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Alkaline Earth Metal Complexes of a Phosphine-Borane-Stabilized Carbanion: Synthesis, Structures, and Stabilities

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The reaction between either MgI_2 or CaI_2 and 2 equiv of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]K$ (**2**) in toluene gives the corresponding organo-alkaline earth metal compounds $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2M$ in moderate to good yields [M = Mg (**3**), Ca (**4**)]. Compound **3** crystallizes solvent-free, whereas X-ray quality crystals of **4** could not be obtained in the absence of coordinating solvents; crystallization of **4** from cold methylcyclohexane/THF gives the solvate $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Ca(THF)_4$ (**4a**). The corresponding heavier alkaline earth metal complexes $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2M(THF)_5$ [M = Sr (**7**), Ba (**8**)] are obtained from the reaction between MI_2 and 2 equiv of **2** in THF, followed by recrystallization from cold methylcyclohexane/THF. Compound **3** degrades over a period of several weeks at room-temperature both in the solid state and in toluene solution to give the free phosphine-borane $(Me_3Si)_2\{Me_2(H_3B)P\}CH$ (**5**) as the sole phosphorus-containing product. In addition, compounds **3**, **4**, and **4a** react rapidly with THF in toluene solution, yielding **5** as the sole phosphorus-containing product; in contrast, compounds **7** and **8** are stable toward this solvent.

Introduction

Since organomagnesium compounds were first described by Barbier and Grignard at the beginning of the 20th century, they have become a mainstay of synthetic organic and organometallic chemists, due largely to the ease with which such compounds may be synthesized and the wide array of reactions that they undergo.[1] The organometallic chemistry of the heavier alkaline earth metals is, by contrast, still in its infancy and, until recently, was largely restricted to complexes of cyclopentadienyl and substituted cyclopentadienyl ligands.[1,2] The more limited development of σ-bonded organometallic derivatives of these metals may be attributed to the difficulties associated with their synthesis and manipulation, due to the large size of the heavier group 2 cations and the highly polar nature of the respective M−C σ-bonds.[3] These factors typically result in highly aggregated (often insoluble) species with very high reactivities, even toward the solvents in which they are prepared.

Organocalcium halides, the heavier alkaline earth metal analogues of Grignard reagents, were first reported by Beckmann in 1905,[4] but it was not until 1991 that the first structurally characterized σ-bonded organocalcium compound, $\{(Me_3Si)_2CH\}_2Ca(1,4\text{-dioxane})$ (**1**),[5] was reported. This compound stood as the sole example of its class for several years, and it is only very recently that significant progress has been made in the synthesis of σ-bonded heavier group 2 organometallic compounds. The range of such compounds has now expanded dramatically to include an array of benzyl,[6] acetylide,[7] aryl,[8] and heteroatom-stabilized

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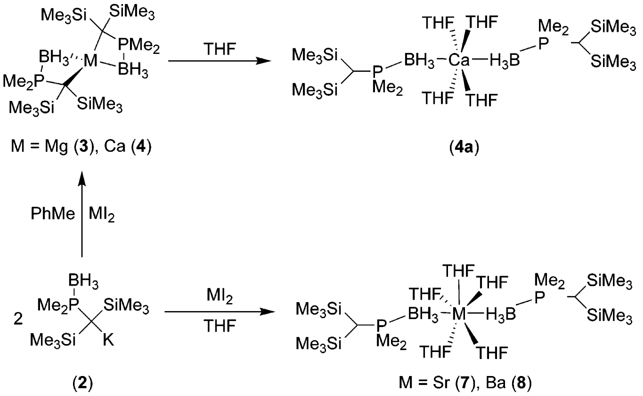
Scheme 1



alkyl compounds[9] and several heterometallic species,[10] culminating in the recent successful low-temperature isolation and structural characterization of several organocalcium halides by Westerhausen and co-workers.[11]

In spite of this recent progress much still remains to be learned about the structures and reactions of these fascinating species. We have recently become interested in the chemistry of phosphine-borane-stabilized carbanions and have shown that the structures of the group 1 derivatives of the silicon- and phosphine-borane-stabilized carbanion $[(Me_3Si)_2\{Me_2(H_3B)P\}C]^-$ are markedly affected by the size and polarizability of the cation.[12,13] We now report the synthesis and structural characterization of a homologous series of group 2 complexes of this carbanion and comment on their stabilities.

Results and Discussion

Treatment of MI_2 [M = Mg, Ca] with 2 equiv of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]K$ (**2**)[12] in toluene yields the complexes $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2M$ [M = Mg (**3**), Ca (**4**)] as colorless solids (Scheme 1); compounds **3** and **4** may be obtained as colorless blocks by recrystallization from cold toluene. While single crystals of **3** may be obtained in this way, we were unable to obtain crystals of **4** suitable for X-ray crystallography in the absence of coligands (see below); however, the identity of **4** was confirmed by multielement NMR spectroscopy and elemental analyses.

