

**Structural Diversity in Alkaline Earth Metal Complexes of a Phosphine-Borane-  
Stabilized 1,3-Dicarbocation**

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## Abstract

The reaction between (4-*t*BuC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>Ca and one equivalent of PhP(BH<sub>3</sub>)(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (**1**) in diethyl ether gives the dimeric complex [[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)<sub>2</sub>}Ca(OEt<sub>2</sub>)<sub>2</sub>]<sub>2</sub> (**2**) in good yield. Similar reactions between **1** and one equivalent of either (PhCH<sub>2</sub>)<sub>2</sub>Sr(THF) or (PhCH<sub>2</sub>)<sub>2</sub>Ba yield the corresponding dimers [[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)<sub>2</sub>}Sr(THF)<sub>1.75</sub>(OEt<sub>2</sub>)<sub>0.25</sub>]<sub>2</sub> (**3**) and [[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)<sub>2</sub>}Ba(OEt<sub>2</sub>)<sub>1.75</sub>(THF)<sub>0.25</sub>]<sub>2</sub> (**4**), respectively. Unexpectedly, an attempt to prepare **3** from a one-pot reaction between SrI<sub>2</sub>, **1** and two equivalents of PhCH<sub>2</sub>K gave the complex [[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>Sr<sub>3</sub>K<sub>2</sub>(OEt<sub>2</sub>)(THF)<sub>2</sub>]<sub>2</sub>.Et<sub>2</sub>O (**5**) in low yield. While superficially similar, compounds **2**, **3** and **4** crystallize with distinct structures, which differ either in the chirality of the carbanion centers, or in the nature of the bridging group. Compounds **2**, **3** and **4** decompose slowly in THF solution to give ethylene, Ae(OEt)<sub>2</sub> (or Ae(OCH=CH<sub>2</sub>)<sub>2</sub>) and the monocarbanion derivatives [PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)}{CH<sub>2</sub>SiMe<sub>3</sub>}]<sub>2</sub>Ae(THF)<sub>*n*</sub>, according to NMR spectroscopy [Ae = Ca, Sr, Ba].

## Introduction

The organometallic chemistry of the heavier alkaline earth metals Ca, Sr and Ba has seen a substantial resurgence of interest over the last 10-15 years, due to the realization that these compounds not only exhibit novel structures and reactivities, but also have potential applications in fields as diverse as materials chemistry and catalysis.<sup>1,2</sup> The use of organo-group 2 compounds in catalysis has a long history, dating back to the 1970s, when it was recognized that dibenzylbarium catalyzes the polymerization of styrene.<sup>3</sup> More recently, organo-group 2 compounds have been shown to act as catalysts for a wide range of alkene transformations, including hydrosilylation, hydroamination and hydrophosphination.<sup>4,5</sup>

For the heavier alkaline earth metals Ca, Sr and Ba the preparation of tractable  $\sigma$ -bonded organometallic derivatives is hampered by the large sizes of the  $Ae^{2+}$  cations and the consequent propensity of their complexes to aggregate, often leading to poor solubility in organic solvents. Additionally, the highly polar Ae-C bonds in such compounds present significant challenges in their isolation. Nonetheless,  $\sigma$ -bonded organometallic complexes of all of the alkaline earth metals are now known and their chemistry is becoming better understood.<sup>1,6,7</sup> In many of these compounds the problems of aggregation and reactivity are mitigated through the use of silicon-containing substituents at the carbanion center, which both increase the steric demands of the ligand, disfavoring aggregation, and reduce its “carbanion” character, due to delocalization of the negative charge into Si-Me  $\sigma^*$  orbitals (negative hyperconjugation).

The diorganophosphine-borane group  $PR_2(BH_3)$  is isoelectronic and isosteric with the corresponding methyl-substituted triorganosilyl substituent  $SiR_2Me$ ; however, in phosphine-borane-stabilized carbanions (PBCs),  $R'_2\{R_2(H_3B)P\}C^-$ , the residual hydridic character of the borane hydrogens permits these atoms to compete with, or supplement, the coordination of a metal by the carbanion center itself. This is perhaps best illustrated by the compounds  $\{(Me_3Si)_3C\}_2Ca^{6a}$  and  $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Ca(THF)_4^{8a}$  which contain isoelectronic

carbanion ligands: whereas the former possesses direct Ca-C  $\sigma$ -bonds, the latter exhibits solely Ca...H-B (and Ca-O) interactions and has no Ca-C contacts.

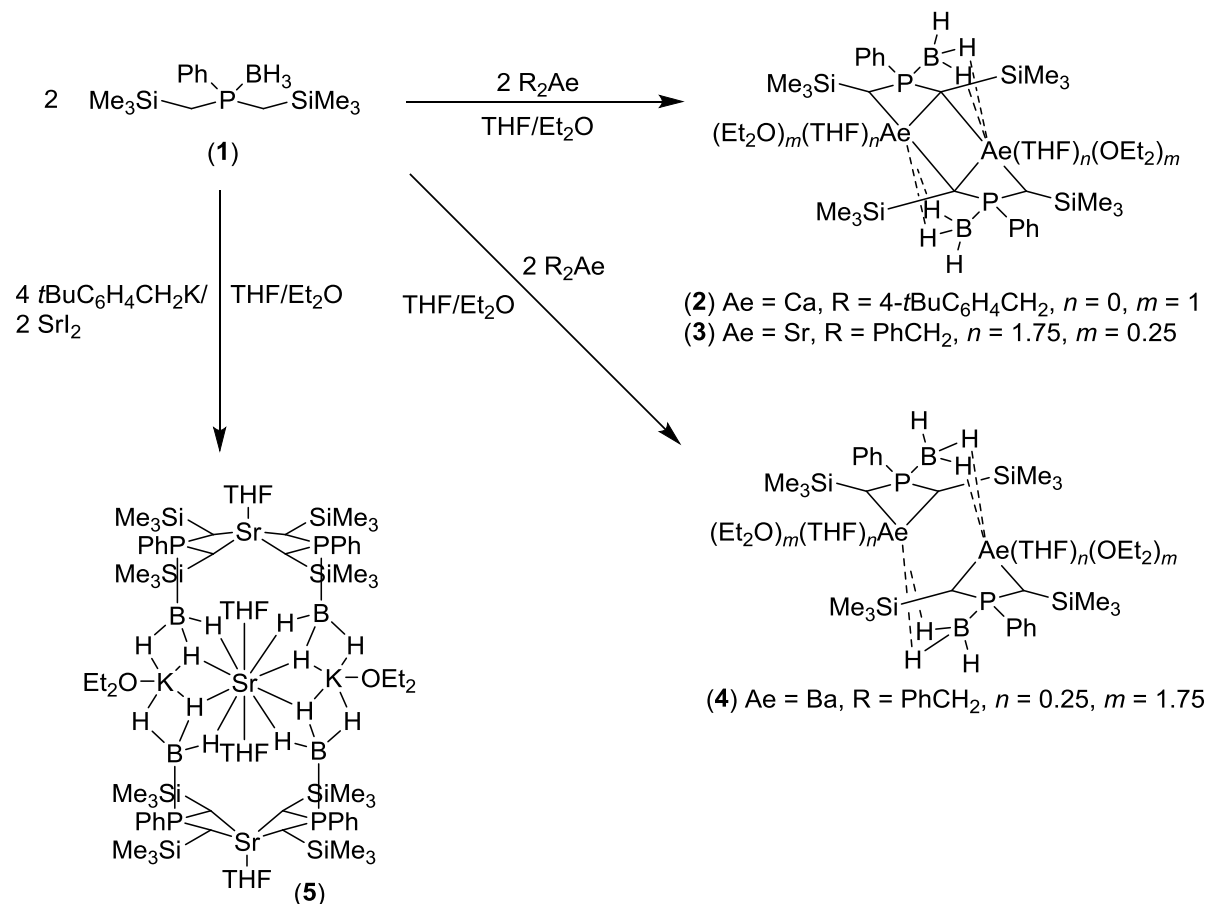
Despite the isoelectronic and isosteric relationship between these two ligand classes, until recently, relatively little was known about the chemistry of PBCs and structurally-characterized complexes were limited to a very few alkali metal derivatives.<sup>9</sup> Over the last ten years we, and others, have striven to expand the range of complexes with these ligands,<sup>8,10-13</sup> however, complexes of the group 2 elements remain scarce.<sup>8</sup>

We recently reported the synthesis and unusual crystal structure of the silicon- and phosphine-borane-stabilized dicarbanion complex  $(\text{THF})_2\text{Li}\{(\text{Me}_3\text{SiCH})_2\text{P}(\text{BH}_3)\text{Ph}\}\text{Li}(\text{THF})_3$ .<sup>10h</sup> The dicarbanion ligand in this complex has the potential to chelate metal centers and so we were keen to explore whether this would favor Ae-C contacts over Ae...H-B contacts in its complexes. We now report the synthesis and structural characterization of the calcium, strontium and barium complexes of this ligand and comment on the stability of these complexes towards ethers.

