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# Lanthanide(II) complexes of a phosphine-borane-stabilised carbanion<sup>†</sup>

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The reaction between two equivalents of the potassium salt  $[(Me_3Si)_2\{Me_2P(BH_3)\}C]K$  (4) and  $SmI_2(THF)_2$  in refluxing THF yields the dialkylsamarium(II) compounds  $[(Me_3Si)_2\{Me_2P(BH_3)\}C]_2Sm(THF)$  (5a) or  $[(Me_3Si)_2\{Me_2P(BH_3)\}C]_2Sm(THF)_3$  (5b), depending on the crystallisation conditions, in good yield as air- and moisture-sensitive crystalline solids. X-ray crystallography shows that, whereas both alkyl ligands chelate the samarium(II) ion in 5a, in 5b one alkyl ligand chelates the metal centre and one binds the metal only through its borane hydrogen atoms. The reaction between YbI<sub>2</sub> and two equivalents of 4 in refluxing benzene yields the solvent-free dialkylytterbium(II) compound  $[(Me_3Si)_2\{Me_2P(BH_3)\}C]_2Yb$  (8). In contrast to 5a and 5b, compound 8 reacts rapidly with THF to give the free phosphine-borane  $(Me_3Si)_2\{Me_2P(BH_3)\}CH$  as the only identifiable product.

## Introduction

Over the last three decades the organometallic chemistry of the lanthanide(II) ions has undergone a period of rapid and sustained expansion, due largely to the unique structures and reactions exhibited by these species.<sup>1,2</sup> The unique reactivity of these compounds is exemplified by the bent metallocene Cp\*<sub>2</sub>Sm, first isolated by Evans and co-workers in 1984, which exhibits remarkable reactivity towards a wide variety of inorganic and organic substrates.<sup>2</sup>

Whilst the chemistry of lanthanide(II) metallocenes is now relatively well developed, surprisingly few σ-bonded organolanthanide(II) species are known and, amongst these, alkyl derivatives are particularly rare.<sup>3–20</sup> The first crystallographically characterised alkyllanthanide(II) compounds  $\{(Me_3Si)_3C\}_2Yb$  (1),<sup>3</sup> [ $\{(Me_3Si)_3C\}Yb(\mu-OEt)(OEt_2)\}_2^{3,4}$  and  $(Tp'^{Bu,Me})Yb\{CH(SiMe_3)_2\}^5$  were reported as recently as 1994 [ $Tp'^{Bu,Me}$  = hydrotris(3-*tert*-butyl-5-methypyrazolyl)borate]. The first alkyleuropium(II) compound { $(Me_3Si)_3C\}_2Eu$  (2) was reported in 1996,<sup>6</sup> and in 1997 we reported the first crystallographically characterised alkylsamarium(II) compound { $(Me_3Si)_2(Me_2MeOSi)C\}_2Sm(THF)$  (3).<sup>7</sup> Very recently Takats and co-workers reported the synthesis of the remarkable σ-bonded organothulium(II) compound ( $Tp'^{Bu,Me}$ )Tm{CH(SiMe\_3)\_2}.C<sub>6</sub>H<sub>14</sub>.<sup>19</sup>

The reactions of alkyllanthanide(II) species have yet to be studied in depth, but early results suggest that these compounds

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often exhibit reactivities and undergo reactions which are different from, but which complement, those of their metallocene cousins. In this regard, compound 1 undergoes reactions which have no precedent in lanthanide metallocene chemistry; for example, 1 reacts with ethyl ethers according to Scheme 1 to give the corresponding heteroleptic alkyl/alkoxyytterbium(II) species.<sup>3,4,6</sup> Neither the europium nor samarium analogues 2 and 3,67 nor the less sterically hindered dialkylytterbium complex  $\{(Me_3Si)_2CH\}_2Yb(OEt_2)_2$  exhibit this behaviour;<sup>4b</sup> indeed, this latter complex is isolated as a stable diethyl ether adduct. Compound 1 also exhibits unusual reactivity towards halocarbons. Typically, lanthanide(II) compounds undergo oxidation to the corresponding lanthanide(III) halide on treatment with an alkyl bromide or iodide. In contrast, the reaction between 1 and either methyl iodide or 1,2-diiodoethane yields the corresponding alkylytterbium iodide  $[{(Me_3Si)_3C}Yb(\mu-I)(OEt_2)]_2$ , without oxidation of the vtterbium(II) centre.3,6

We have recently developed a number of phosphine-boranestabilised carbanions and dicarbanions and have shown that these are excellent ligands for the synthesis of complexes of the main group elements from groups 1, 2 and 14.<sup>21</sup> We now show that one of these ligands enables the stabilisation of novel Yb(II) and Sm(II) complexes and that the binding mode of this ligand is dependent on the exact crystallisation conditions.