Compounds **3** and **4** are soluble in hydrocarbon solvents, but compound **3** decomposes slowly over a matter of weeks in toluene solution at room temperature. This decomposition reaction is accelerated at higher temperatures: significant degradation is observed after heating under reflux in toluene for 2 h, and complete decomposition of **3** is observed after 12 h under these conditions. The decomposition reaction yields the free phosphine-borane $(Me_3Si)_2\{Me_2(H_3B)P\}CH$ (**5**) as the only toluene-soluble component along with a significant amount of white precipitate. This precipitate is insoluble, even in hot THF, and appears to be largely inorganic in nature; elemental analyses indicate very low carbon and hydrogen content for this material, and hydrolysis experiments yield a gelatinous solid (most likely a magnesium hydroxide) along with a very small amount of **5**, which was identified spectroscopically. There is no evidence for deprotonation of the toluene solvent under the conditions employed, and experiments conducted in d_8-toluene do not result in incorporation of deuterium into **5**. These observations suggest that decomposition may involve proton transfer from one carbanion ligand to another, possibly from a PMe_2 or $SiMe_3$ group to give a phosphorus- or silicon-stabilized carbanion, respectively, followed by further decomposition to an inorganic species (e.g., MgH_2 or $Mg(BH_4)_2$).

The ^1H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectra of **3** and **4** are as expected; the $^{31}P\{^1H\}$ NMR spectra consist of broad quartets at −3.8 ppm ($J_{PB} = 88.9$ Hz) and −5.8 ppm ($J_{PB} = 102.7$ Hz), respectively [cf. 6.5 ppm ($J_{PB} = 59.5$ Hz) for the free phosphine-borane **5**; −5.9 ppm ($J_{PB} = 98.5$ Hz) for the potassium salt **2**].[13] Compound **3** crystallizes with two crystallographically independent molecules in the asymmetric unit which differ only trivially in their bond lengths and angles; the molecular structure of **3** is shown in Figure 1 along with details of selected bond lengths and angles. Compound **3** crystallizes solvent-free as discrete monomers, in which the Mg ions are bound by the carbanion centers and, in an η^2-fashion, by the hydrogen atoms of the BH_3 groups of the ligands. This generates two pseudo-four-membered chelate rings and confers a pseudotetrahedral geometry on the magnesium ion. This is in contrast to the exactly isoelectronic analogue $\{(Me_3Si)_3C\}_2Mg$ (**6**),[14] which has a strictly linear C−Mg−C core, with a two-coordinate magnesium ion. The Mg−C distances of 2.270(5) and 2.262(5) Å in **3** [2.287(5) and 2.285(4) Å in the second molecule in the asymmetric unit] are substantially longer than the corresponding distance in **6** [2.116(2) Å], consistent with the low coordination number of the magnesium ion in this latter compound. The Mg−C distance in **3** is also rather long in comparison to typical Mg−C σ-bonds in Grignard reagents in which the Mg ion is four- or six-coordinate [2.09−2.25 Å];[1] this may be a consequence of the formation of a strained pseudo-four-membered chelate ring in **3**. The Mg...B distances of 2.549(6) and 2.527(6) Å [2.546(6) and 2.518(6) Å in molecule 2] and the Mg−H distances of 1.94(5)−2.40(5) Å [2.03(4)−2.53(6) Å in molecule 2] are similar to the Mg...B and Mg−H distances in a range of Lewis base adducts of

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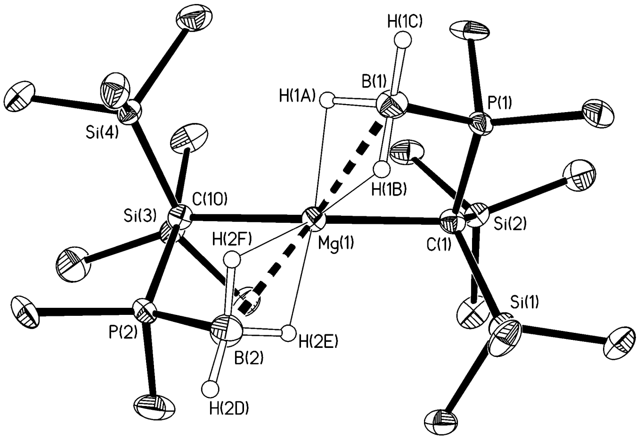


