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Metalation of Trimethylphosphine−Borane. Unexpected Reactivity of a Simple Phosphine−Borane-Stabilized Carbanion toward Siloxanes

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The reaction between trimethylphosphine−borane (**3**) and 1 equiv of MeNa in diethyl ether gives the polymeric complex $[\{Me_2P(BH_3)CH_2\}Na(THF)]_\infty$ (**5a**) in good yield after recrystallization from THF. In contrast, the reaction between **3** and 1 equiv of *n*-BuLi in diethyl ether gives the unusual complex $\{Me_2P(BH_3)CHSiMe_2OLi\}_4Li_4(Et_2O)_{2.75}(THF)_{1.25}$ (**6**), which crystallizes as a cluster containing $[Me_2P(BH_3)CHSiMe_2O]^{2-}$ siloxy-functionalized carbanions formed via the reaction between the α-lithiated intermediate $\{Me_2P(BH_3)CH_2\}Li$ (**4**) and silicone grease. Although the intermediate **4** could not be isolated, reactions between *in situ*-generated **4** and sources of Me_2SiO (Dow Corning silicone grease, silicone oil, hexamethylcyclotrisiloxane (**8**)) proceed cleanly to give good yields of **6**; no reaction was observed between **4** and hexamethyldisiloxane. Reactions between **4** and **8** generate half an equivalent of **3** per equivalent of **4** consumed, and the cluster **6** reacts with excess siloxane to give **3** and unidentified products that contain silicon, but not phosphorus; thus, the optimum ratio of **4** to **8** in these reactions is 6:1. Variable-temperature ^1H, ^7Li, $^{11}B\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy suggests that **6** is subject to dynamic equilibria in solution that involve deaggregation of the cluster.

Introduction

α-Metalated phosphine−boranes are important intermediates in the synthesis of a wide range of both chiral and achiral mono- and polyphosphines.[1,2] In the majority of cases these species are generated *in situ* from the reaction of a phosphine−borane adduct with an alkali metal alkyl such as *n*- or *s*-BuLi. There have been very few structural studies of this class of compound (see below),[3−8] and little consideration appears to have been given to how their structures and reactivities might be related. This is in contrast to borane-free phosphine-stabilized carbanions $[R_2PCR_2]^-$ and their oxide and sulfide counterparts $[R_2P(E)CR_2]^-$ (E = O, S), for which underlying trends in structure and reactivity have been quite well established.[9]

Until recently only one alkali metal derivative of a phosphine−borane-stabilized carbanion had been structurally characterized: the complex $[Li(tmeda)_2][Me_2P(BH_3)CHPMe_2(BH_3)]$ (**1**), reported by Weiss and Schmidbaur in 1979, crystallizes as a separated ion pair with no close contacts between the cation and anion [tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine].[3] We recently reported the unusual dicarbanion complex $[[(Me_3Si)\{n\text{-}Pr_2P(BH_3)\}CCH_2]Li(pmdeta)]_2$ (**2**),[5] which exhibits contacts between the lithium ions and the borane hydrogen atoms, but not between lithium and the carbanion centers [pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine]. This structural motif has significant consequences for the reactions of **2**; protonolysis of the (−)-sparteine analogue of **2**, i.e., $[[(Me_3Si)\{n\text{-}Pr_2P(BH_3)\}CCH_2]Li\{(-)\text{-sparteine}\}]_2$, under a variety of conditions leads to a 1:1 mixture of the *rac* and *meso* diastereomers of the bis(phosphine−borane) $[\{n\text{-}Pr_2P(BH_3)\}(Me_3Si)CHCH_2]_2$, with no evidence for stereocontrol. This clearly implies that the structure observed in the solid state, in which the lithium ion is remote from the carbanion center, is maintained in solution.