## Results and Discussion

**Synthesis and stability:** The reaction between the phosphine-borane  $\text{PhP}(\text{BH}_3)(\text{CH}_2\text{SiMe}_3)_2$  (**1**)<sup>10h</sup> and one equivalent of  $(4\text{-}t\text{BuC}_6\text{H}_4\text{CH}_2)_2\text{Ca}(\text{THF})_4$ <sup>6f</sup> in toluene gives an orange oil from which the dicarbanion complex  $[[\text{PhP}(\text{BH}_3)\{\text{CH}(\text{SiMe}_3)\}_2]\text{Ca}(\text{OEt}_2)]_2$  (**2**) may be obtained after crystallization from diethyl ether (Scheme 1). Similar reactions between **1** and one equivalent of either  $(\text{PhCH}_2)_2\text{Sr}(\text{THF})$ <sup>14</sup> or  $(\text{PhCH}_2)_2\text{Ba}$ <sup>6g</sup> give the corresponding complexes  $[[\text{PhP}(\text{BH}_3)\{\text{CH}(\text{SiMe}_3)\}_2]\text{Sr}(\text{THF})_{1.75}(\text{OEt}_2)_{0.25}]_2$  (**3**) and  $[[\text{PhP}(\text{BH}_3)\{\text{CH}(\text{SiMe}_3)\}_2]\text{Ba}(\text{OEt}_2)_{1.75}(\text{THF})_{0.25}]_2$  (**4**). An alternative attempt to prepare **3** by a one-pot procedure unexpectedly gave a small amount of an unusual ate complex: the reaction between **1**,  $\text{SrI}_2$  and two equivalents of  $4\text{-}t\text{BuC}_6\text{H}_4\text{CH}_2\text{K}$ <sup>6f</sup> in THF gave a small

number of pale yellow single crystals of  $[\text{PhP}(\text{BH}_3)\{\text{CH}(\text{SiMe}_3)\}_2]_4\text{Sr}_3\text{K}_2(\text{OEt}_2)_2(\text{THF})_4\cdot\text{Et}_2\text{O}$  (**5**) after crystallization from diethyl ether.



**Scheme 1.** Syntheses of **2-5**.

Compounds **2**, **3**, **4** and **5** were characterized by multi-element NMR spectroscopy and X-ray crystallography. The X-ray crystal structure of **2** contains only diethyl ether co-ligands, while the structures of both **3** and **4** contain both diethyl ether and THF each with partial occupancy at one coordination site; the  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of all three compounds indicate that both diethyl ether and THF are present in each case. It therefore appears that there is no significant preference for the coordination of either diethyl ether or THF in these compounds and that they may be isolated with an arbitrary mixture of each co-ligand. In addition, the coordinated solvent appears to be partially lost under vacuum and the

foregoing, along with the reactivity of these compounds towards diethyl ether and THF (see below), prevents the acquisition of accurate elemental analyses.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of **2**, **3** and **4** consist of broad multiplets at 6.5, 5.0 and 3.4 ppm, respectively, while the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of these compounds consist of broad doublets at -31.6, -30.7 and -28.1 ppm, respectively. In each case the  $^{31}\text{P}$ - $^{11}\text{B}$  coupling constant [91, 106 and 106 Hz, respectively] is significantly larger than the corresponding coupling constant in the free phosphine-borane **1** (59 Hz). This is consistent with  $\alpha$ -deprotonation of **1** in these compounds; we have previously shown that  $\alpha$ -metalation of phosphine-boranes leads to an increase in the  $^{31}\text{P}$ - $^{11}\text{B}$  coupling constant of between 30 and 50 Hz.<sup>10</sup> X-ray crystallography (see below) shows that in the solid state, the two carbanion centers in **2** and **3** occupy very different environments: in each case, one carbanion center bridges two metal ions, while the second coordinates a single metal center. However, the two methine protons in both **2** and **3** give rise to a single signal in their  $^1\text{H}$  NMR spectra [**2** -0.46 ppm, coupling unresolved; **3** -0.42 ppm, doublet,  $J_{\text{PH}} = 15.0$  Hz], while the two  $\text{SiMe}_3$  groups give rise to a single singlet in each case [**2** -0.24, **3** -0.27 ppm]. While **4** adopts a different dimeric structure to **2** and **3** in the solid state (see below), the  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ ,  $^{31}\text{P}\{^1\text{H}\}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of all three compounds are remarkably similar. The foregoing is consistent either with rapid dynamic exchange between the two different carbanion centers in **2** and **3**, or with fragmentation of the dimeric units into mononuclear species. Although it is difficult to be certain about the nuclearity of these species in solution, a  $^1\text{H}$  DOSY NMR experiment on **3** (used as a suitable example) in  $d_8$ -THF yields a diffusion coefficient of  $5.34 \times 10^{-10} \text{ m}^2\text{s}^{-1}$ . This experimentally determined value of  $D$  gives an apparent hydrodynamic radius of 7.3 Å using the Stokes Einstein equation. This is consistent with retention of the dimeric structure, for which a hydrodynamic radius of 6.8 Å was obtained from DFT calculations. The  $^{31}\text{P}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectra of **2** in  $d_8$ -THF do not change significantly

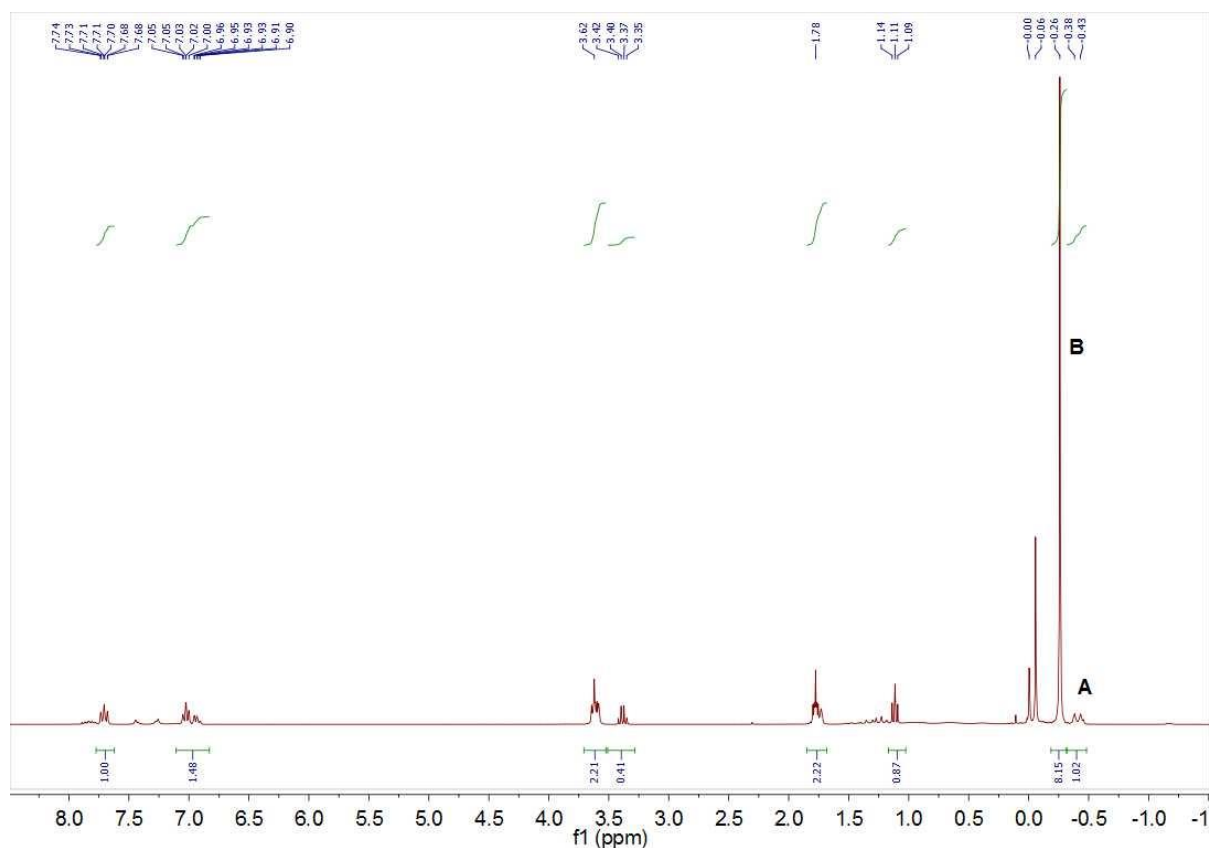
over the temperature range 20 to  $-40^{\circ}\text{C}$ , suggesting that exchange between the bridging and non-bridging carbanion centers is too rapid to be frozen out under these conditions.

