,  $\text{CHMeMe}$ ), 2.14 (m, 1H,  $\text{CHMeMe}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR

(*d*<sub>8</sub>-toluene, 25 °C):  $\delta$  3.09 (d,  $J_{PC} = 2.1$  Hz, SiMe<sub>3</sub>), 17.34 (CHMeMe), 17.78 (CHMeMe), 17.84 (SnCH), 18.01 (CHMeMe), 19.13 (CHMeMe), 26.53 (d,  $J_{PC} = 32.3$  Hz, CHMeMe), 26.84 (d,  $J_{PC} = 27.8$  Hz, CHMeMe). <sup>11</sup>B{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene, 25 °C):  $\delta$  -37.6 (d,  $J_{PB} = 76$  Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene, 25 °C):  $\delta$  38.5 (q,  $J_{PB} = 76$  Hz). <sup>119</sup>Sn{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene, 25 °C):  $\delta$  403 (br, FWHM = 380 Hz).

**Crystal Structure Determination of 6a and 7:** All data were collected at 150 K on an Oxford Diffraction Gemini A Ultra diffractometer using graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell parameters were refined from the observed positions of all strong reflections. An empirical absorption correction was applied to the final data for each compound, based on symmetry equivalent and repeated reflections. The structures were solved by direct methods and refined on  $F^2$  values for all unique data. Further details are given in Table 1. All non-hydrogen atoms were refined anisotropically, and C-bound H atoms were constrained with a riding model, while B-bound H atoms were freely refined; U(H) was set at 1.2 (1.5 for methyl groups) times  $U_{eq}$  for the parent atom. The tmeda ligand in **6a** is disordered over two positions with equal occupancy. Data were collected and processed using Oxford Diffraction CrysAlisPro and structure solution and refinement completed using the OLEX2 interface to the SHELXTL suite (CrysAlisPro 2010; Dolomanov et al 2009; Sheldrick 2008).

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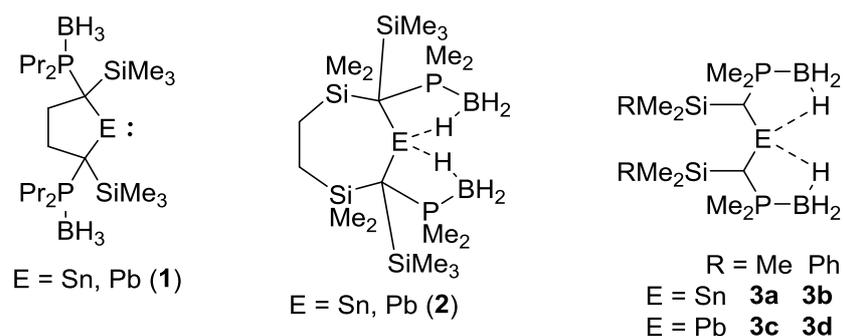
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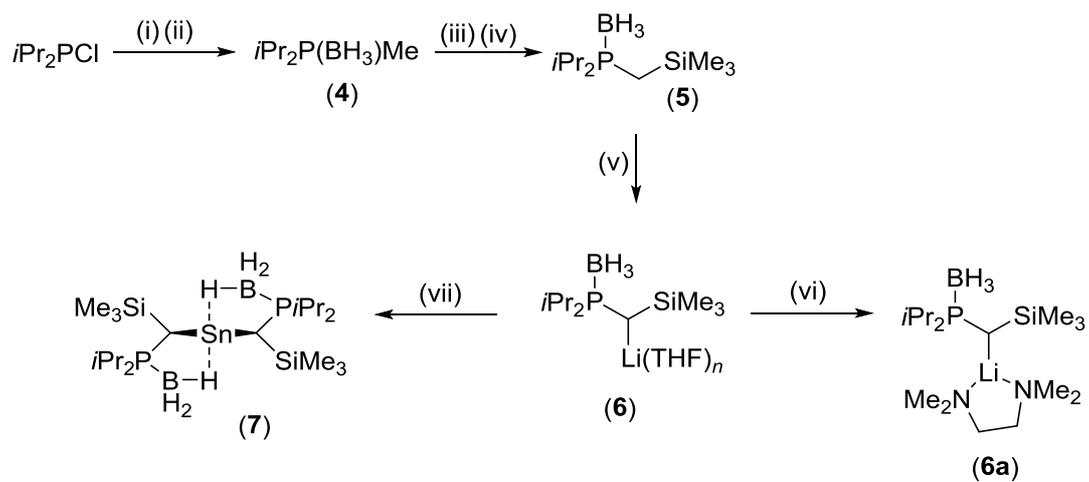
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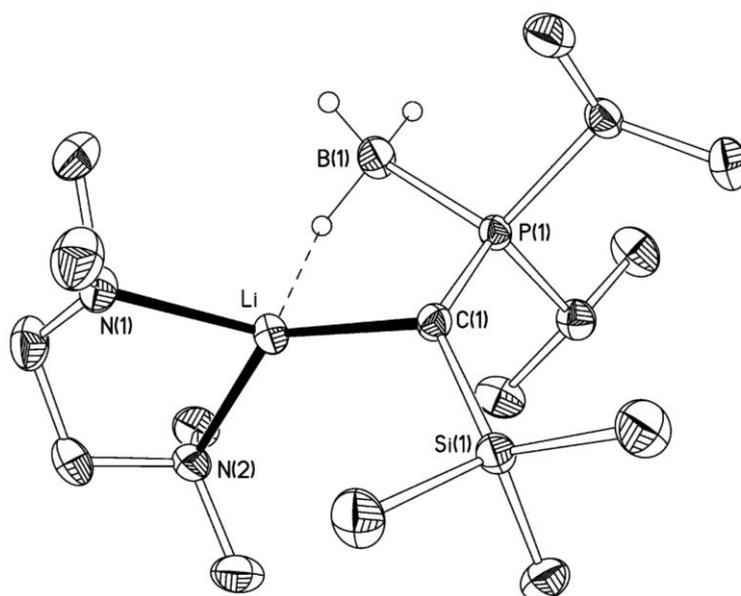
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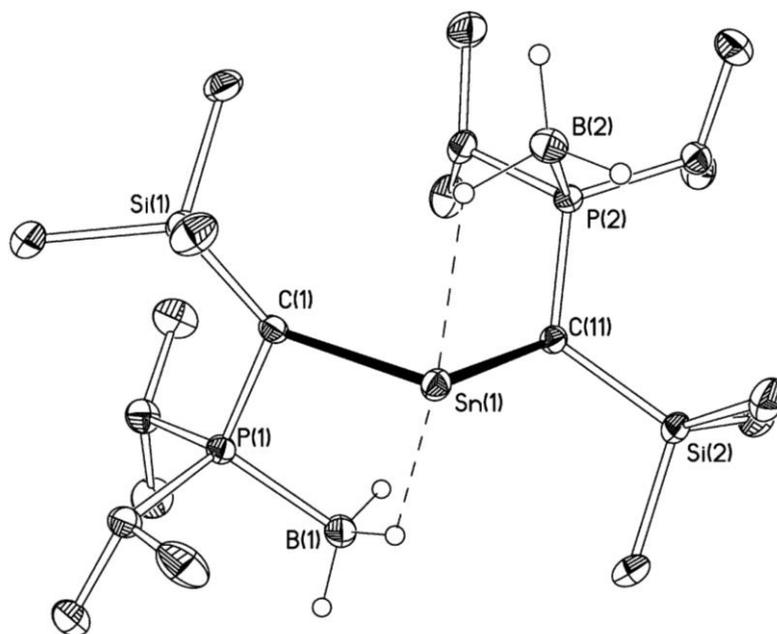
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**Scheme 1.** Reagents and conditions: (i) MeMgBr, Et<sub>2</sub>O, -78 °C; (ii) BH<sub>3</sub>·SMe<sub>2</sub>; (iii) *n*BuLi, THF; (iv) Me<sub>3</sub>SiCl, -78 °C, THF; (v) *n*BuLi, THF; (vi) TMEDA, THF/Et<sub>2</sub>O; (vii) Cp<sub>2</sub>Sn, toluene.