This finding, combined with the acute lack of information regarding the structures and reactivities of phosphine−borane-stabilized carbanions generally, prompted us to begin a detailed investigation of these compounds.[6−8] In our initial experiments we concentrated on the carbanion $[(Me_3Si)_2C\{PMe_2(BH_3)\}]^-$, in which the negative charge may be delocalized across both the silyl and phosphine−borane groups and which is exactly isoelectronic with the well-established "trisyl" carbanion $(Me_3Si)_3C^-$. Our investigations have revealed that this carbanion adopts a variety of coordination modes in its complexes with alkali and alkaline earth metal cations, including a chelating mode (**I**), a variety of bridging modes (**II**−**IV**), and a terminal BH_3-donor mode (**V**) (Chart 1). In each case coordination of

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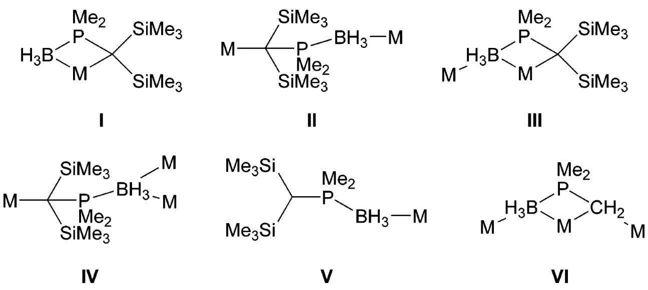
Chart 1



the metal center by the borane hydrogen atoms appears to be a key feature of the structure.

Although this ligand has yielded a range of interesting and novel compounds, its binding modes are likely to be significantly influenced by the steric and electronic properties of the bulky, charge-stabilizing silyl groups. In order to obtain information on a system in which charge stabilization would be solely effected by a phosphine−borane group, we have now examined the metalation of the archetypal tertiary phosphine−borane $Me_3P(BH_3)$ (**3**). We report below the results of this investigation, including the unexpected reactivity of the corresponding α-metalated derivatives toward siloxanes.

Results and Discussion

Treatment of **3** with 1 equiv of either *n*-BuLi or MeNa in diethyl ether, when conducted in silicone grease-free apparatus (see below), gives solutions whose $^{31}P\{^1H\}$ NMR spectra indicate complete metalation of the phosphine−borane to give the phosphine−borane-stabilized carbanion complexes $\{Me_2P(BH_3)CH_2\}M$ [M = Li (**4**), Na (**5**)]; these crude $^{31}P\{^1H\}$ spectra exhibit broad quartets at −1.6 ppm (J_{PB} = 87.6 Hz) and −3.3 ppm (J_{PB} = 93.4 Hz) for **4** and **5**, respectively [cf. 0.2 ppm (J_{PB} = 57.4 Hz) for $Me_3P(BH_3)$ in the same solvent]. The relatively small chemical shift differences between **3** and **4**/**5** and the large J_{PB} coupling constants in the latter compounds are consistent with deprotonation of one of the methyl groups of **3**; we have typically observed a near doubling of the $^{31}P-^{11}B$ coupling constant upon α-deprotonation of a phosphine−borane.[5−8]

Despite numerous attempts we were unable to isolate a solid sample of **4** for analysis; however, the sodium complex $[\{Me_2P(BH_3)CH_2\}Na(THF)]_\infty$ (**5a**) may be obtained in good yield by crystallization of **5** from cold THF. The ^1H, $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **5a** are as expected; in the ^1H spectrum the CH_2 protons give rise to a moderately broad doublet at −0.92 ppm (J_{PH} = 10.7 Hz) and the CH_3 protons give rise to a doublet at 0.99 ppm (J_{PH} = 9.8 Hz), whereas the BH_3 protons give rise to a well-resolved quartet of doublets centered at 0.32 ppm ($^2J_{PH}$ = 13.2 Hz, J_{BH} = 89.4 Hz). The coordinated THF observed in the crystal structure of **5a** (see below) is rapidly lost under vacuum and is not observed in either its NMR spectra or its elemental analyses. The $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **5a** consist of a doublet and a broad quartet at −32.5 and −4.2 ppm, respectively (J_{PB} = 89.7 Hz).