#### **Results and discussion**

We have previously shown that the samarium(II) dialkyl  $\{(Me_3Si)_2(Me_2MeOSi)C\}_2Sm(THF)$  (3) is readily prepared by a metathesis reaction between  $SmI_2(THF)_2$  and two equivalents of  $\{(Me_3Si)_2(Me_2MeOSi)C\}K$ .<sup>7</sup> It is perhaps somewhat surprising, therefore, that the corresponding reaction between



Scheme 1



Scheme 2  $[R = SiMe_3]$ 

 $SmI_2(THF)_2$  and two equivalents of the potassium alkyl [(Me<sub>3</sub>Si)<sub>2</sub>- $\{Me_2P(BH_3)\}C]K$  (4)<sup>21d</sup> in THF at room temperature is rather sluggish, much of the potassium salt remaining after 48 h; however, this reaction may be forced to completion by heating under reflux for 2 h in the same solvent (Scheme 2). Removal of the solvent and extraction of the residue into methylcyclohexane gives a deep purple-brown solution from which dark purple-black blocks of the mono-THF adduct  $[(Me_3Si)_2 \{Me_2P(BH_3)\}C]_2Sm(THF)$  (5a) deposit as a methylcyclohexane solvate on cooling to -30 °C for several days. The <sup>1</sup>H NMR spectrum of 5a is consistent with this formulation, although the solvent of crystallisation is readily lost under vacuum and so is not observed: singlets are observed at -1.87 and 0.53 ppm due to the PMe<sub>2</sub> and SiMe<sub>3</sub> protons, respectively, whilst signals due to the THF co-ligand are observed at 4.13 and 14.10 ppm. However, we were unable to observe a signal due to the BH<sub>3</sub> protons, even in the  ${}^{1}H{}{}^{11}B{}$  spectrum, probably due to a combination of the quadrupolar nature of the <sup>11</sup>B nucleus and the proximity of these protons to the paramagnetic Sm(II) centre. The  ${}^{31}P{}^{1}H$  and  ${}^{11}B{}^{1}H$  NMR spectra of **5a** consist of broad singlets at -1.9 and -41.6 ppm, respectively; <sup>31</sup>P-<sup>11</sup>B coupling is not resolved on either signal.

The molecular structure of **5a** is shown in Fig. 1, along with selected bond lengths and angles. Compound **5a** crystallises as a discrete molecular species in which the phosphine-borane-substituted alkyl ligands bind the samarium(II) ion through their carbanion centres and the borane groups (for which the hydrogen atoms were not located), generating two pseudo-four-membered chelate rings [the C–Sm–B "bite angle" is  $66.2(3)^{\circ}$  for both ligands]; the coordination of the samarium ion is completed by a molecule of THF.

The Sm–C distances of 2.853(8) and 2.827(9) Å are similar to the corresponding distances in the few previously reported alkylsamarium(II) compounds; for example, the Sm–C distances in { $(Me_3Si)_2(Me_2MeOSi)C$ }\_2Sm(THF) are 2.787(5) and 2.845(5) Å,<sup>7</sup> whereas the Sm–C distances in { $(Me_3Si)(C_6H_4-2-NMe_2)CH$ }\_2Sm(THF)<sub>2</sub> are 2.768(3) and 2.789(3) Å.<sup>8</sup> To the best of our knowledge, there has been no previous report of a crystallographically characterised Sm(II)  $\cdots$  BH<sub>n</sub> contact, although there are several examples of Sm(III) borohydride complexes. According to Shannon the ionic radii of Sm(II) and Sm(III) are 1.22 and 1.02 Å, respectively,<sup>22</sup> for eight-coordination and so a difference of approximately 0.2 Å might be expected between