While compounds **2-4** are stable both in the solid state and in solution below  $-30^{\circ}\text{C}$ , all three compounds undergo slow decomposition at room temperature in THF solution, with the rate of decomposition increasing in the order **2**<**3**<**4**. We have, as yet, been unable to isolate this decomposition product; however, NMR spectroscopy provides some clues to the decomposition pathway. In each case, the decomposition pathway and resulting spectra are similar and so the following discussion refers the strontium compound **3** as an exemplar. The  $^{31}\text{P}\{^1\text{H}\}$  NMR signal for the decomposition product **3<sub>dec</sub>** is coincident with the signal due to **3**; however, the formation of this compound may be monitored by  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopy: over several weeks the  $^{11}\text{B}\{^1\text{H}\}$  NMR signal for **3** at  $-30.7$  ppm ( $J_{\text{PB}} = 106$  Hz) is gradually replaced by a new doublet at  $-28.9$  ppm ( $J_{\text{PB}} = 97$  Hz) due to **3<sub>dec</sub>**.

The  $^1\text{H}$  NMR spectra of **3** are more informative (Figure 1). Over a period of several weeks the high-field doublet at  $-0.40$  ppm (**A**;  $J_{\text{PH}} = 15.0$  Hz), due to the methine protons at the carbanion centers in **3**, and the  $\text{SiMe}_3$  signal at  $-0.27$  ppm (**B**) decrease significantly in intensity, along with the signals due to the phenyl ring. This is accompanied by the appearance of a new doublet at  $-1.20$  ppm (**C**;  $J_{\text{PH}} = 8.5$  Hz) and a pair of multiplets at  $1.19$  and  $1.49$  ppm (**D** and **E**), which collapse to a straightforward AB spin system on decoupling the  $^{31}\text{P}$  NMR nuclei, along with two equal intensity  $\text{SiMe}_3$  signals. An edited HSQC experiment confirms that **D** and **E**, which each have the same intensity as **C**, arise from the diastereotopic protons of a  $\text{CH}_2$  group adjacent to phosphorus. The presence of diastereotopic methylene, methine and  $\text{BH}_3$  groups within a single species was confirmed by a  $^{11}\text{B}$ -decoupled  $^1\text{H}$  NOESY experiment, which exhibits clear cross-peaks for these four signals (see Supporting Information).

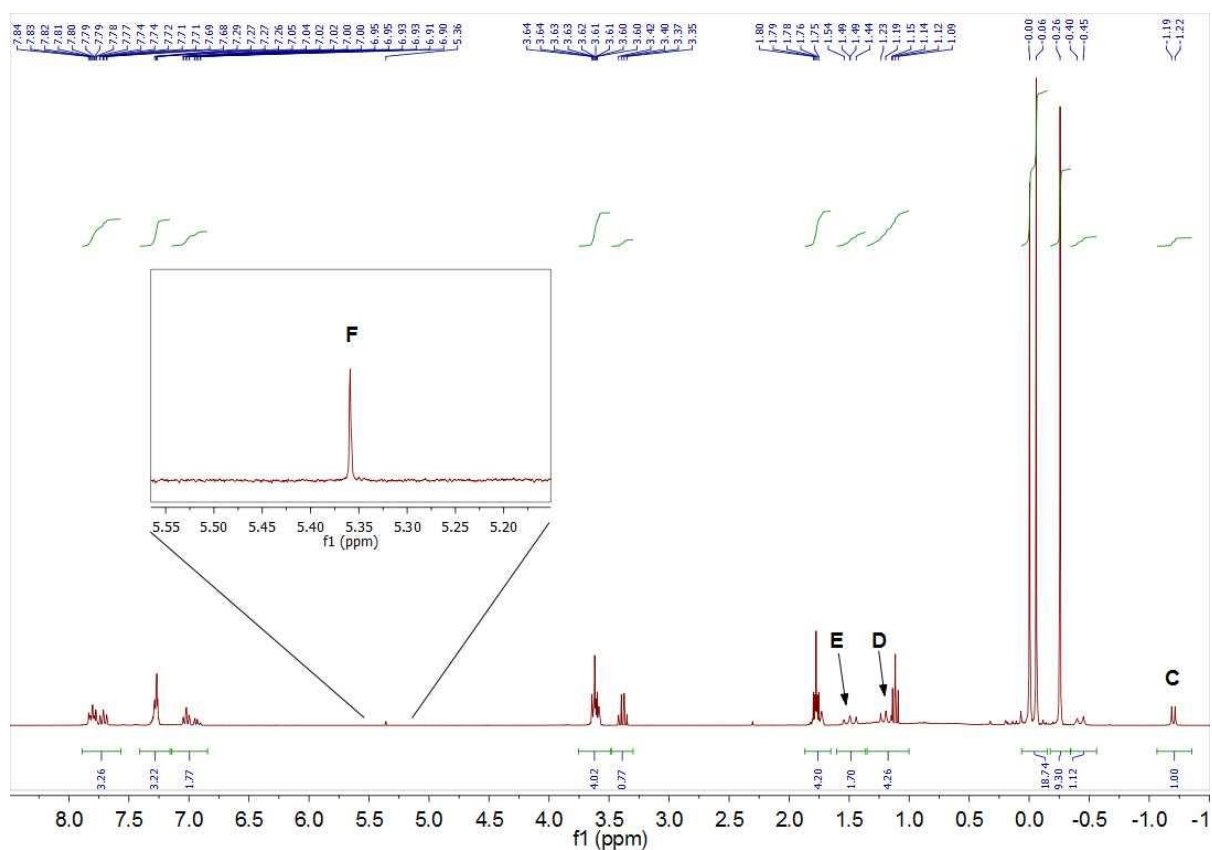
The foregoing suggests that decomposition of **3** proceeds via protonation of the dicarbanion ligands to give the mono-carbanion  $[(\text{Me}_3\text{Si})\text{CH}_2\text{PPh}(\text{BH}_3)\text{CH}(\text{SiMe}_3)]^-$ . To

confirm the formation of a mono-carbanion, we deliberately prepared the potassium salt  $[\text{PhP}(\text{BH}_3)\{\text{CH}(\text{SiMe}_3)\}\{\text{CH}_2\text{SiMe}_3\}]\text{K}(\text{THF})_n$  (**6**) through the reaction of **1** with one equivalent of benzylpotassium in THF. The  $^{31}\text{P}\{^1\text{H}\}$  and  $^{11}\text{B}\{^1\text{H}\}$  spectra of **6** exhibit a broad quartet at 4.5 ppm and a broad doublet at -31.8 ppm ( $J_{\text{PB}} = 91$  Hz), respectively, and are similar to those of **3<sub>dec</sub>** [a multiplet at approx. 5.0 ppm and a broad doublet at -28.9 ppm ( $J_{\text{PB}} = 97$  Hz), respectively]. In addition to the signals due to the phenyl ring, the  $^1\text{H}$  NMR spectrum of **6** exhibits a doublet at -0.87 ppm ( $J_{\text{PH}} = 11.6$  Hz) [*cf.* -1.20 ppm,  $J_{\text{PH}} = 8.3$  Hz for **3<sub>dec</sub>**], along with two  $\text{SiMe}_3$  signals (-0.07 and -0.04 ppm) and a pair of multiplets at 1.11 and 1.17 ppm due to the diastereotopic  $\text{CH}_2$  protons (these simplify to a straightforward pair of doublets ( $J_{\text{HH}} = 13.9$  Hz) on decoupling the  $^{31}\text{P}$  nucleus) [*cf.* multiplets at 1.19 and 1.49 ppm for **3<sub>dec</sub>**].



(a)



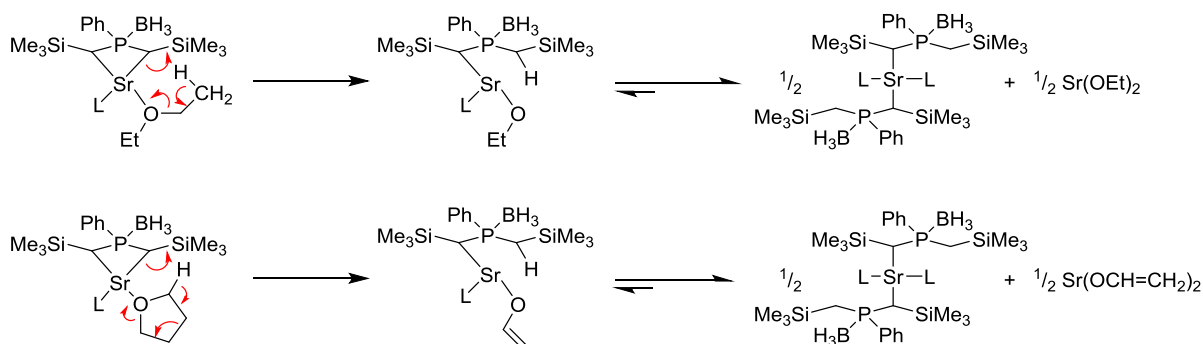


(b)

**Figure 1.**  $^1\text{H}$  NMR spectra of (a) **3** in  $d_8$ -THF, and (b) the same sample after standing at room temperature for 5 weeks.