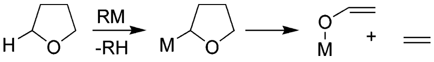
Figure 1. Molecular structure of one of the two independent molecules of **3** with 40% displacement ellipsoids and with H atoms bonded to carbon omitted for clarity. Selected bond lengths (Å) and angles (deg): Mg(1)−C(1) 2.270(5), Mg(1)−C(10) 2.262(5), Mg(1)...B(1) 2.527(6), Mg(1)...B(2) 2.549(6), Mg(1)−H(1A) 1.94(5), Mg(1)−H(1B) 2.35(5), Mg(1)−H(2E) 1.98(5), Mg(1)−H(2F) 2.40(5), C(1)−P(1) 1.781(5), C(10)−P(2) 1.791(4), C(1)−Si(1) 1.896(5), C(1)−Si(2) 1.890(5), C(10)−Si(3) 1.880(4), C(10)−Si(4) 1.878(5), P(1)−B(1) 1.912(5), P(2)−B(2) 1.922(6), Mg(2)−C(19) 2.285(4), Mg(2)−C(28) 2.287(5), Mg(2)...B(3) 2.546(6), Mg(2)...B(4) 2.518(6), Mg(2)−H(3D) 2.03(4), Mg(2)−H(3E) 2.53(6), Mg(2)−H(4D) 2.37(5), Mg(2)−H(4E) 2.09(6), C(19)−P(3) 1.782(4), C(28)−P(4) 1.776(5), C(19)−Si(5) 1.877(4), C(19)−Si(6) 1.893(4), C(28)−Si(7) 1.886(5), C(28)−Si(8) 1.879(4), P(3)−B(3) 1.908(6), P(4)−B(4) 1.919(5), Si−$C(Me)_{av}$ 1.886, C(1)−Mg(1)−B(1) 76.49(17), C(10)−Mg(1)−B(2) 77.00(18), C(19)−Mg(2)−B(3) 76.48(17), C(28)−Mg(2)−B(4) 76.84(17).

$Mg(BH_4)_2$ and related compounds;[15,16] for example, the Mg...B distances in $(Bu^tNH_2)_3Mg(BH_4)_2$, in which the BH_4 ligands adopt an η^2-binding mode, are 2.549(2) and 2.521(2) Å, while the average Mg−H distance in this compound is 2.08 Å.[15]

Although the calcium derivative **4** could not be obtained as single crystals in the absence of coligands, X-ray quality crystals of the adduct $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Ca(THF)_4$ (**4a**) were obtained by recrystallization of **4** from cold methylcyclohexane/THF. In contrast to its unsolvated analogue, compound **4a** is unstable in solution; samples of **4a** decompose at room temperature in toluene to give the free phosphine-borane **5** as the sole phosphorus-containing product within a few weeks. Addition of an excess of THF to samples of either **4** or **4a** results in a dramatic increase in the rate of decomposition, samples degrading completely within 20 min. Similarly, the magnesium derivative **3** decomposes rapidly on exposure to THF, again yielding **5** as the sole phosphorus-containing species. Careful monitoring of the reaction between **3** and THF by $^{31}P\{^1H\}$ NMR spectroscopy indicates that this reaction proceeds via the formation of at least two phosphine-borane-containing intermediates and that these are formed within minutes of dissolution of the crystals; unfortunately, we were unable to isolate these intermediates for further study.

Reactions between polar organometallic compounds and THF are well-known and typically proceed via α-deprotonation, followed by fragmentation to give ethylene and the corresponding metal enolate (Scheme 2).[17] However, although this would appear to be a plausible decomposition mechanism for **3** and **4**/**4a** when treated with THF, we were unable to observe the formation of ethylene in sealed tube NMR experiments and so are unable to confirm this unambiguously. Neither was there any evidence from ^1H or ^{13}C NMR experiments for ring-opened THF fragments or enolate ligands, although such products are likely to be rather insoluble in the C_6D_6 solvent employed and so may not be easy to detect.

Scheme 2



The strontium and barium derivatives $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2M(THF)_5$ [M = Sr (**7**), Ba (**8**)] are isolated as THF adducts which, in contrast to **4a**, are stable indefinitely in solution, even in THF itself (see below). This is in spite of the expected increase in polarity, and hence reactivity, of the M−C bonds in these species in comparison to **3** and **4**. Although the carbanion centers in the magnesium complex **3** are significantly pyramidalized, indicating substantial charge localization at carbon in this compound, the calcium complex **4a** contains ligands with planar, substantially charge-delocalized carbanion centers similar to those found in **7** and **8** (see below). This clearly suggests that the reactivity of **3** and **4** toward THF is governed by the Lewis acidity of the metal center in these complexes rather than the "carbanion" character of the ligand. In this regard, it is of note that the alkali metal derivatives $(THF)_3Li\{(Me_3Si)_2CPMe_2(BH_3)\}_2Li$ (**9**) and $[(Me_3Si)_2\{Me_2P(BH_3)\}C]ML]_n$ [ML = Na(THF)₂ (**10**), K (**11**), Rb (**12**), $n = \infty$; ML = Cs(pmdeta), $n = 2$ (**13**); pmdeta = *N*,*N*,*N*′,*N*″*N*″-pentamethyldiethylenetriamine] are indefinitely stable in THF solution.[12,13]