Fig. 1 Molecular structure of **5a** with H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Sm–C(1) 2.853(8), Sm–C(10) 2.827(9), Sm–O 2.565(6), Sm $\cdots$ B(1) 2.895(11), Sm $\cdots$ B(2) 2.861(11), C(1)–P(1) 1.760(9), C(1)–Si(1) 1.865(9), C(1)–Si(2) 1.832(9), C(10)–P(2) 1.752(9), C(10)–Si(3) 1.850(10), C(10)–Si(4) 1.862(9), P(1)–B(1) 1.962(11), P(2)–B(2) 1.943(12), C(1)–Sm–B(1) 66.2(3), C(10)–Sm–B(2) 66.2(3), C(1)–Sm–C(10) 135.0(3), B(1)–Sm–B(2) 165.2(4).

bond lengths to the samarium ion in **5a** and the corresponding distances in comparable Sm(III) compounds. Unfortunately, the crystallographic data for **5a** are not of sufficient quality for the precise location of the borane hydrogen atoms in this compound; however, the Sm(II)  $\cdots$  B distances are 2.895(11) and 2.861(11) Å. For comparison, typical Sm  $\cdots$  B distances in samarium(III) borohydride complexes lie in the range 2.58–3.03 Å; for example, the Sm(III)  $\cdots$  B distances in the dimer [(1,3-Bu'\_2C\_5H\_3)\_2Sm(BH\_4)]\_2 are 2.833(6) and 2.882(6) Å,<sup>23</sup> whereas the Sm  $\cdots$  B distances in Cp\*<sub>2</sub>Sm(BH<sub>4</sub>)(THF) are 2.62(2) and 2.58(2) Å (for the two independent molecules in the asymmetric unit),<sup>24</sup> and the Sm  $\cdots$  B distances in the cluster [( $\eta^5$ -Me<sub>4</sub>Pr<sup>*n*</sup>C\_5)Sm(BH<sub>4</sub>)<sub>2</sub>]<sub>6</sub> range from 2.64 to 3.03 Å.<sup>25</sup> The similarity between the Sm(II)  $\cdots$  B distances in **5a** are relatively strong.

The C(1)–Sm–C(10) and B(1)–Sm–B(2) angles are 135.0(3) and  $165.2(4)^{\circ}$ , respectively, and so the geometry at the samarium(II) ion

is best described as lying somewhere between square pyramidal, with an apical THF, and trigonal bipyramidal, with axial borane groups.

Somewhat unexpectedly, a second batch of crystals of this compound, obtained by an identical synthetic route, was found by X-ray crystallography to have the composition  $[(Me_3Si)_2\{Me_2P(BH_3)\}C]_2Sm(THF)_3$  (5b), also as a methylcy-clohexane solvate. These crystals have an essentially identical appearance to those of 5a, but rapidly lose crystallinity on exposure to vacuum. This is associated with rapid loss of both the solvent of crystallisation (methylcyclohexane) and two of the three molecules of THF, as demonstrated by <sup>1</sup>H NMR spectroscopy. The molecular structure of 5b is shown in Fig. 2, along with selected bond lengths and angles.



Fig. 2 Molecular structure of **5b** with H atoms bonded to carbon omitted for clarity. Selected bond lengths (Å) and angles (°): Sm–C(1) 2.873(3), Sm–O(1) 2.5743(18), Sm–O(2) 2.608(2), Sm–O(3) 2.6020(17), Sm–H(1C) 2.53(3), Sm–H(1B) 2.68(3), Sm–H(2A) 2.60(3), Sm–H(2B) 2.55(2), Sm–H(2C) 2.61(3), Sm $\cdots$  B(1) 2.959(4), Sm $\cdots$  B(2) 2.783(3), C(1)–P(1) 1.756(3), C(1)–Si(1) 1.855(3), C(1)–Si(2) 1.855(3), C(10)–P(2) 1.719(3), C(10)–Si(3) 1.820(3), C(10)–Si(4) 1.827(3), P(1)–B(1) 1.939(4), P(2)–B(2) 1.928(3), C(1)–Sm–B(1) 64.68(10), Si(1)–C(1)–Si(2) 112.80(16), Si(1)–C(1)–P(1) 114.70(15), Si(2)–C(1)–P(1) 116.04(16), Si(3)–C(10)–Si(4) 118.58(17), Si(3)–C(10)–P(2) 120.52(17), Si(4)–C(10)–P(2) 115.55(16).