The NMR spectra of the decomposition product are inconsistent with transfer of a proton from either a  $\text{SiMe}_3$  group or the  $\text{BH}_3$  group; a proton-coupled  $^{11}\text{B}$  NMR spectrum of the sample of **3** after 5 weeks reveals two pseudo-quintets, one each from **3** and **3<sub>dec</sub>**, due to coupling of  $^{11}\text{B}$  to three equivalent protons and the  $^{31}\text{P}$  center. We therefore believe the proton source to be the coordinated THF/ $\text{Et}_2\text{O}$ . Consistent with this, the ratio of the sum of the integrals of the low field THF and  $\text{Et}_2\text{O}$  signals and the sum of the aromatic signals in the  $^1\text{H}$  NMR spectra decreases from 0.76:1 to 0.57:1, over the five-week period (while the THF: $\text{Et}_2\text{O}$  ratio remains essentially constant). Careful examination of the spectrum also reveals the emergence of a small singlet at 5.36 ppm (**F**) due to the formation of ethylene;<sup>13</sup> the low intensity of this signal may be attributed to loss of ethylene from solution into the

headspace of the sample, which was sealed under vacuum. It therefore appears that decomposition of **3** occurs via abstraction of a proton from the coordinated solvent by one of the carbanion centers, resulting in a mixed alkylstrontium ethoxide/enolate (Scheme 2). We do not observe signals due to the ethoxide or enolate ligands in the  $^1\text{H}$  NMR spectra of the decomposition product, presumably due to the operation of a Schlenk-type equilibrium, which favors the dialkylstrontium and insoluble strontium ethoxide/enolate, the latter of which we observe as a precipitate from the solution.

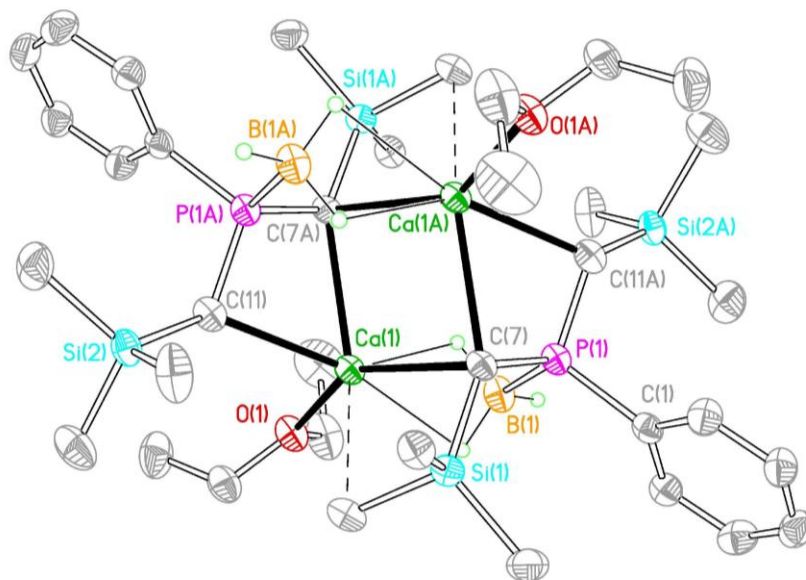


**Scheme 2.** Possible decomposition pathways for **3** (L = THF or Et<sub>2</sub>O).

Such decomposition pathways have some precedent:  $\alpha$ -proton abstraction from THF by polar organometallic compounds is well known,<sup>15</sup> while  $\beta$ -proton abstraction from diethyl ether has been observed in several related complexes of calcium and ytterbium(II) with sterically-demanding silicon-stabilized carbanions.<sup>6a,16</sup>

**Molecular structures:** Compounds **2**, **3** and **4** each crystallize as discrete molecular species; however, each adopts a unique structure which differs from the others in several key respects. Compound **2** crystallizes as a centrosymmetric dimer; the molecular structure of **2** is shown in Figure 2, along with selected bond lengths and angles. Each calcium ion is coordinated by the two carbanion centers of a dicarbanion ligand [bite angle 65.71(10) $^\circ$ ], by the oxygen atom of a molecule of diethyl ether, and, in an  $\eta^2$  manner, by the borane hydrogen atoms, and by one of the carbanion centers of the second dicarbanion ligand in the

dimer; in addition there is a short contact between each calcium ion and one of the methyl groups of a trimethylsilyl substituent. Thus, each dicarbanion ligand bridges the two calcium ions via one carbanion center.

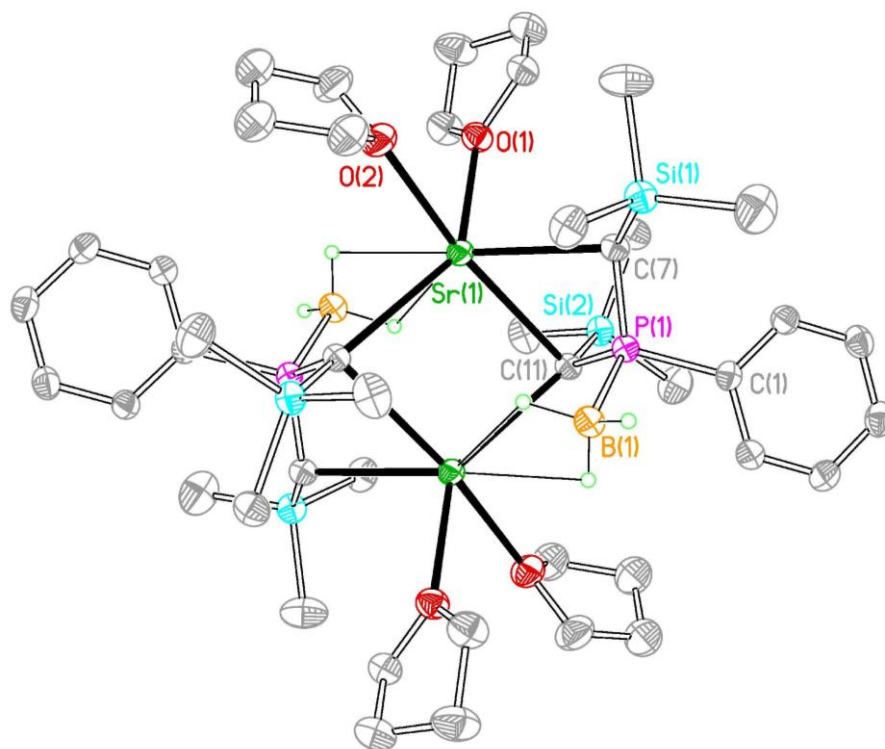


**Figure 2.** Molecular structure of **2** with 40% probability ellipsoids and with C-bound H atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ca(1)-C(7) 2.683(3), Ca(1)-C(7A) 2.683(3), Ca(1)-C(11) 2.550(3), Ca(1)-O(1) 2.370(2), Ca(1)-H(1B) 2.51(3), Ca(1)-H(1C) 2.40(3), Ca(1)...B(1) 2.809(4), C(7)-P(1) 1.791(3), C(11)-P(1) 1.747(3), C(7)-Si(1) 1.849(3), C(11A)-Si(2) 1.840(3), P(1)-B(1) 1.937(4), C(7)-Ca(1)-C(11A) 65.71(10), Ca(1)-C(7)-Ca(1A) 80.22(9), C(7)-Ca(1)-C(7A) 99.78(9).

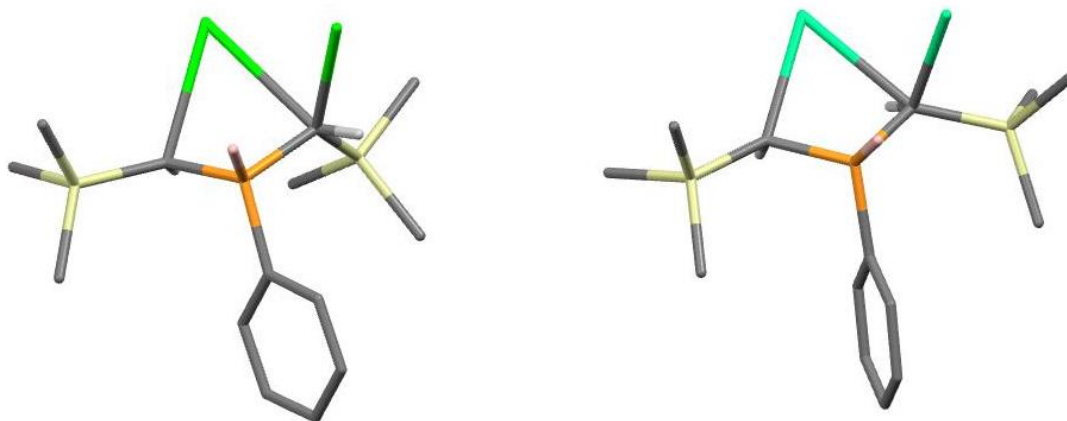
The Ca-C distance to the terminal carbanion center [Ca(1)-C(11) 2.550(3) Å] is somewhat shorter than the Ca-C distances to the bridging carbanion center [Ca(1)-C(7) and Ca(1)-C(7A) both 2.683(3) Å], as expected, and is similar to previously reported Ca-C distances; however, the Ca(1)-C(7)/C(7A) distances are rather long compared to typical Ca-C distances, even for systems where a carbanion center bridges two calcium ions. For example, the Ca-C distance in (PhCH<sub>2</sub>)<sub>2</sub>Ca(THF)<sub>4</sub> range from 2.568(5) to 2.595(5) Å,<sup>6f</sup> for the two

independent molecules in the asymmetric unit, whereas the Ca-C distances in dimeric  $[(\text{Me}_4\text{EtC}_5)\text{Ca}(\text{CH}_2\text{C}_6\text{H}_4\text{-2-NMe}_2)]_2$  are 2.607(2) and 2.621(2) Å.<sup>6d</sup> The Ca-H(B) distances in **2** are 2.40(3) and 2.51(3) Å, while the Ca...B distance is 2.809(4) Å; these are similar to the Ca-H and Ca...B distances in  $[\{\text{Ph}_2\text{P}(\text{BH}_3)\}_2\text{CH}]_2\text{Ca}(\text{THF})$  [Ca-H 2.45(3) (average), Ca...B 2.815(4)-2.908(4)],<sup>8b</sup> which exhibits similar  $\eta^2$ -BH<sub>3</sub>-Ca contacts.