We have previously observed a related phenomenon in alkaline earth metal phosphide chemistry. The reaction between CaI_2 and 2 equiv of the ether-functionalized potassium phosphide $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]K$ yields the heterocubane cluster species $[[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}O)P]Ca(THF)]_4$, which contains a novel dianionic alkoxophosphide ligand, via a C−O cleavage reaction.[18] In contrast, reactions between SrI_2 or BaI_2 and 2 equiv of $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]K$ yield the expected bis(phosphide) products $[\{(Me_3Si)_2CH\}(C_6H_4\text{-}2\text{-}OMe)P]_2M(THF)_n$ [M = Sr, $n = 2$; M = Ba, $n = 3$].[19]

Although the instability of **4a** prevented us from obtaining an accurate elemental analysis, this compound was fully characterized by ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy and X-ray crystallography. Compound **4a** crystallizes as discrete, centrosymmetric monomers; the molecular structure of **4a** is shown in Figure 2 along with details of selected bond lengths and angles. The phosphine-

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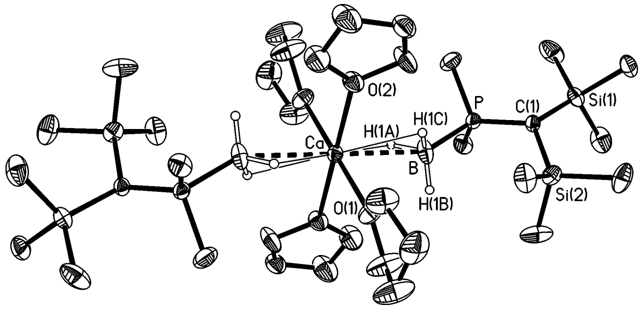
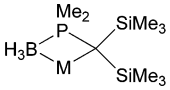


Figure 2. Molecular structure of **4a** with 40% probability ellipsoids and with H atoms bound to carbon omitted for clarity. Selected bond lengths (Å) and angles (deg): Ca...B 2.751(2), Ca−H(1A) 2.40(2), Ca−H(1C) 2.43(2), Ca−O(1) 2.3724(14), Ca−O(2) 2.4168(13), C(1)−P 1.7151(17), C(1)−Si(1) 1.8205(18), C(1)−Si(2) 1.8183(17), P−B 1.926(2), Si−C(Me)$_{av}$ 1.886, B−Ca−O(1) 87.22(7), B−Ca−O(2) 93.52(7), O(1)-Ca−O(2) 91.46(5), Ca−B−P 152.97(15), P−C(1)−Si(1) 119.63(9), P−C(1)−Si(2) 115.82(10), Si(1)−C(1)−Si(2) 118.64(9).

borane-stabilized carbanion coordinates to the metal center in an η^2-fashion solely via its BH_3 hydrogen atoms; there is no contact between the calcium ion and the essentially planar carbanion center [sum of angles at C(1) = 354.09°]. This is the first time that such a binding mode has been observed for this type of ligand; in complexes with the alkali metals this ligand adopts either a chelating mode similar to that observed in **3** (**I**) or one of a variety of bridging modes (**II**−**IV**).[12,13]



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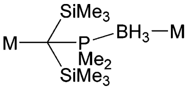

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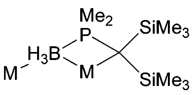

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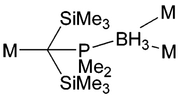

IV

The coordination sphere of the calcium ion is completed by the oxygen atoms of four molecules of THF to afford a slightly distorted *trans*-octahedral geometry. The Ca...B distance of 2.751(2) Å and the Ca−H distances of 2.40(2) and 2.43(2) Å are similar to the corresponding distances in the few other compounds containing Ca−H(B) contacts; for example, the Ca−H(B) distances in $(DME)_2Ca(BH_4)_2$, range from 2.35(3) to 2.58(3) Å.[20] In contrast, the Ca−H(B) distances in **4a** are substantially longer than the corresponding distance in $\{1,2,4\text{-}(Me_3Si)_3C_5H_2\}Ca(HBEt_3)(THF)_2$ [2.21(4) Å],[21] although the coordination environments of the calcium ions differ significantly between these two compounds.

Whereas we encountered problems in the isolation of **4**, the syntheses of the corresponding strontium and barium analogues proceeded smoothly (Scheme 1). The reaction of 2 equiv of **2** with either SrI_2 or BaI_2 in THF, followed by crystallization from cold methylcyclohexane/THF, gives the compounds $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2M(THF)_5$ [M = Sr (**7**), Ba (**8**)] in moderate to good yields. Compounds **7** and **8** are soluble in ethers and toluene but are only sparingly soluble in light petroleum. The ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **7** and **8** are as expected; the $^{31}P\{^1H\}$ NMR spectra of **7** and **8** consist of broad, poorly resolved quartets centered at −8.6 ppm (J_{PB} = 97.8 Hz) and −8.4 ppm (J_{PB} = 95.6 Hz), respectively. In contrast to the rapid degradation observed for **4a**, the THF adducts **7** and **8** are indefinitely stable in the solid state and in solution, including in THF, showing no signs of decomposition even after several weeks.