Compound **5a** crystallizes as an infinite chain polymer; the structure of **5a** is shown in Figure 1, along with selected bond lengths and angles. Each phosphine−borane-stabilized carbanion binds to a sodium ion via its carbanion center and one of its borane hydrogen atoms to give a pseudo-four-membered chelate ring. Two such subunits are arranged in a head-to-tail fashion around a 2-fold rotation axis, generating a slightly puckered Na_2C_2 square with the phosphine−borane substituents adopting a *syn* arrangement [C(1)−Na−C(1′) 106.22(6)°; Na−C(1)−Na′ 72.61(5)°; dihedral angle between the two Na_2C planes = 14.1°]. These squares are further linked into a polymeric array via μ_2-η^1:η^1 BH_3−Na interactions to give planar centrosymmetric $Na_2(BH_3)_2$ squares [B···Na···B″ 93.30(7)°; Na···B···Na″ 86.70(7)°]; the coordination sphere of each sodium ion is completed by a molecule of THF to give five-coordinate metal centers. The Na_2C_2 and $Na_2(BH_3)_2$ squares alternate along the chain to give a sinusoidal, ribbon-type polymer. The carbanions thus adopt a new binding mode for this type of ligand in which the ligand chelates the metal center, while simultaneously bridging to adjacent metals via both the carbanion center and the borane group (**VI**, Chart 1). This C-bridging mode may be attributed to the lack of charge-stabilizing, bulky silyl groups at the carbanion center, which results in decreased steric hindrance and increased charge localization at the C atom, in comparison to the silyl-substituted ligand $[(Me_3Si)_2C\{PMe_2(BH_3)\}]^-$.

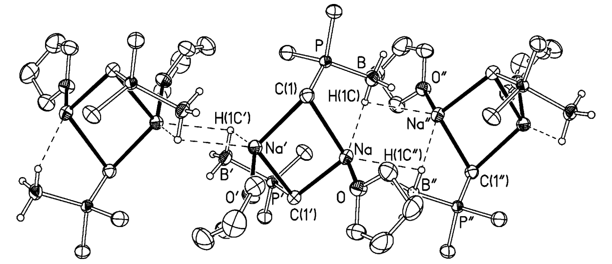


Figure 1. Extended polymeric structure of **5a** with 40% probability ellipsoids and with H atoms bonded to carbon omitted for clarity. Selected bond lengths (Å) and angles (deg): Na−C(1) 2.742(2), Na−C(1′) 2.583(2), Na−O 2.3261(15), Na−H(1C) 2.53(2), Na−H(1C″) 2.65(3), Na···B 2.987(3), Na···B″ 2.872(2), P−C(1) 1.7368(19), P−B 1.923(2), O−Na−C(1) 90.69(6), O−Na−C(1′) 105.42(6), O−Na···B 124.91(7), O−Na···B″ 90.43(7), B···Na···B″ 93.30(7), Na···B···Na″ 86.70(7), C(1)−Na−C(1′) 106.22(6), Na′−C(1)−Na 72.61(5), C(1)−Na···B 64.16(6), Na−C(1)−P 94.72(8), Na′−C(1)−P 122.73(10). Symmetry operators: ′ 3/2−*x*, y, 1−*z*; ″ 3/2−*x*, 3/2−*y*, 3/2−*z*.

The Na−C distances in **5a** are 2.583(2) and 2.742(2) Å, the longer distance corresponding to the ligand that directly chelates the sodium ion; this longer distance may be attributed to the formation of a strained pseudo-four-membered chelate ring. The Na−C(1′) distance is similar to the bridging Na−C distances in $[\{(Me_3Si)_2CH\}Na]_\infty$ [2.551(4) and 2.549(5) Å],[10] whereas the Na−C(1) distance is similar to the Na−C distance within the four-membered chelate ring in $[\{(Me_3Si)(Me_2MeOSi)CH\}Na(PhH)_{0.5}]_\infty$ [2.7692(18) Å].[11] The Na−H [2.53(2) and 2.65(3) Å] and the Na···B [2.872(2) and 2.987(3) Å] distances are similar to the corresponding distances in a range of sodium complexes of the BH_4^- anion; for example, the Na−H distances in $[(pmdeta)Na(\mu-BH_4)]_2$ range from 2.49(3) to 2.58(3) Å, and the Na···B distances in this compound are 2.727(4) and 2.867(4) Å.[12]