The structure of **3** is shown in Figure 3, along with selected bond lengths and angles. Compound **3** adopts a similar structure to **2** in the solid state, crystallizing as centrosymmetric dimers in which the two strontium ions are bridged by one of the carbanion centers of each of the dicarbanion ligands. Each strontium ion is coordinated by the two carbanion centers of a dicarbanion ligand, generating a 4-membered chelate ring [bite angle 60.80(8)°], by a further carbanion center and, in an  $\eta^2$  manner, the borane hydrogen atoms of the second dicarbanion ligand, and by the oxygen atoms of a molecule of THF and a disordered mixture of diethyl ether and THF (with 25:75% occupancy). However, while **2** and **3** are similar, the orientation of the SiMe<sub>3</sub> group on the bridging carbanion centers differs between the two structures: in **2** this trimethylsilyl group lies on the same side of the molecules as the borane group, whereas in **3** the methine H atom occupies this position (Figure 4). Thus the ligands in **2** and **3** adopt diastereomerically related configurations in the solid state.



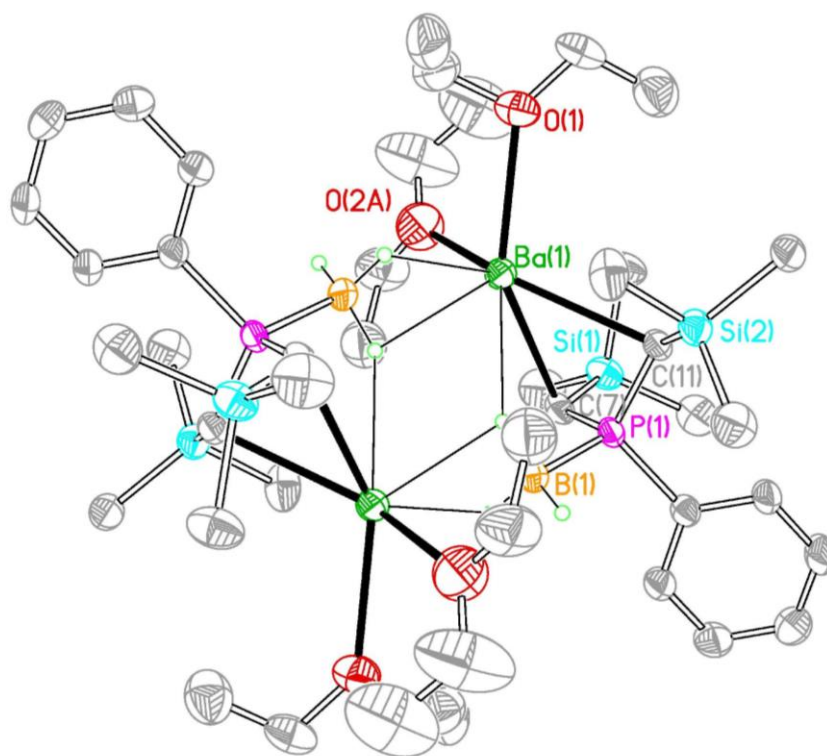
**Figure 3.** Molecular structure of **3** with 40% probability ellipsoids and with C-bound H atoms and disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): Sr(1)-C(7) 2.732(3), Sr(1)-C(11) 2.912(3), Sr(1)-C(11A) 2.953(3), Sr(1)-O(1) 2.5282(19), Sr(1)-O(2) 2.595(7), Sr(1)-H(1AA) 2.57(4), Sr(1)-H(1BA) 2.67(4), Sr(1)...B(1A) 2.992(3), C(7)-P(1) 1.747(3), C(11)-P(1) 1.790(3), C(7)-Si(1) 1.816(4), C(11)-Si(2) 1.860(3), P(1)-B(1) 1.935(3), C(7)-Sr(1)-C(11) 60.80(8), Sr(1)-C(11)-Sr(1A) 79.50(6), C(11)-Sr(1)-C(11A) 100.50(6).



**Figure 4.** Dicarbanion ligand configurations in **2** (right) and **3** (left). Key: C grey, H white, P orange, B pink, Si yellow, Ca/Sr green.

The Sr-C(terminal carbanion) distance in **3** [2.732(3) Å] is similar to other Sr-C distances to terminal carbanion ligands; for example, the Sr-C distances in  $\{(\text{Me}_3\text{Si})_2\text{CH}\}_2\text{Sr}(\text{THF})_3$ <sup>6j</sup> and  $[\{(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\text{N}\}\text{C}_6\text{H}_4\text{-2-}\{\text{CH}=\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\}\}\text{Sr}\{\text{CH}(\text{SiMe}_3)_2\}(\text{THF})_2$ <sup>17</sup> are 2.692(3) and 2.681(3) Å, and 2.706(4) Å, respectively. In comparison, the Sr-C(bridging carbanion) distances in **3** [2.912(3) and 2.953(3) Å] are longer than other reported Sr-C(carbanion) distances, although we note that there is no previously reported example of an  $\text{sp}^3$  carbanion center bridging two Sr ions. The Sr-H(B) distances in **3** [2.57(4) and 2.67(4) Å] are similar to the corresponding distances in  $\text{Sr}[\text{HC}\{\text{C}(\text{Me})\text{N}(2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)\}_2](\text{BH}_4)(\text{THF})_2$  [2.62(1)-2.65(1) Å],<sup>18</sup> whereas the Sr...B distance of 2.992(3) Å in **2** is somewhat longer than the Sr...B distance [2.8206(18) Å] in the latter compound, due to the  $\eta^2\text{-BH}_3$  coordination mode in the former compared to the  $\eta^3\text{-BH}_4$  coordination mode in the latter.

Compound **4** also crystallizes as discrete centrosymmetric dimers; however, **4** adopts a somewhat different structure in the solid state to those of **2** and **3**. The molecular structure of **4** is shown in Figure 5, along with selected bond lengths and angles.



**Figure 5.** Molecular structure of **4** with 40% probability ellipsoids and with C-bound H atoms and disordered THF component omitted for clarity. Selected bond lengths (Å) and angles (°): Ba(1)-C(7) 2.921(3), Ba(1)-C(11) 2.917(3), Ba(1)-O(1) 2.764(2), Ba(1)-O(2) 2.743(3), Ba(1)-H(1AA) 2.71(3), Ba(1)-H(1B) 2.81(3), Ba(1)...B(1) 3.603(3), Ba(1)...B(1A) 3.040(3), Ba(1A)-H(1A) 2.93(3), C(7)-P(1) 1.749(3), C(11)-P(1) 1.750(3), C(7)-Si(1) 1.822(3), C(11)-Si(2) 1.811(3), P(1)-B(1) 1.935(3), C(7)-Ba(1)-C(11) 58.46(7).