**Figure 1:** Molecular structure of **6a** with 40% probability ellipsoids; disorder component and C-bound H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Li–C(1) 2.213(3), Li–N(1) 2.115(3), Li–N(2) 2.139(3)(4), Li–H(1B) 2.02(2), Li...B 2.633(3), P–C(1) 1.7374(15), Si–C(1) 1.8178(15), P–B 1.9322(19), C(1)–Li...B 76.06(10), N(1)–Li–N(2) 87.02(11), P–C(1)–Si 133.09(9), P–C(1)–Li 91.30(10), Si–C(1)–Li 122.35(10).



**Figure 2:** Molecular structure of **7** with 40% probability ellipsoids and with C-bound H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg.): Sn–C(1) 2.306(2), Sn–C(11) 2.293(2), C(1)–P(1) 1.802(2), C(11)–P(2) 1.789(2), C(1)–Si(1) 1.881(2), C(11)–Si(2) 1.879(2), P(1)–B(1) 1.905(3), P(2)–B(2) 1.924(3), Sn...H(1C) 2.36(2) , Sn...H(2C) 2.32(2), C(1)–Sn–C(11) 100.43 (7).

**Table 1.** Crystallographic data for **6a** and **7**

Compound	<b>6a</b>	<b>7</b>
Formula	C <sub>16</sub> H <sub>42</sub> BLiN <sub>2</sub> PSi	C <sub>20</sub> H <sub>54</sub> B <sub>2</sub> P <sub>2</sub> Si <sub>2</sub> Sn
M	339.33	553.06
Crystal System	Monoclinic	Monoclinic
Space Group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/n</i>
<i>a</i> /Å	9.4986(4)	14.3694(6)
<i>b</i> /Å	16.8836(6)	11.8551(5)
<i>c</i> /Å	14.7898(5)	17.8704(8)
$\beta$ /Å	103.494(4)	98.335(4)
<i>V</i> /Å <sup>3</sup>	2306.37(15)	3012.1(2)
<i>Z</i>	4	4
$\mu$ /mm <sup>-1</sup>	0.977	1.039
Data collected	15617	30055
Unique data	4997	7505
<i>R</i> <sub>int</sub>	0.0259	0.0523
Data with $F^2 > 2\sigma$	4099	5289
Refined parameters	251	276
<i>R</i> (on <i>F</i> , $F^2 > 2\sigma$ )	0.041	0.031
<i>R</i> <sub>w</sub> (on $F^2$ , all data)	0.107	0.052
Goodness of fit on $F^2$	1.033	0.897
Min, max electron density /eÅ <sup>-3</sup>	0.42, -0.38	0.49, -0.44