Although our attempts to isolate the lithium complex **4** in solid form were unsuccessful, we find that when a solution of **4** in diethyl ether is left to stand for 2 h in the presence of Dow Corning silicone grease (used to seal the ground glass joints of the glassware), crystals of the unusual cluster complex $\{Me_2P(BH_3)CHSiMe_2OLi\}_4Li_4(Et_2O)_{2.75}(THF)_{1.25}$ (**6**) deposit; in the presence of an excess of silicone grease compound **6** may

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be isolated in good yield as colorless blocks suitable for X-ray crystallography. Compound **6** contains a new siloxy-functionalized alkyl ligand, $[Me_2P(BH_3)CHSiMe_2O]^{2-}$, apparently derived from the reaction between **4** and poly(dimethylsiloxane) from the grease. Reactions between organometallic compounds and silicone grease are rare but have some precedent; these, usually serendipitous, reactions have recently been reviewed.[13] Such reactions typically fall into six categories: (i) siloxane chain cyclization into silacrown rings;[14] (ii) siloxane chain fragmentation and incorporation of di- and trisiloxane units;[15] (iii) "dimethylsilanone" insertion into M−X bonds;[16] (iv) inorganic ring formation through incorporation of Me_2SiO_2 units;[17] (v) incorporation of dimethylsilylene groups;[18] and (vi) incorporation of trimethylsiloxy groups.[19]

The reaction between **4** and silicone grease appears to involve the formal insertion of a Me_2SiO fragment into a Li−C bond. Similar "dimethylsilanone" insertion products are obtained from the prolonged reactions of either CuCl/($Me_3SiNPMe_2$)Li or Et_2PLi with silicone grease, which generate $[Li\{Me_3SiNPMe_2CH_2CuCH(PMe_2NSiMe_3)(SiMe_2OLi)\}]_2$ and $[LiOSiMe_2PEt_2]_6$, respectively, in low yield.[16a,f]

The NMR spectra of **6** indicate the presence of a single ligand and a single lithium environment in d_8-THF at 50 °C. The ^1H spectrum at this temperature exhibits a broad doublet at −0.72 ppm (J_{PH} = 18.3 Hz) due to the methine proton and a singlet at −0.03 ppm and a doublet at 1.05 ppm (J_{PH} = 9.8 Hz) due to the $SiMe_2$ and PMe_2 groups, respectively, along with signals due to THF and diethyl ether; the BH_3 protons were detected by a $^1H\{^{11}B\}$ experiment as a broad doublet at 0.43 ppm (J_{PH} = 12.9 Hz). As the temperature is reduced to ambient, these signals broaden and de-coalesce to give multiple, overlapping signals that are not amenable to meaningful interpretation, but which suggest that **6** is subject to dynamic equilibria in solution.

Variable-temperature $^{31}P\{^1H\}$ spectra also indicate that **6** is subject to multiple dynamic equilibria in solution. At 50 °C the $^{31}P\{^1H\}$ spectrum consists of a broad quartet at −9.9 ppm (J_{PB} = 84.8 Hz), along with low-intensity peaks due to hydrolysis products. As the temperature is decreased, this peak broadens and partially de-coalesces into overlapping multiplets, which it is not possible to assign unambiguously. The dynamic nature of **6** is exemplified by its ^7Li spectra: at 50 °C the ^7Li spectrum consists of a singlet at 1.68 ppm; as the temperature is decreased, this signal broadens and de-coalesces, until, at −41 °C, the spectrum consists of seven signals spanning the range 1.3−2.3 ppm (Figure 2). As the temperature is reduced further, these signals sharpen and change in intensity such that, at −60 °C, the spectrum consists of six major signals at 2.3, 2.1, 1.7, 1.6, 1.5, and 1.3 ppm in the approximate ratio 1:2:2:6:2:4. These spectra strongly suggest that **6** undergoes at least partial deaggregation to a variety of monomeric and/or oligomeric species in donor solvents and that the dynamic equilibria between these species are fast on the NMR time scale at elevated temperatures.