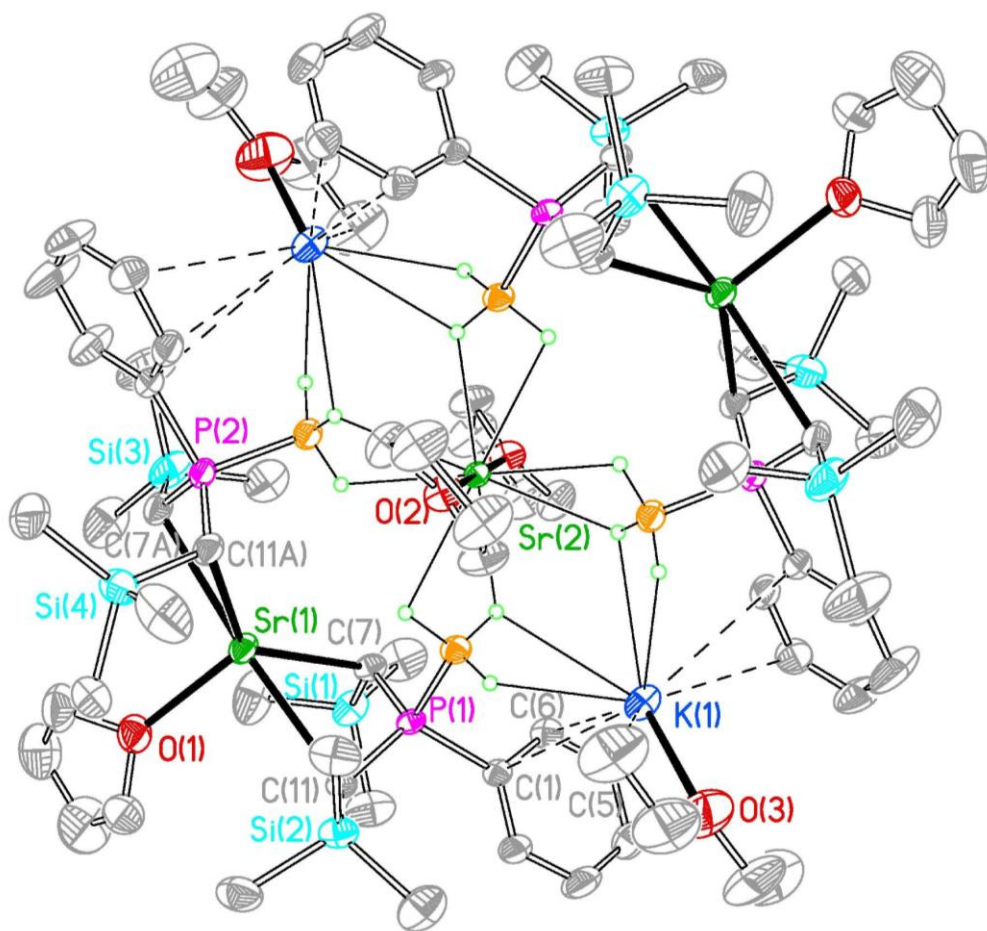
While compounds **2** and **3** crystallize as C-bridged dimers, compound **4** crystallizes as borane-bridged dimers in which the two barium ions are bridged in a  $\mu_2\text{-}\eta^1\text{:}\eta^2$  manner by the borane groups of two dicarbanion ligands. Each barium ion is coordinated by the two carbanion centers of a dicarbanion ligand to give a four-membered chelate ring [bite angle 58.46(7)°], one  $\eta^1\text{-BH}_3$  and one  $\eta^2\text{-BH}_3$  contact. The coordination of each barium ion is completed by two oxygen atoms, one from a molecule of diethyl ether and one from a disordered mix of diethyl ether and THF (which have occupancies of 75:25%), such that the

dimer as a whole contains half a molecule of THF. The two carbanion centers in **4** are chiral and this molecule crystallizes with a  $C_5C_5$  (*rac*) configuration.

Crystallographically characterized,  $\sigma$ -bonded organobarium compounds remain rather rare; however, the Ba-C distances in **4** [2.921(3) and 2.917(3) Å] lie between those reported for  $\{(Me_3Si)_2CH\}_2Ba(THF)_3$  [2.879(3) and 2.827(3) Å]<sup>6j</sup> and  $(Ph_2CH)_2Ba(18\text{-crown-}6)$  [3.065(3) and 3.096(3) Å].<sup>19</sup> The Ba-H distances [2.71(3), 2.81(3) and 2.93(3) Å] are typical for (B)H-Ba contacts; for example, the Ba-H distances in  $(diglyme)_2Ba(\eta^3\text{-}BH_4)_2$  range from 2.69(3) to 2.95(5) Å.<sup>20</sup> The Ba(1)...B(1A) distance [3.040(3) Å] is also similar to the Ba...B distance in  $(diglyme)_2Ba(\eta^3\text{-}BH_4)_2$  [3.058(7) Å], while the Ba(1)...B(1) distance [3.603(3) Å] is somewhat longer, consistent with the binding modes in each case.

The ate complex **5** also crystallizes as discrete molecular units; these contain three strontium ions, two potassium ions and four dicarbanion ligands. The molecular structure of **5** is shown in Figure 6, along with selected bond lengths and angles.





**Figure 6.** Molecular structure of **5** with 40% probability ellipsoids and with C-bound H atoms and disorder components omitted for clarity. Selected bond lengths (Å) and angles (°): Sr(1)-C(7) 2.764(2), Sr(1)-C(11) 2.875(2), Sr(1)-C(7A) 2.861(3), Sr(1)-C(11A) 2.770(2), Sr(1)-O(1) 2.5329(19), Sr(2)-H(1A) 2.54(2), Sr(2)-H(1B) 2.60(2), Sr(2)-H(2B) 2.62(2), Sr(2)-H(2D) 2.58(2), Sr(2)...B(1) 2.980(3), Sr(2)...B(2) 3.028(3), Sr(1)-O(2) 2.5419(16), K(1)-O(3) 2.653(3), K(1)-H(1A) 2.96(2), K(1)-H(1C) 2.72(2), K(1)-H(2C) 2.76(2), K(1)-H(2D) 2.89(2), K(1)...B(1) 3.267(3), K(1)...B(2A) 3.274(3), K(1)...C(1) 3.322(2), K(1)...C(5) 3.445(3), K(1)...C(6) 3.218(3), K(1)...C(1A) 3.523(3), K(1)...C(5A) 3.539(3), K(1)...C(6A) 3.245(3), K(1)...C(24) 3.441(15), C(7)-P(1) 1.752(2), C(11)-P(1) 1.739(2), C(7)-Si(1) 1.823(3), C(11)-Si(2) 1.813(2), C(7A)-P(2) 1.747(3), C(11A)-P(2) 1.744(3),

C(7A)-Si(3) 1.813(3), C(11A)-Si(4) 1.823(2), P(1)-B(1) 1.930(3), P(2)-B(2) 1.930(3), C(7)-Sr(1)-C(11) 61.12(7), C(7A)-Sr(1)-C(11A) 61.37(8).

Compound **5** contains two distinct types of strontium ion: Sr(1) and its symmetry equivalent lie at the periphery of the complex and are coordinated by four carbanion centers from two dicarbanion ligands [bite angles 61.12(7) and 61.37(8) $^{\circ}$ ] and by a molecule of THF. Thus, these two Sr ions adopt a distorted trigonal bipyramidal geometry in which two of the carbanion centers occupy the axial positions [C(7A)-Sr(1)-C(11) 175.57(7) $^{\circ}$ ]. In contrast, Sr(2) lies at the center of the cluster and is coordinated solely by the hydrogen atoms of four BH<sub>3</sub> groups and by two molecules of THF in a pseudo-octahedral geometry. The two potassium ions are each coordinated by a molecule of diethyl ether, two  $\eta^3$ -Ph contacts and two  $\eta^2$ -BH<sub>3</sub> contacts to two adjacent dicarbanion ligands. Thus, the BH<sub>3</sub> groups act as  $\mu_2$ - $\eta^2$ : $\eta^2$  bridges between the potassium ions and the central strontium ion in the cluster.

The Sr-C distances in **5** [2.875(2), 2.764(2), 2.861(3) and 2.770(2) Å] are similar to the Sr-C(terminal carbanion) distance in **3** and to previously reported Sr-C distances (see above). Similarly, the Sr...B distances in **5** [2.980(3) and 3.028(3) Å] are similar to the Sr...B distance in **3** and are comparable to Sr...B distances in the few previously reported complexes in which there is a Sr...BH<sub>n</sub> interaction; for example, the Sr...B distances in [(Me<sub>3</sub>Si)<sub>2</sub>CH]Sr( $\mu$ -Me<sub>2</sub>NBH<sub>3</sub>)(THF)<sub>2</sub>]<sub>2</sub> are 2.912 and 2.960 Å.<sup>21</sup> The K-H distances [2.72(2)-2.96(2) Å] and the K...B distances [3.267(3) and 3.274(3) Å] in **5** are also similar to previously reported distances of this type; for example, the K-H distances in [(Me<sub>3</sub>Si)<sub>2</sub>{Me<sub>2</sub>P(BH<sub>3</sub>)}C]K]<sub>∞</sub> range from 2.71(5) to 2.92(4) Å, while the K...B distances in this compound range from 3.108(7) to 3.340(7) Å.<sup>10b</sup>

## Conclusions

While coordination of the metal in the majority of previously reported PBC complexes of the alkaline earth metals is dominated by B-H...Ae contacts, complexes of the

silicon- and phosphine-borane-stabilized dicarbanion  $[\text{PhP}(\text{BH}_3)\{\text{CH}(\text{SiMe}_3)\}_2]^{2-}$  exhibit both B-H...Ae and C-Ae contacts. Each of the alkaline earth metal complexes of this dicarbanion (**2-4**) crystallizes as a dimer; however, these adopt significantly different structures in the solid state. Both **2** and **3** crystallize as C-bridged dimers, which differ in the stereochemistry of the bridging carbanion centers and the coordination number of the metal centers. In contrast, the larger  $\text{Ba}^{2+}$  ion in **4** favors a dimeric structure in which the two metal centers are bridged by Ba...H-B interactions. All three compounds, although isolated as complexes with diethyl ether and/or THF co-ligands, decompose slowly in solution due to  $\alpha$ - or  $\beta$ -abstraction of a proton from the coordinated ether, generating the corresponding alkaline earth metal complexes of the mono-carbanion  $[(\text{Me}_3\text{Si})\text{CH}_2\text{PPh}(\text{BH}_3)\text{CH}(\text{SiMe}_3)]^-$ .