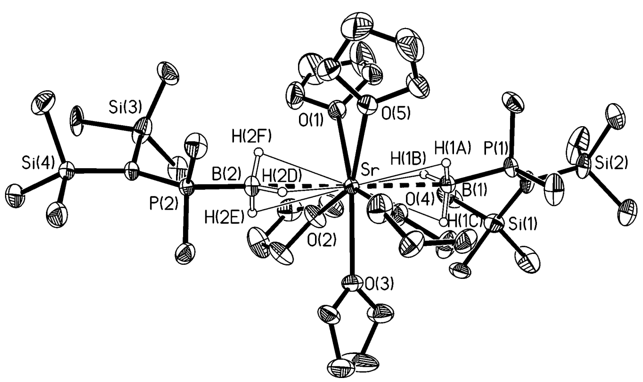

Figure 3. Molecular structure of **7** with 40% probability ellipsoids. H atoms bonded to carbon and minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (deg) for **7** [values in square brackets refer to the isostructural compound **8**]: M...B(1) 2.893(4) [3.027(8)], M...B(2) 2.873(4) [3.023(8)], M−H(1A) 2.65(3) [2.65(4)], M−H(1B) 2.76(3) [2.84(4)], M−H(1C) 2.89(4) [3.06(4)], M−H(2D) 2.59(3) [2.72(4)], M−H(2E) 2.79(3) [2.91(4)], M−H(2F) 2.73(3) [2.89(4)], M−O(1) 2.586(2) [2.761(5)], M−O(2) 2.620(2) [2.758(6)], M−O(3) 2.606(2) [2.762(5)], M−O(4) 2.591(2) [2.754(5)], M−O(5) 2.652(2) [2.790(5)], C(1)−P(1) 1.704(3) [1.711(7)], C(1)−Si(1) 1.819(4) [1.800(9)], C(1)−Si(2) 1.835(3) [1.845(8)], P(1)−B(1) 1.935(4) [1.944(9)], C(10)−P(2) 1.719(3) [1.729(7)], C(10)−Si(3) 1.817(3) [1.802(7)], C(10)−Si(4) 1.809(3) [1.831(7)], P(2)−B(2) 1.924(4) [1.930(8)], Si−C(Me)$_{av}$ 1.897 [1.875], O(1)−M−O(2) 74.69(7) [75.01(14)], O(2)−M−O(3) 73.33(8) [73.05(19)], O(3)−M−O(4) 71.27(8) [70.0(2)], O(4)−M−O(5) 70.81(8) [72.5(2)], O(1)−M−O(5) 71.31(8) [71.16(17)], B(1)−M−O(1) 84.89(10) [84.3(2)], B(1)−M−O(2) 91.91(10) [95.0(2)], B(1)−M−O(3) 91.80(10) [91.4(2)], B(1)−M−O(4) 84.97(10) [83.9(2)], B(1)−M−O(5) 93.80(10) [92.6(2)], B(2)−M−O(1) 94.37(10) [96.3(2)], B(2)−M−O(2) 89.34(9) [89.3(2)], B(2)−M−O(3) 89.62(10) [90.3(2)], B(2)−M−O(4) 94.66(9) [93.1(2)], B(2)−M−O(5) 84.54(10) [83.6(2)].

Compounds **7** and **8** are both isostructural and isomorphous; the molecular structure of **7** is shown in Figure 3 along with details of selected bond lengths and angles for both **7** and **8**. Once again, the phosphine-borane-stabilized carbanion ligands bind the metal centers via their BH_3 hydrogen atoms alone; there are no contacts between the essentially planar carbanion centers and the metal ions [sum of angles at C(1) and C(10) = 358.9 and 355.0°, respectively, for **7**, and 358.1 and 354.4°, respectively, for **8**]. In each case the BH_3 groups are bound in an η^3-fashion to the metal centers, and the coordination spheres of the metal ions are completed by five molecules of THF, giving the metal ions a distorted pentagonal bipyramidal geometry in which the borane groups occupy the axial positions. The atoms in the MO_5 mean pentagonal planes in both **7** and **8** deviate little from this plane [maximum deviation 0.27 Å].