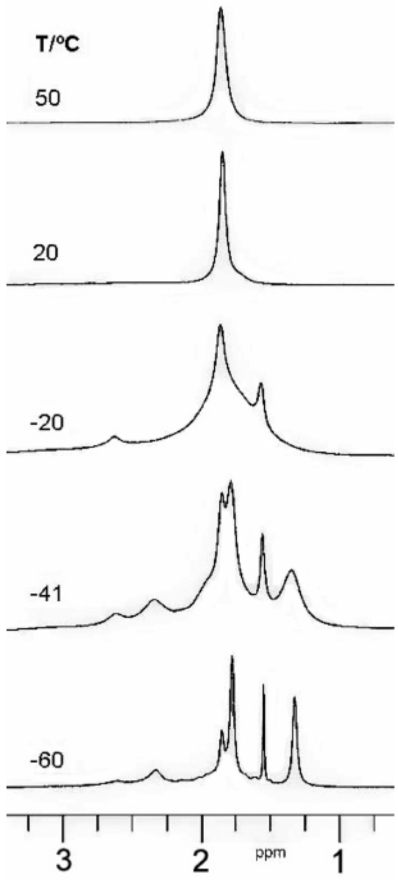

Figure 2. Variable-temperature ^7Li NMR spectra of **6** in d_8-THF.

The molecular structure of **6** is shown in Figure 3 along with selected bond lengths. Compound **6** crystallizes with two independent molecules in the asymmetric unit, which differ in the coordination of two of the lithium ions; in molecule 1 Li(4) is coordinated by a disordered mixture of THF and diethyl ether, each of which has 50% occupancy, and Li(5) is coordinated by a molecule of THF, whereas in molecule 2 Li(9) is coordinated by a molecule of diethyl ether and Li(10) by a molecule of THF, giving **6** the overall formula $[\{Me_2P(BH_3)CHSiMe_2OLi\}_4Li_4(THF)_{1.25}(Et_2O)_{2.75}]$. In all other respects the bond lengths and angles within the two molecules differ only trivially, and so the following discussion is confined to molecule 1. In an investigation of another sample of this compound we have found other combinations of THF and diethyl ether in these positions.

The cluster has exact, crystallographic C_2 symmetry along the axis joining Li(4) and Li(5) and is built around a Li_6O_4 adamantoid core in which the O atoms occupy the apexes (Figure 3b). The core contains three distinct lithium environments; Li(1/1′) is coordinated by the carbanion centers and siloxide oxygen atoms of two of the dianionic ligands in a distorted tetrahedral geometry. Lithium ions Li(2/2′), Li(4), and Li(5) are coordinated by the O atoms of these ligands and have

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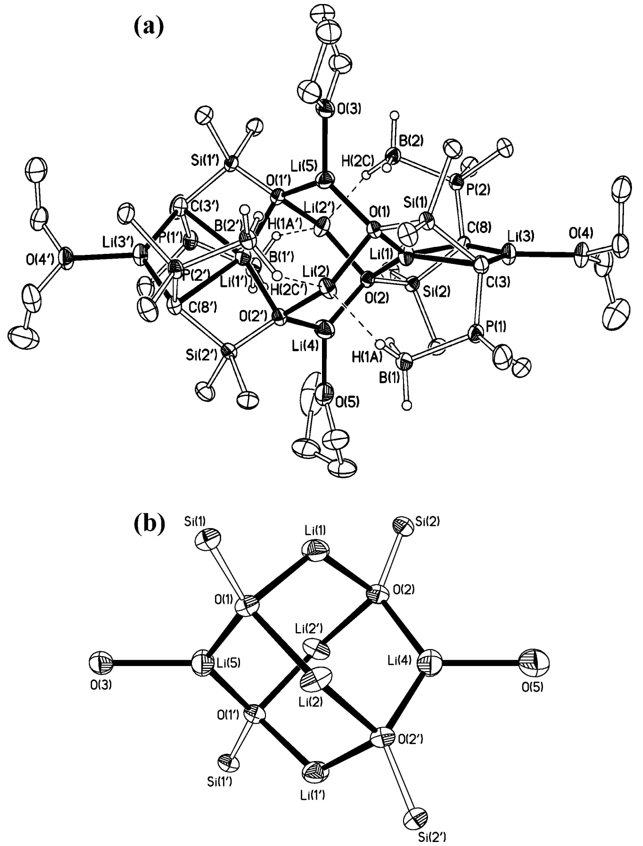