### Experimental

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF, diethyl ether, and toluene were dried prior to use by distillation under nitrogen from sodium, potassium, or sodium/potassium alloy, as appropriate. THF was stored over activated 4A molecular sieves; all other solvents were stored over a potassium film. Deuterated THF and toluene were distilled from potassium under nitrogen, deoxygenated by three freeze-pump-thaw cycles and were stored over activated 4A molecular sieves. Dibenzylstrontium,<sup>14</sup> dibenzylbarium,<sup>6g</sup>  $(4\text{-}t\text{BuC}_6\text{H}_4\text{CH}_2)\text{K}$ ,<sup>6f</sup>  $(4\text{-}t\text{BuC}_6\text{H}_4\text{CH}_2)_2\text{Ca}(\text{THF})_4$ ,<sup>6f</sup> and  $\text{PhP}(\text{BH}_3)(\text{CH}_2\text{SiMe}_3)_2$  (**1**)<sup>10h</sup> were prepared by previously published procedures. All other compounds were used as supplied by the manufacturer.

$^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra were recorded on a JEOL ECS500 or a Bruker AvanceIII HD500 spectrometer operating at 500.16 and 125.65 MHz, respectively, or a Bruker AvanceIII300 spectrometer operating at 300.15 and 75.47 MHz, respectively; chemical shifts are quoted in ppm relative to tetramethylsilane. The assignment of peaks in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra was accomplished with the aid of standard HSQC and DEPT spectra, where appropriate.  $^{31}\text{P}\{^1\text{H}\}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra were recorded on a JEOL

ECS500 spectrometer operating at 202.35 and 160.16 MHz, respectively, or a Bruker AvanceIII300 spectrometer operating at 121.49 and 96.29 MHz, respectively; chemical shifts are quoted in ppm relative to external 85% H<sub>3</sub>PO<sub>4</sub> and BF<sub>3</sub>.Et<sub>2</sub>O, respectively. A 2D phase-sensitive <sup>1</sup>H NOESY experiment conducted under conditions of selective decoupling of <sup>11</sup>B at -28.93/-31.02 ppm during the *t*<sub>1</sub> and *t*<sub>2</sub> periods was acquired on a Bruker AvanceIII HD500 spectrometer. The experiment was recorded with a mixing time of 600 ms, and with 16 scans per increment to generate a 4096 x 512 matrix which was transformed using a sinebell window in each dimension. The sample was not spun and the temperature was stabilized at 298 +/- 0.1 K. <sup>1</sup>H DOSY measurements of **3** were performed on the same spectrometer using a BBO probe and shielded z-gradient coils. The standard Bruker pulse program, ledbpgp2s, employing a stimulated echo sequence, bipolar gradient pulses for diffusion, and two spoil gradients was utilized. The diffusion time was constant at 100 ms and the gradient pulse strength was varied from 0.025 Tm<sup>-1</sup> to 0.49 Tm<sup>-1</sup> in 16 linear steps. The experiment was run non-spinning, with a 5mm NMR tube, a sample depth of 58 mm and was stabilized at 298 +/- 0.1 K. Individual FIDs were transformed into 64k data points using an exponential line broadening of 1.0 Hz, and were phased and baseline corrected.

The theoretical hydrodynamic radius of **3** was calculated using the *volume* keyword in the Gaussian09 software package;<sup>22</sup> a single point energy calculation was carried out, using the Cartesian coordinates obtained by X-ray crystallography, with the wB97XD hybrid functional<sup>23</sup> and an Lanl2dz effective core potential basis set<sup>24</sup> on Sr and the 6-31G(d,p) basis set<sup>25</sup> on the remaining atoms.

We were unable to obtain consistent elemental analyses for compounds **2**, **3**, **5**, or **6** due to a combination of partial solvent loss, unequal substitution of the metal centers by diethyl ether and THF, and the decomposition of samples via ether cleavage (see text); for **4** we were able to isolate a sample having a consistent Et<sub>2</sub>O/THF ratio and this compound decomposes sufficiently slowly to permit elemental analysis.

**[[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)<sub>2</sub>]Ca(OEt<sub>2</sub>)<sub>2</sub> (2):** To a solution of **1** (0.68 g, 2.30 mmol) in toluene (20 mL) was added a solution of (4-*t*BuC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>)<sub>2</sub>Ca(THF)<sub>4</sub> (1.43 g, 2.30 mmol) in toluene (20 mL). The resulting solution was stirred overnight, then filtered and the solvent was removed *in vacuo* to yield a yellow oily solid. Recrystallization of this solid from diethyl ether (20 mL) at 5 °C yielded **2** as colorless blocks. Yield (0.90 g, 96%). Accurate elemental analyses could not be obtained for this compound (see text). <sup>1</sup>H{<sup>11</sup>B} NMR (*d*<sub>8</sub>-THF, 25 °C): δ -0.46 (broad, 4H, PCHSi), -0.24 (s, 36H, SiMe<sub>3</sub>), 0.79 (d, <sup>2</sup>J<sub>HP</sub> = 12.1 Hz, 6H, BH<sub>3</sub>), 1.11 (t, 2H, Et<sub>2</sub>O), 1.77 (m, 12H, THF) 3.38 (q, 1.5H, Et<sub>2</sub>O), 3.62 (m, 12H, THF), 6.96 (m, 2H, Ph), 7.05 (m, 4H, Ph), 7.75 (m, 4H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 25 °C): δ 5.11 (d, <sup>2</sup>J<sub>CP</sub> = 4.4 Hz, SiMe<sub>3</sub>), 15.96 (Et<sub>2</sub>O), 24.24 (d, <sup>1</sup>J<sub>PC</sub> = 7.9 Hz, PCHSi), 25.37 (THF), 66.66 (Et<sub>2</sub>O), 67.67 (THF) 125.44 (Ph), 126.78 (d, *J* = 8.0 Hz, Ph), 130.45 (d, *J*<sub>PC</sub> = 9.2 Hz, Ph), 155.28 (d, *J*<sub>PC</sub> = 17.9 Hz, Ph). <sup>11</sup>B{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 25 °C): δ -32.6 (br). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 25 °C): δ 6.5 (q, *J*<sub>PB</sub> = 91 Hz).

**[[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)<sub>2</sub>]Sr(THF)<sub>1.75</sub>(OEt<sub>2</sub>)<sub>0.25</sub>]<sub>2</sub> (3):** To a solution of (PhCH<sub>2</sub>)<sub>2</sub>Sr(THF) (0.97 g 2.84 mmol) in THF (20 mL) was added a solution of **1** (0.84 g, 2.83 mmol) and this mixture was stirred for 16 h. The solvent was removed *in vacuo* and the orange foam was treated with diethyl ether (20 mL), whereupon pale yellow crystals began to form. After 2 h the yellow crystals were isolated by filtration and residual solvent was removed *in vacuo*. Yield 1.06 g, 73%. Accurate elemental analyses could not be obtained for this compound (see text). <sup>1</sup>H NMR (*d*<sub>8</sub>-THF, 21 °C): δ -0.40 (d, *J*<sub>PH</sub> = 15.0 Hz, 4H, PCHSi), -0.27 (s, 36H, SiMe<sub>3</sub>), 0.80 (br. q, *J*<sub>BH</sub> = ca 81 Hz, 6H, BH<sub>3</sub>), 1.11 (t, 3H, Et<sub>2</sub>O), 1.77 (m, 8H, THF), 3.39 (q, 2H, Et<sub>2</sub>O), 3.62 (m, 8H, THF), 6.94 (m, 2H, Ph), 7.02 (m, 4H, Ph), 7.71 (m, 4H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 21 °C): δ 4.32 (SiMe<sub>3</sub>), 22.01 (br, PCHSi), 25.40 (THF), 63.32 (THF), 124.74 (d, *J*<sub>PC</sub> = 2.3 Hz, Ph), 125.74 (d, *J*<sub>PC</sub> = 7.9 Hz, Ph), 130.22

(d,  $J_{PC} = 10.1$  Hz, Ph), 152.17 (d,  $J_{PC} = 19.8$  Hz, Ph).  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 21 °C):  $\delta$  -30.7 (d,  $J_{PB} = 106$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 21 °C):  $\delta$  5.0 (br q,  $J_{PB} = 106$  Hz).