The Sr...B distances of 2.893(4) and 2.873(4) Å and the Sr−H distances, which range from 2.59(3) to 2.89(4) Å, are

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similar to the corresponding distances in the borohydride complex $(diglyme)_2Sr(\eta^3\text{-}BH_4)_2$ [Sr...B 2.916(7), Sr−H 2.64(4)−2.77(4) Å].[22] Similarly, the Ba...B distances of 3.027(8) and 3.023(8) Å and the Ba−H distances, which range from 2.65(4) to 3.06(4) Å, are similar to the corresponding distances in $(diglyme)_2Ba(\eta^3\text{-}BH_4)_2$ [Ba...B 3.058(7), Ba−H 2.69(3)−2.95(5) Å].[22] The greater hapticity of the borane groups and the increased coordination number of the metal centers in **7** and **8** compared to **3** and **4a** are consistent with the greater ionic radii of Sr^{2+} and Ba^{2+} compared to Mg^{2+} and Ca^{2+}.

The bond lengths and angles within the CSi_2P skeletons of the ligands differ markedly between compound **3**, in which the ligand chelates the metal center, and compounds **4a**, **7**, and **8**, in which the ligands act as terminal η^2- or η^3-BH_3 donors. In **3** the carbanion center is distinctly pyramidal [sum of angles in the CSi_2P skeleton = 337.0 and 339.3° (molecule 1) and 339.4 and 339.7° (molecule 2)], whereas in **4a**, **7**, and **8**, where the carbanions have no short contacts with the metal ions, the carbanion centers are close to planar, as expected [sum of angles at C(1) = 354.1 (**4a**), 358.9 (**7**) and 358.1° (**8**); C(10) = 355.0 (**7**), 354.4° (**8**)]. The C−P distances of 1.781(5) and 1.791(4) Å in **3** [1.782(4) and 1.776(5) Å in molecule 2] are significantly shorter than the corresponding distance in the free phosphine-borane **5** [1.8508(13) Å] but are longer than the corresponding distances in **4a**, **7**, and **8**, which range from 1.704(3) to 1.715(2) Å, and than the C−P distances in the alkali metal derivatives **9**−**13**, which range from 1.735(5)−1.755(5) Å.[11,12] Similarly, the C−Si distances in the central CSi_2P skeleton of **3** range from 1.877(4) to 1.896(5) Å; these are significantly longer than the corresponding distances in **4a**, **7**, and **8**, which range from 1.800(9) to 1.845(8) Å and longer than the C−Si distances in **9**−**13**, which range from 1.824(4) to 1.868(9) Å. Indeed, the C−Si distances in **3** are similar to the corresponding C−Si distances in **5** [1.8831(13) and 1.9118(13) Å]. The greater C−P and C−Si distances are found in the complexes with the more polarizing, charge localizing metal ions Li^+ and Mg^{2+}. This is consistent with delocalization of charge through negative hyperconjugation being at a maximum in complexes with larger, more polarizable cations, especially in those cases where the carbanion is not directly in contact with the metal, and, conversely, with charge localization being at a maximum in complexes with small, polarizing cations, as expected.

Conclusions

Although heavier alkali metal complexes of the phosphine-borane-stabilized carbanion $[(Me_3Si)_2\{Me_2(H_3B)P\}C]^-$ are accessible, their stabilities, especially toward solvents, are markedly dependent upon the nature of the cation. The Mg complex **3** is unstable both in the solid state and solution and reacts rapidly with THF to generate the free phosphine-borane **5** as the sole phosphorus-containing product. Although stable in hydrocarbon solutions, compound **4** is also unstable toward THF, whereas the heavier alkaline earth metal derivatives **7** and **8** are isolated as THF adducts which are stable toward this solvent. Compound **3** crystallizes solvent-free, with chelating ligands, whereas compounds **4a**, **7**, and **8** crystallize as THF solvates, in which the phosphine-borane-stabilized carbanion binds the metal centers via its borane H atoms only; there is no contact between the metal and carbanion centers in these latter compounds.

Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. Diethyl ether, THF, toluene, methylcyclohexane, and light petroleum (bp 40−60 °C) were distilled under nitrogen from potassium or sodium/potassium alloy. THF was stored over activated 4Å molecular sieves; all other solvents were stored over a potassium film. C_6D_6 was distilled from potassium and was deoxygenated by three freeze−pump−thaw cycles and stored over activated 4Å molecular sieves. The compound $[(Me_3Si)_2\{Me_2(H_3B)P\}C]K$ (**2**)[13] was prepared by a previously published procedure.