Figure 3. (a) Molecular structure of one of the independent molecules of **6**, with 40% probability ellipsoids; disorder components and H atoms bonded to C omitted for clarity. (b) The adamantoid core of **6**. Selected bond lengths (Å): Li(1)−O(1) 1.890(4), Li(1)−O(2) 1.893(4), Li(1)−C(3) 2.660(4), Li(1)−C(8) 2.525(4), Li(2)−O(1) 1.901(3), Li(2)−O(2′) 1.902(4), Li(2)···B(1) 2.650(4), Li(2)···B(2′) 2.738(4), Li(2)−H(1A) 2.06(3), Li(2)−H(2C′) 2.07(2), Li(3)−O(4) 1.932(3), Li(3)−C(3) 2.170(4), Li(3)−C(8) 2.177(4), Li(4)−O(2) 1.881(3), Li(4)−O(5) 1.973(7), Li(5)−O(1) 1.884(3), Li(5)−O(3) 1.924(6), P(1)−C(3) 1.7364(19), P(1)−B(1) 1.931(2), P(2)−C(8) 1.7456(18), P(2)−B(2) 1.925(2), Si(1)−C(3) 1.8555(19), Si(1)−O(1) 1.6277(12), Si(2)−C(8) 1.8503(18), Si(2)−O(2) 1.6262(13). Symmetry operator: ′ −x, −y, z.

no contacts with the carbanion centers; the coordination sphere of Li(2/2′) is completed by η^1-BH_3 contacts to two different carbanion ligands, whereas the coordination sphere of Li(5) is completed by a molecule of THF and that of Li(4) by a 50/50 mixture of THF and diethyl ether, as described above. The remaining lithium ions, Li(3/3′), are coordinated by the carbanion centers of two phosphine−borane-stabilized carbanion ligands at the edges of the cluster and have their coordination spheres completed by a molecule each of diethyl ether; thus Li(3/3′) is three-coordinate and adopts a trigonal-planar geometry. Each carbanion center therefore bridges two adjacent Li ions [Li(3) and Li(1)] to give Li_2C_2 squares in which the phosphine−borane substituents adopt an *anti* arrangement.

The Li(3)−C distances of 2.170(4) and 2.177(4) Å are significantly shorter than the Li(1)−C distances of 2.525(4) and 2.660(4) Å. These latter distances are rather long for this type of contact, for which the typical average value is 2.28 Å.[20] The Li(3)−C distances are similar to the Li−C distances in a range of silicon- and/or phosphorus-stabilized carbanion complexes; for example, the Li−C distances in (tmeda)Li{$(Me_3Si)_2C(PMe_2)$}$_2$Li are 2.16(1) and 2.17(1) Å,[21] while the Li−C distance in $[Li(tmeda)_2][\{(Me_3Si)_2(Me_2SiCH_2)C\}_2Li]$ is 2.156(4) Å.[22] The Li−O(Si) distances in **6** range from 1.890(4) to 1.902(3) Å and lie in the typical range for such contacts;[23] the Li−H distances in **6** [2.06(3) and 2.07(2) Å] are similar to the Li−H distances in the ate complex $(THF)_3Li\{(Me_3Si)_2CPMe_2(BH_3)\}_2$-Li, which range from 2.03(8) to 2.31(6) Å.[6]