**[[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)<sub>2</sub>]}Ba(OEt<sub>2</sub>)<sub>1.75</sub>(THF)<sub>0.25</sub>]<sub>2</sub> (4):** To a solution of **1** (1.50 g, 4.91 mmol) in THF (30 mL) was added a solution of (PhCH<sub>2</sub>)<sub>2</sub>Ba (1.57 g, 4.91 mmol) in THF (40 mL). The resulting solution was stirred for 3 h, then filtered and the solvent was removed *in vacuo* to yield an orange oily solid. Recrystallization from diethyl ether (20 mL) at 5 °C yielded **4** as colorless blocks. Yield 0.98 g, 34%. Anal. Calcd for C<sub>44</sub>H<sub>94</sub>B<sub>2</sub>Ba<sub>2</sub>O<sub>4</sub>P<sub>2</sub>Si<sub>4</sub> (1157.78): C 45.65, H 8.18. Found: C 45.54, H 8.06.  $^1\text{H}\{^{11}\text{B}\}$  NMR ( $d_8$ -THF, 25 °C):  $\delta$  -0.39 (d,  $^2J_{HP} = 14.2$  Hz, 4H, PCHSi), -0.19 (s, 36H, SiMe<sub>3</sub>), 1.06 (d,  $^2J_{HP} = 14.2$  Hz, 6H, BH<sub>3</sub>), 1.18 (t, 12H, Et<sub>2</sub>O), 1.78 (m, 4H, THF), 3.39 (q, 8H, Et<sub>2</sub>O), 3.63 (m, 4H, THF), 6.94 (m, 2H, Ph), 7.04 (m, 4H, Ph), 7.67 (m, 4H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 25 °C):  $\delta$  4.14 (d,  $^2J_{CP} = 4.5$  Hz, SiMe<sub>3</sub>), 14.78 (Et<sub>2</sub>O), 23.54 (d,  $^2J_{CP} = 27.3$  Hz, PCHSi), 24.57 (THF), 66.36 (Et<sub>2</sub>O), 68.27 (THF), 124.88 (Ph), 125.84 (d,  $J = 8.1$  Hz, Ph), 130.11 ( $J = 10.5$  Hz, Ph), 152.61 (Ph).  $^{11}\text{B}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 25 °C):  $\delta$  -28.1 (d,  $J_{PB} = 106$  Hz).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $d_8$ -THF, 25 °C):  $\delta$  3.4 (q,  $J_{PB} = 106$  Hz).

**[[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)<sub>2</sub>]}Sr<sub>3</sub>K<sub>2</sub>(OEt<sub>2</sub>)<sub>2</sub>(THF)<sub>4</sub>.Et<sub>2</sub>O (5):** To a suspension of SrI<sub>2</sub> (0.58 g, 1.70 mmol) in THF (10 mL) was added a solution of 4-*t*BuC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>K (0.63 g, 3.38 mmol) in THF (30 mL). This mixture was stirred for 2 h and then a solution of **1** (0.50 g, 1.69 mmol) in THF (10 mL) was added. This mixture was stirred for 1.5 h and then the pale solids were removed by filtration. Solvent was removed *in vacuo* from the filtrate and the resulting orange oily solid was dissolved in diethyl ether (20 mL) and cooled to 5 °C for 16 h. The pale yellow crystals of **5** were isolated by filtration and washed with a little light petroleum. Yield 0.09 g, 11% [based on molecular formula without solvent of crystallization]. Accurate elemental analyses could not be obtained for this compound (see text).  $^1\text{H}$  NMR ( $d_8$ -toluene, 21 °C):  $\delta$  -0.03 (br s, 8H, PCHSi), 0.26 (s, 72H, SiMe<sub>3</sub>), 1.10 (t,

12H, Et<sub>2</sub>O), 1.49 (br s, 16H, THF), 3.26 (q, 8H, Et<sub>2</sub>O), 3.73 (br s, 16H, THF), 7.08 (m, 4H, Ph), 7.30 (m, 8H, Ph), 8.09 (m, 8H, Ph) [BH<sub>3</sub> signal too broad to observe]. <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene, 21 °C): δ 5.13 (SiMe<sub>3</sub>), 15.18 (Et<sub>2</sub>O), 23.06 (br s, PCHSi), 25.17 (THF), 65.51 (Et<sub>2</sub>O), 68.41 (THF), 130.43 (Ph) [remaining aromatic signals obscured]. <sup>11</sup>B{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene, 21 °C): δ -27.2 (d, *J*<sub>PB</sub> = 108 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-toluene, 21 °C): δ 0.2 (br q, *J*<sub>PB</sub> = 108 Hz).

**[PhP(BH<sub>3</sub>){CH(SiMe<sub>3</sub>)}{CH<sub>2</sub>SiMe<sub>3</sub>]}K(THF)<sub>0.25</sub> (6):** To a solution of **1** (0.30 g, 1.01 mmol) in THF (10 mL) was added a solution of PhCH<sub>2</sub>K (0.13 g, 1.00 mmol) and this mixture was stirred for 2 h. Solvent was removed *in vacuo* to give a pale yellow solid, which was washed with light petroleum (5 mL). Residual solvent was removed *in vacuo* to give **6** as a pale yellow powder. Yield 0.28 g, 81%. <sup>1</sup>H{<sup>11</sup>B} NMR (*d*<sub>8</sub>-THF, 25 °C): δ -0.87 (d, *J*<sub>PH</sub> = 11.6 Hz, PCHSi), -0.07 (s, 9H, SiMe<sub>3</sub>), -0.04 (s, 9H, SiMe<sub>3</sub>), 0.70 (d, *J*<sub>PH</sub> = 13.1 Hz, 3H, BH<sub>3</sub>), 1.11 (m, 1H, CHH), 1.17 (m, 1H, CHH), 1.78 (m, 1H, THF), 3.61 (m, 1H, THF), 7.09 (m, 1H, Ph), 7.18 (m, 2H, Ph), 7.85 (m, 2H, Ph). <sup>13</sup>C{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 25 °C): δ 1.54 (d, *J*<sub>PC</sub> = 1.9 Hz, SiMe<sub>3</sub>), 4.93 (d, *J*<sub>PC</sub> = 48.5 Hz, CHK), 5.67 (d, *J*<sub>PC</sub> = 3.4 Hz, SiMe<sub>3</sub>), 24.75 (d, *J*<sub>PC</sub> = 24.1 Hz, PCH<sub>2</sub>Si), 26.43 (THF), 67.96 (THF), 127.25 (d, *J*<sub>PC</sub> = 2.0 Hz, Ph), 127.38 (d, *J*<sub>PC</sub> = 8.3 Hz, Ph), 131.65 (d, *J*<sub>PC</sub> = 8.6 Hz, Ph), 149.42 (d, *J*<sub>PC</sub> = 39.0 Hz, Ph). <sup>11</sup>B{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 25 °C): δ -31.8 (d, *J*<sub>PB</sub> = 91 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (*d*<sub>8</sub>-THF, 25 °C): δ 4.5 (*J*<sub>PB</sub> = 91 Hz).

**Crystal Structure Determinations of 2, 3, 4, and 5:** Measurements were made at 150 K on an Oxford Diffraction (Agilent Technologies) Gemini A Ultra diffractometer or a Nonius KappaCCD diffractometer, using CuKα radiation (λ = 1.54178 Å; **3**) or MoKα radiation (λ = 0.71073 Å; **2**, **4**, and **5**). Cell parameters were refined from the observed positions of all strong reflections. Intensities were corrected for absorption either semi-empirically, based on symmetry-equivalent and repeated reflections, or analytically, using a

multi-faceted crystal model.<sup>26</sup> The structures were solved by direct methods and refined on  $F^2$  values for all unique data; Table S1 in the Supporting Information gives further details. 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;  $U(\text{H})$  was set at 1.2 (1.5 for methyl groups) times  $U_{\text{eq}}$  for the parent C atom. Disorder in was successfully modelled with the use of restraints in the following cases: **3** one trimethylsilyl group and one Et<sub>2</sub>O/THF co-ligand (25:75% occupancy); **4** one Et<sub>2</sub>O and one Et<sub>2</sub>O/THF co-ligand (the latter with 75:25% occupancy); **5** one trimethylsilyl group, one Et<sub>2</sub>O and one THF ligand. Programs were Oxford Diffraction CrysAlisPro for data collection and processing, and the Olex2 interface to the SHELX suite for structure solution, refinement, and molecular graphics.<sup>27</sup>

**Supporting Information:** For **2**, **3**, **4**, and **5** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in CIF and tabular format. <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} NMR spectra of **2-6** and the <sup>1</sup>H{<sup>11</sup>B} NOESY NMR spectrum of **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

**Acknowledgment:** The authors are grateful to Newcastle University and the Libyan government for support. The authors thank Prof W. McFarlane for writing the pulse sequence for the <sup>1</sup>H{<sup>11</sup>B} NOESY NMR experiment.

**Dedication:** Dedicated to the memory of Prof. Mike F. Lappert FRS.

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