^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL Lambda500 spectrometer operating at 500.16, 125.65, 160.35, and 202.35 MHz, respectively; ^1H and ^{13}C chemical shifts are quoted in ppm relative to tetramethylsilane; and ^{11}B and ^{31}P chemical shifts are quoted in ppm relative to $BF_3(OEt_2)$ and 85% H_3PO_4, respectively. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

Preparation of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Mg$ (3). To a slurry of MgI_2 (0.24 g, 0.86 mmol) in toluene (10 mL) was added a solution of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]K$ (0.49 g, 1.80 mmol) in toluene (20 mL). The resulting solution was stirred for 12 h and then filtered to remove the KI side product. The filtrate was concentrated to ca. 5 mL and cooled to −30 °C for 12 h yielding **3** as colorless blocks. Isolated yield 0.21 g, 47.5%. Anal. Calcd for $C_{18}H_{54}B_2MgP_2Si_4$ (490.84): C 44.05, H 11.09. Found: C 43.88, H 11.00. $^1H\{^{11}B\}$ NMR (C_6D_6, 25 °C): δ 0.34 (s, 36H, $SiMe_3$), 1.19 (d, J_{PH} = 9.8 Hz, 12H, PMe_2), 1.42 (d, J_{PH} = 8.3 Hz, 6H, BH_3). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 7.64 (d, J_{PC} = 3.6 Hz, $SiMe_3$), 16.21 ($PCSi_2$) 17.94 (d, J_{PC} = 34.1 Hz, PMe_2). $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C): δ −24.6 (d, J_{PB} = 88.9 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −3.8 (q, J_{PB} = 88.9 Hz).

Preparation of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Ca$ (4). To a slurry of CaI_2 (0.44 g, 1.51 mmol) in toluene (10 mL) was added a solution of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]K$ (0.82 g, 3.01 mmol) in toluene (20 mL). The reaction mixture was stirred for 16 h and filtered, and the filtrate was concentrated to ca. 5 mL and cooled to −30 °C for 12 h to give **4** as colorless crystals. Isolated yield 0.39 g, 51%. Anal. Calcd for $C_{18}H_{54}B_2CaP_2Si_4$ (506.60): C 42.67, H 10.74. Found: C 42.61, H 10.65. $^1H\{^{11}B\}$ NMR (C_6D_6, 25 °C): δ 0.40 (s, 36H, $SiMe_3$), 0.59 (d, J_{PH} = 14.3 Hz, 6H, BH_3), 1.42 (d, J_{PH} = 9.5 Hz, 12H, PMe_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 8.31 ($SiMe_3$), 22.85 (d, J_{PC} = 34.7 Hz, PMe_2), [quaternary carbon not observed]. $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C): δ −27.2 (d, J_{PB} = 102.7 Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −5.8 (q, J_{PB} = 102.7 Hz).

The adduct $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Ca(THF)_4$ (**4a**) was obtained by recrystallization of **4** from cold (−30 °C) methylcyclohexane containing a few drops of THF as colorless needles suitable for X-ray crystallography. $^1H\{^{11}B\}$ NMR (C_6D_6, 25 °C): δ 0.47 (s, 36H, $SiMe_3$), 1.00 (d, J_{PH} = 14.4 Hz, 6H, BH_3), 1.38 (m, 16H,

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Table 1. Crystallographic Data for **3**, **4a**, **7**, and **8**

compound	**3**	**4a**	**7**	**8**
formula	$C_{18}H_{54}B_2MgP_2Si_4$	$C_{34}H_{86}B_2CaO_4P_2Si_4$	$C_{38}H_{94}B_2O_5P_2Si_4Sr$	$C_{38}H_{94}B_2BaO_5P_2Si_4$
M	490.8	795.0	914.7	964.4
crystal system	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$C2$	$P2_1/c$	$Pca2_1$	$Pca2_1$
a/Å	15.800(2)	10.837(2)	17.455(3)	17.541(4)
b/Å	8.9292(13)	13.824(3)	13.611(2)	13.8433(7)
c/Å	44.332(7)	17.219(4)	22.757(3)	22.928(11)
β/deg	96.972(2)	105.666(2)		
V/Å^3	6208.3(16)	2483.7(9)	5406.4(14)	5568(3)
Z	8	2	4	4
cryst size/mm	0.42 × 0.30 × 0.15	0.30 × 0.25 × 0.18	0.55 × 0.54 × 0.18	0.40 × 0.40 × 0 .18
μ/mm^{-1}	0.319	0.317	1.179	0.890
data collected	22041	21949	46675	74183
unique data	10685	6038	13041	9755
R_{int}	0.040	0.028	0.051	0.038
data with $F^2 > 2\sigma$	10211	4743	9733	8000
refined parameters	567	253	591	489
R (on F, $F^2 > 2\sigma$)^a	0.056	0.043	0.039	0.049
R_w (on F^2, all data)^a	0.121	0.122	0.091	0.128
goodness of fit on F^{2a}	1.204	1.030	1.014	1.056
min, max electron density /e Å^{-3}	0.42, −0.55	0.76, −0.41	0.54, −0.33	1.00, −0.63

[a] Conventional $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. data} - \text{no. params})]^{1/2}$ for all data.

THF), 1.43 (d, $J_{PH} = 9.8$ Hz, 12H, PMe_2), 3.64 (m, 16H, THF). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 8.10 ($SiMe_3$), 21.97 (d, $J_{PC} = 36.7$ Hz, PMe_2), 26.16 (THF), 69.40 (THF) [quaternary carbon not observed]. $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C): δ −25.8 (d, $J_{PB} = 105.2$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −9.7 (q, $J_{PB} = 105.2$ Hz).