The samarium(II) ion in **5b** is coordinated by the carbanion centre and the borane hydrogen atoms of one alkyl ligand, generating a pseudo-four-membered chelate ring [C-Sm-B "bite angle" 64.68(10)°], by the borane hydrogen atoms of the second alkyl ligand, and by three molecules of THF; the carbanion centre of the second alkyl ligand has no short contact with the samarium ion. This gives the samarium ion a highly distorted pseudo-octahedral geometry, in which the THF ligands adopt a meridional disposition.

The Sm–C distance [2.873(3) Å] is similar to the corresponding distances in **5a** and related compounds. For compound **5b** the borane hydrogen positions were located and freely refined; the borane group of the monodentate alkyl ligand binds in an  $\eta^3$ -fashion whereas the borane group of the chelating alkyl ligand binds the Sm(II) ion in an  $\eta^2$ -fashion. Although there are no previous examples of Sm(II)…H–B contacts, a small number of crystallographically characterised europium(II) borohydrides have been reported; since the ionic radii of Eu(II) and Sm(II) differ by just 0.02 Å,<sup>22</sup> Eu(II)…H distances may act as a

useful comparator for the Sm(II)...H contacts in **5b**. The Sm...H contacts fall in the range 2.53(3)–2.68(3) and these compare with Eu...H distances ranging from 2.30(6) to 2.57(4) Å in the europium(II) bis((cyclooctane-1,5-diyl)dihydroborate) (THF)<sub>4</sub>Eu{( $\mu$ -H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}<sup>26</sup> and from 2.41(4) to 2.56(3) Å in the related salt [NMe<sub>4</sub>]<sub>2</sub>[Ln{( $\mu$ -H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}]<sub>4</sub>].<sup>27</sup>

The carbanion centre in the chelating alkyl ligand has a distinctly pyramidal  $CSi_2P$  skeleton [sum of angles at  $C(1) = 343.54^\circ$ ; displacement of C(1) from the Si(1)-Si(2)-P(1) plane = 0.433 Å]. In contrast, the carbanion centre in the monodentate, boranedonor ligand is much closer to planar [sum of angles at C(10) = $354.65^\circ$ ; displacement of C(10) from the Si(3)-Si(4)-P(2) plane = 0.241 Å]. Consistent with this the C(1)-P(1), C(1)-Si(1) and C(1)-Si(2) distances [1.756(3), 1.855(3) and 1.855(3), respectively] are significantly longer than the C(10)-P(2), C(10)-Si(3) and C(10)-Si(4) distances [1.719(3), 1.820(3) and 1.827(3), respectively]. This is in accord with a greater degree of charge localisation when the carbanion is coordinated to the samarium ion compared to the essentially sp<sup>2</sup>-hybridised monodentate ligand, where charge is extensively delocalised from the carbanion centre onto the adjacent heteroatoms.

The difference in structure between 5a and 5b clearly suggests that there is a delicate balance between solvation and ligand coordination mode in these systems. In this regard, it is instructive to compare the structures of 5a and 5b with that of the corresponding strontium derivative. According to Shannon, the ionic radii of Sr<sup>2+</sup> and Sm<sup>2+</sup> differ by just 0.01 Å [the ionic radii of Sr<sup>2+</sup> and Sm<sup>2+</sup> are 1.21 and 1.22 Å for a seven-coordinate ion]<sup>22</sup> and these ions often display very similar coordination chemistries.8 It is, therefore, notable that the strontium analogue of 5 adopts a different structure again in the solid state from those of 5a and 5b. This compound crystallises from methylcyclohexane/THF as the adduct  $[(Me_3Si)_2 {Me_2P(BH_3)}C]_2 Sr(THF)_5$  (6), in which the strontium is bound by both alkyl ligands through their borane hydrogen atoms only, with no short Sr-C contacts, and by five molecules of THF.<sup>21e</sup> Interestingly, the THF ligands in 6 appear to be more tightly held than those in 5b and are not lost when this compound is exposed to vacuum.