Table 1. Crystallographic Data for 5a and 6

	5a	**6**
formula	$C_7H_{19}BNaOP$	$C_{72}H_{203}B_8Li_{16}O_{16}P_8Si_8$[b]
fw	184.0	1995.3
cryst size/mm	0.54 × 0.45 × 0.40	0.15 × 0.12 × 0.10
cryst syst	monoclinic	tetragonal
space group	$I2/a$	$P4_2bc$
a/Å	12.534(2)	19.7951(6)
b/Å	14.6996(12)	
c/Å	13.079(3)	31.9497(18)
β/deg	102.279(8)	
V/Å^3	2354.5(7)	12519.4(9)
Z	8	4
μ/mm^{-1}	0.223	0.234
transmn coeff range	0.889−0.916	0.966−0.977
no. of reflns measd	11 758	91 233
no. of unique reflns	2626	18 534
R_{int}	0.030	0.039
no. of reflns with $F^2 > 2\sigma$	2061	16921
no. of params	122	704
R (on F, $F^2 > 2\sigma$)[a]	0.039	0.039
R_w (on F^2, all data)[a]	0.115	0.111
goodness of fit[a]	1.119	1.028
min., max. electron density/e Å^{-3}	0.55, −0.29	0.82, −0.39

[a] Conventional $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $S = [\sum w(F_o^2 - F_c^2)^2/(\text{no. data - no. params})]^{1/2}$ for all data. [b] This formula is for the two slightly different molecules together.

In order to gain greater insight into the mechanism by which **6** is formed, we have investigated the reaction of **4** with a variety of siloxane species. We find that, whereas **4** reacts rapidly with Dow Corning silicone grease, silicone oil, or hexamethylcyclotrisiloxane $(Me_2SiO)_3$ (**8**), it is inert toward hexamethyldisiloxane, clearly implying that Me_2SiO units are required in the starting material; the cleanest reactions were observed between **4** and **8**, which in the correct stoichiometry (see below) reproducibly give **6** in good yield.

Compound **6** reacts with excess **8** (or fragments thereof) in THF over approximately 48 h to give unidentified silicon-containing products and **3**; no other phosphorus-containing products are evident in the $^{31}P\{^1H\}$ NMR spectrum after this time. In contrast, in the absence of siloxanes **6** appears to be stable in solution for long periods.

We also observe that 1 equiv of the phosphine−borane **3** is formed for each equivalent of $[Me_2P(BH_3)CHSiMe_2O]^{2-}$ dianion produced; this clearly suggests that the optimum ratio of **4** to **8** is 6:1 (i.e., 2 equiv of the carbanion for each Me_2SiO unit), since half of the initial amount of **4** is converted into **3**, rather than **6**. Indeed, the reaction between **8** and 6 equiv of **4** proceeds cleanly according to eq 1; however, this reaction is significantly slower than the 2:1 reaction, taking several days

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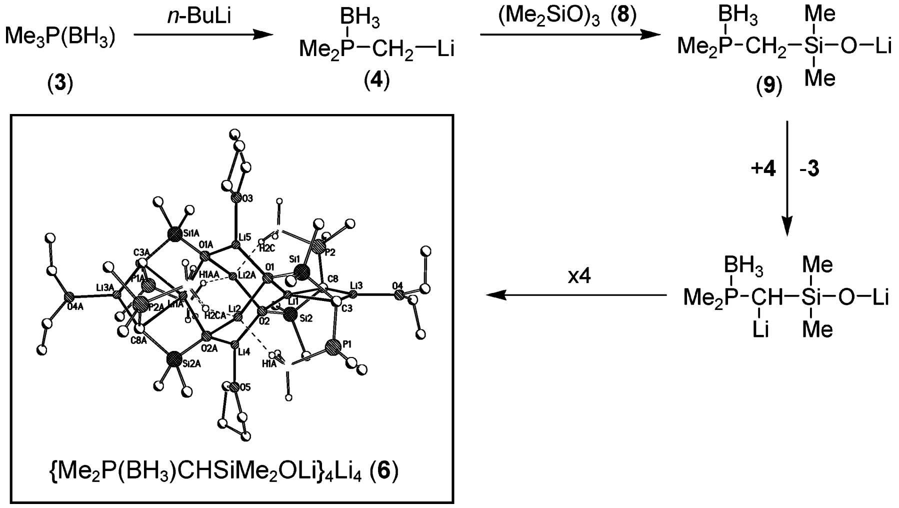
Scheme 1



to reach completion, consistent with **4** exhibiting a preference for reaction with the intact cyclic siloxane **8** rather than fragments of this siloxane produced during the reaction.