Preparation of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Sr(THF)_5$ (7). To a slurry of SrI_2 (0.15 g, 0.44 mmol) in THF (10 mL) was added a solution of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]K$ (0.25 g, 0.92 mmol) in THF (20 mL). The resulting solution was stirred for 12 h, and then the solvent was removed in vacuo. The product was extracted into diethyl ether (30 mL) and filtered, and solvent was removed in vacuo from the filtrate. Recrystallization of the resulting colorless solid from cold (−30 °C) methylcyclohexane (10 mL) containing a few drops of THF yielded colorless needles of **7** suitable for X-ray crystallography. Isolated yield 0.33 g, 82%. Anal. Calcd for $C_{38}H_{94}B_2O_5P_2Si_4Sr$ (914.68): C 49.90, H 10.36. Found: C 49.71, H 10.27. $^1H\{^{11}B\}$ NMR (C_6D_6, 25 °C): δ 0.46 (s, 36H, $SiMe_3$), 1.15 (d, $J_{PH} = 12.8$ Hz, 6H, BH_3), 1.39 (m, 20H, THF), 1.44 (d, $J_{PH} = 9.8$ Hz, 12H, PMe_2), 3.65 (m, 20H, THF). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 7.95 ($SiMe_3$), 21.77 (d, $J_{PC} = 35.7$ Hz, PMe_2), 26.17 (THF), 69.29 (THF) [quaternary carbon not observed]. $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C): δ −25.0 (d, $J_{PB} = 97.8$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −8.6 (q, $J_{PB} = 97.8$ Hz).

Preparation of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]_2Ba(THF)_5$ (8). To a slurry of BaI_2 (0.43 g, 1.10 mmol) in THF (10 mL) was added a solution of $[(Me_3Si)_2\{Me_2(H_3B)P\}C]K$ (0.54 g, 1.98 mmol) in THF (20 mL). The resulting solution was stirred for 12 h, and the solvent was removed in vacuo. The product was extracted into diethyl ether (30 mL) and filtered, and the solvent was removed in vacuo from the filtrate. Recrystallization of the resulting colorless solid from cold (−30 °C) methylcyclohexane (10 mL) containing a few drops of THF yielded **8** as colorless blocks suitable for X-ray crystallography. Isolated yield 0.41 g, 39%. Anal. Calcd for $C_{38}H_{94}B_2BaO_5P_2Si_4$ (964.39): C 47.33, H 9.82. Found: C 47.11, H 9.71. $^1H\{^{11}B\}$ NMR (C_6D_6, 25 °C): δ 0.41 (s, 36H, $SiMe_3$), 1.37 (m, 20 H, THF), 1.41 (d, $J_{PH} = 9.5$ Hz, 12H, PMe_2) 1.49 (d, $J_{PH} = 12.2$ Hz, 6H, BH_3), 3.58 (m, 20H, THF). $^{13}C\{^1H\}$ NMR (C_6D_6, 25 °C): δ 7.49 ($SiMe_3$), 21.62 (d, $J_{PC} = 34.1$ Hz, PMe_2), 26.25 (THF), 68.88 (THF) [quaternary carbon not observed]. $^{11}B\{^1H\}$ NMR (C_6D_6, 25 °C): δ −23.3 (d, $J_{PB} = 95.6$ Hz). $^{31}P\{^1H\}$ NMR (C_6D_6, 25 °C): δ −8.4 (q, $J_{PB} = 95.6$ Hz).

Crystal Structure Determinations of 3, 4a, 7, and 8. Measurements were made at 150 K on Bruker AXS SMART CCD and Nonius KappaCCD diffractometers using graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). For all compounds cell parameters were refined from the observed positions of all strong reflections in each data set. Intensities were corrected semiempirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and were refined on F^2 values for all unique data. Table 1 gives further details. All non-hydrogen atoms were refined anisotropically and H atoms bonded to boron were refined isotropically, while the remaining H atoms were constrained with a riding model; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Disorder was resolved and successfully modeled for one THF ligand in **4a**, one trimethylsilyl group in each of the phosphine-borane ligands, and one THF molecule in **7**. Although some probable disorder is indicated in **8** by highly anisotropic displacement parameters for some ligand atoms, a satisfactory model could not be refined. Both **7** and **8** have a degree of inversion twinning. Programs were Bruker AXS SMART (control) and SAINT (integration), Nonius COLLECT and associated programs, and SHELXTL for structure solution, refinement, and molecular graphics.[22]

Observed and calculated structure factor details are available from the authors upon request.

Acknowledgment. The authors thank the Royal Society for support.

Supporting Information Available: Details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters for **3**, **4a**, **7**, and **8** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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