In contrast to the ready synthesis of 5, the reaction between YbI<sub>2</sub> and two equivalents of 4 in THF at room temperature does not proceed cleanly, yielding a mixture of unreacted 4 and the free phosphine-borane  $(Me_3Si)_2\{Me_2P(BH_3)\}CH$  (7) as the major products, even after extended reaction times. Heating this reaction mixture under reflux leads to complete decomposition, yielding 7 as the only identifiable product. Nevertheless, the desired dialkylytterbium compound  $[(Me_3Si)_2 \{Me_2P(BH_3)\}C]_2Yb$ (8) may be accessed in good yield from the reaction between  $YbI_2$ and two equivalents of 4 after heating under reflux in benzene for 16 h. Deep orange crystals of 8 may be obtained from cold n-hexane, although, despite repeated efforts, we were unable to obtain single crystals suitable for X-ray crystallography. However, the composition of this compound was confirmed unambiguously by elemental analysis and multi-element NMR spectroscopy. The <sup>1</sup>H NMR spectrum of 8 consists of a singlet at 0.32 ppm due to the SiMe<sub>3</sub> protons, a doublet at 1.20 ppm due to the PMe<sub>2</sub> protons and a broad 1:1:1:1 quartet at 1.96 ppm ( $J_{BH} = 88.4$  Hz) due to the BH<sub>3</sub> protons, the latter of which collapses to a doublet on decoupling of the <sup>11</sup>B nucleus ( $J_{PH} = 9.2$  Hz). The <sup>31</sup>P{<sup>1</sup>H} and <sup>11</sup>B{<sup>1</sup>H} NMR spectra consist of a broad quartet at -11.7 ppm and a broad doublet at -24.8 ppm, respectively; the <sup>171</sup>Yb spectrum consists of a singlet at 794 ppm.

Unfortunately, the solution NMR data for **8** do not provide unambiguous evidence for the coordination modes of the carbanions in this compound. Previously reported <sup>171</sup>Yb chemical shifts span the range from –500 to 2000 ppm and the chemical shifts of even very similar Yb(II) compounds often vary dramatically; for example, the <sup>171</sup>Yb chemical shifts of the metallocenes ( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>YbL<sub>2</sub> are 0 (L = THF),<sup>28</sup> 98 (L = 1/2DME)<sup>29</sup> and 949 ppm (L = py).<sup>28</sup> However, the <sup>171</sup>Yb chemical shift of **8** is in the same region as the shifts of related dialkylytterbium compounds; for example the <sup>171</sup>Yb chemical shift of formally two-coordinate **1** is 812 ppm,<sup>3</sup> whereas the chemical shift of the five-coordinate complex {(Me<sub>3</sub>Si)(Me<sub>2</sub>MeOSi)C(SiMe<sub>2</sub>CH<sub>2</sub>)}<sub>2</sub>Yb(THF) is 1049 ppm<sup>13</sup> and the chemical shift of the four-coordinate complex {(Me<sub>3</sub>Si)<sub>2</sub>(Me<sub>2</sub>(EtOCH<sub>2</sub>CH<sub>2</sub>)Si)C}<sub>2</sub>Yb is 544 ppm.<sup>6</sup>

Although **8** appears to be indefinitely stable in benzene solution, treatment of a crystalline sample of **8** with THF results in rapid decomposition, again yielding the free phosphine-borane **7** as the only identifiable product, suggesting that the failure of the attempted synthesis of **8** in THF may be attributed to its instability towards this solvent and its consequent decomposition immediately it is formed in the reaction. This behaviour is reminiscent of that of the isoelectronic dialkylytterbium compound **1**, which reacts rapidly with THF to give (Me<sub>3</sub>Si)<sub>3</sub>CH as the only identifiable product.<sup>3,6</sup>

There is often a strong correlation between the chemistries of Yb(II) and Ca(II)<sup>30</sup> [the ionic radii of Ca<sup>2+</sup> and Yb<sup>2+</sup> are 1.00 and 1.02 Å, respectively]<sup>22</sup> and the decomposition chemistry of 8 has parallels with the behaviour of the calcium analogue  $[(Me_3Si)_2 \{Me_2P(BH_3)\}C]_2Ca$  (9): although this latter compound may be isolated as the THF adduct  $[(Me_3Si)_2 {Me_2P(BH_3)}C]_2Ca(THF)_4$  (9a), it rapidly decomposes in the presence of excess THF to give 7 as the sole phosphoruscontaining product.<sup>20e</sup> The corresponding strontium and barium compounds  $[(Me_3Si)_2 \{Me_2P(BH_3)\}C]_2M(THF)_5 [M = Sr, Ba]$  are stable for long periods in THF solution and show no evidence for decomposition. This parallels the behaviour of 5, which is prepared in refluxing THF and is clearly stable towards this solvent, and suggests that the stability of dialkyllanthanide(II) compounds is dependent upon both the size of the metal ion and the steric demands of the ligands.

In summary, we have isolated new alkyl complexes of samarium(II) (5a/5b) and ytterbium(II) (8), the former of which may be crystallised in two different modifications, which differ both in the number of THF co-ligands bound to the metal centre and in the binding mode of the alkyl ligands. While the ytterbium compound 8 is unstable towards THF, compound 5 is isolated as one of two THF adducts, suggesting that the reactivity of these compounds is subtly affected by the size of the metal ion.

#### Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Methylcyclohexane, n-hexane, THF, benzene and light petroleum (b.p. 40–60 °C) were dried prior to use by distillation under nitrogen from sodium or sodium/potassium alloy and were stored over a potassium film. Deuterated benzene was distilled from potassium and was deoxygenated by three freeze-pump-thaw cycles and stored over activated 4Å molecular sieves.  $[(Me_3Si)_2\{Me_2P(BH_3)\}C]K$  (4),<sup>21d</sup> YbI<sub>2</sub>,<sup>31</sup> and SmI<sub>2</sub>(THF)<sub>2</sub><sup>32</sup> were prepared by previously published procedures. All other compounds were used as supplied by the manufacturer.

NMR spectra were recorded on a JEOL ECS500 spectrometer operating at 500.16 (<sup>1</sup>H), 125.65 (<sup>13</sup>C), 160.47 (<sup>11</sup>B), 202.47 (<sup>31</sup>P), and 87.52 (<sup>171</sup>Yb) MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane (<sup>1</sup>H and <sup>13</sup>C), external BF<sub>3</sub>(OEt<sub>2</sub>) (<sup>11</sup>B), external 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P), and external Cp\*<sub>2</sub>Yb(THF)<sub>2</sub> (<sup>171</sup>Yb). Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

#### $[(Me_{3}Si)_{2}{Me_{2}P(BH_{3})}C]_{2}Sm(THF) (5)$

To a solution of SmI<sub>2</sub>(THF)<sub>2</sub> (0.76 g, 1.38 mmol) in THF (15 ml) was added a solution of **4** (0.96 g, 3.54 mmol) in THF (15 ml). The resulting solution was heated under reflux for 2 h. Solvent was removed *in vacuo* and the sticky residue was extracted into methylcyclohexane (15 ml) and filtered. The filtrate was concentrated to *ca* 5 ml and was cooled to -30 °C for 2 days to give purple-black crystals of the mono-THF adduct **5a** as its methylcyclohexane solvate. The solvent of crystallisation is rapidly lost under vacuum and is not observed in the following analyses. Isolated yield: 0.71 g, 75%. Anal. Calcd for C<sub>22</sub>H<sub>62</sub>B<sub>2</sub>OP<sub>2</sub>Si<sub>4</sub>Sm: C 38.35, H 9.07. Found C 38.27, H 9.11. <sup>1</sup>H{<sup>11</sup>B} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –1.87 (s, 6H, PMe<sub>2</sub>), 0.53 (s, 18H, SiMe<sub>3</sub>), 4.13 (s, 4H, THF), 14.10 (s, 4H, THF). <sup>11</sup>B{<sup>11</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –41.6 (br s). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  –1.9 (br s).

Crystallisation of a second batch of **5**, prepared by the same route, from methylcyclohexane at -30 °C gave crystals of the tris-THF adduct [(Me<sub>3</sub>Si)<sub>2</sub>{Me<sub>2</sub>P(BH<sub>3</sub>)}C]<sub>2</sub>Sm(THF)<sub>3</sub> (**5b**) as a methylcyclohexane solvate. The extra two molecules of THF and the solvent of crystallisation are rapidly lost under vacuum and all analyses of this material are identical with those of **5a**.

#### $[(Me_3Si)_2 {Me_2P(BH_3)}C]_2 Yb (8)$

To a suspension of YbI<sub>2</sub> (0.46 g, 1.08 mmol) in benzene (20 ml) was added a solution of **4** (0.59 g, 2.17 mmol) in warm benzene (20 ml). The resulting mixture was heated under reflux for 16 h, and then solvent was removed *in vacuo*. The sticky orange residue was extracted into n-hexane (20 ml) and filtered. The filtrate was concentrated to *ca* 5 ml and was cooled to  $-30 \,^{\circ}$ C for 3 days to give **8** as poor quality orange crystals. Isolated yield: 0.39 g, 57%. Anal. Calcd for C<sub>18</sub>H<sub>54</sub>B<sub>2</sub>P<sub>2</sub>Si<sub>4</sub>Yb: C 33.80, H 8.51. Found C 33.88, H 8.47. <sup>1</sup>H{<sup>11</sup>B} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  0.32 (s, 18H, SiMe<sub>3</sub>), 1.20 (d, <sup>2</sup>J<sub>PH</sub> = 9.2 Hz, 6H, PMe<sub>2</sub>), 1.96 (d, <sup>2</sup>J<sub>PH</sub> = 8.3 Hz, 3H, BH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  6.61 (SiMe<sub>3</sub>), 18.65 (d, <sup>1</sup>J<sub>PC</sub> = 35.5 Hz, PMe). <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  -11.7 (q, <sup>1</sup>J<sub>PB</sub> = 85.6 Hz). <sup>171</sup>Yb NMR (C<sub>6</sub>D<sub>6</sub>, 25 °C):  $\delta$  794 (s)

#### Crystal structure determinations of 5a and 5b

Measurements were made at 150 K on an Oxford Diffraction Gemini A Ultra diffractometer using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected semi-empirically for absorption, based on

#### Table 1 Crystallographic data for 5a and 5b

Compound	5a	5b
Formula	$C_{22}H_{42}B_2OP_2Si_4Sm$	$C_{30}H_{78}B_2O_3P_2Si_4Sm$
M	689.0	833.2
Crystal size/mm	$0.32 \times 0.20 \times 0.20$	$0.25 \times 0.20 \times 0.20$
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\overline{1}$
a/Å	11.9950(2)	13.7414(8)
b/Å	29.7059(5)	13.7832(7)
c/Å	12.4072(2)	15.9703(8)
$\alpha$ (°)		66.697(5)
β(°)	93.442(2)	88.844(5)
γ (°)		70.297(5)
$V/Å^3$	4412.99(13)	2592.9(2)
Ζ	4	2
$\mu/\mathrm{mm}^{-1}$	1.52	1.31
Data collected	41414	27058
Unique data	7755	10171
$R_{ m int}$	0.043	0.037
Data with $F^2 > 2\sigma$	7166	7815
Refined parameters	305	419
$R$ (on $F, F^2 > 2\sigma$ )	0.076	0.028
$R_{\rm w}$ (on $F^2$ , all data)	0.177	0.062
Goodness of fit on $F^2$	1.351	0.921
Min, max electron density/e Å <sup>-3</sup>	1.23, -1.65	0.45, -0.32

symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined on  $F^2$  values for all unique data: Table 1 gives further details. All non-hydrogen atoms were refined anisotropically, and all H atoms in 5a and the C-bound H atoms in 5b were constrained with a riding model, while B-bound H atoms in **5b** were freely refined; U(H) was set at 1.2 (1.5 for methyl groups) times  $U_{eq}$  for the parent C atom. Difference maps revealed methylcyclohexane molecules present in both structures, but these could not be satisfactorily refined due to apparent disorder and partial occupancy, so they were treated with the SQUEEZE procedure of PLATON<sup>33</sup> and omitted subsequently from the refined structure models. These solvent molecules are not included in the chemical formulae and derived properties, but the unplaced BH<sub>3</sub> atoms of **5a** are included. Other programs were Oxford Diffraction CrysAlisPro and SHELXTL for structure solution, refinement, and molecular graphics.<sup>34</sup> CCDC reference numbers 763178 and 763179.†

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