$$24\ Me_2P(BH_3)CH_2Li + 4\ (Me_2SiO)_3 \rightarrow 3\ \{Me_2P(BH_3)CHSiMe_2OLi\}_4Li_4 + 12\ Me_3P(BH_3) \quad (1)$$

These data strongly suggest that the initial reaction between **4** and **8** involves extraction of an Me_2SiO unit from the cyclic siloxane, i.e., formal insertion of an Me_2SiO unit into the Li−C bond of **4**, generating the phosphine−borane-substituted lithium siloxide intermediate $[\{Me_2P(BH_3)\}CH_2SiMe_2O]Li$ (**9**) (Scheme 1). This then reacts rapidly with a second equivalent of **4**, resulting in deprotonation of the methylene carbon to give a carbanion that is stabilized by both a silyl and a phosphine−borane group, along with 1 equiv of **3**; aggregation of these dianions then gives **6**.

The apparent difference in reactivity between the lithium and sodium derivatives **4** and **5** toward siloxanes may reasonably be attributed to differences in their solubility. Compound **4** is soluble in THF and diethyl ether and so remains in solution for sufficient time to react with dissolved polysiloxanes; however, compound **5** is rather insoluble in these solvents and so crystallizes from solution before any reaction with the polysiloxane can take place. Thus, **5** is isolated cleanly from reactions carried out in glassware sealed with silicone grease, whereas solutions of **4** yield crystals of the cluster species **6** under these conditions. Indeed, compound **5** reacts rapidly with siloxanes when these species are deliberately introduced; treatment of **5** with one-third of an equivalent of **8** in THF gives a solution containing **3** and an unidentified phosphorus-containing product, which we were unable to isolate. Although this compound could not be isolated cleanly, a $^{31}P\{^1H\}$ NMR spectrum of the crude reaction solution exhibits, in addition to a strong signal due to **3**, a poorly resolved quartet at −9.21 ppm ($J_{PB} = 95.1$ Hz) [cf. the $^{31}P\{^1H\}$ spectra of **3** and **5a** exhibit broad, poorly resolved quartets at −0.6 ppm ($J_{PB} = 58.6$ Hz) and −4.2 ppm ($J_{PB} = 89.7$ Hz), respectively], which may be assigned to a new species containing a phosphine−borane-stabilized carbanion, possibly corresponding to the sodium analogue of **6**.

Conclusions

Metalation of $Me_3P(BH_3)$ (**3**) by either *n*-BuLi or MeNa proceeds rapidly to give the corresponding phosphine−borane-stabilized carbanion complexes $\{Me_2P(BH_3)CH_2\}M$ [M = Li (**4**), Na (**5**)]. The less soluble sodium complex may be recrystallized from THF to give polymeric $[\{Me_2P(BH_3)CH_2\}Na(THF)]_\infty$ (**5a**), whereas the more soluble lithium compound **4** reacts *in situ* with dissolved silicone grease to give the unusual cluster complex $\{Me_2P(BH_3)CHSiMe_2OLi\}_4Li_4(Et_2O)_{2.75}(THF)_{1.25}$ (**6**), which contains a novel siloxy-functionalized alkyl ligand; in the absence of silicone grease we were unable to isolate **4** cleanly. Compound **6** is accessible from the reaction of **4** with a variety of Me_2SiO sources, but not from siloxanes containing only Me_3SiO units; compound **5** also reacts with sources of Me_2SiO when these are deliberately introduced into the reaction solution. The formation of **6** appears to proceed via the formal insertion of dimethylsilanone into the Li−C bond of **4**, followed by deprotonation at the methylene carbon of the resulting intermediate $[\{Me_2P(BH_3)\}CH_2SiMe_2O]Li$ (**9**), generating 1 equiv of the free phosphine−borane **3** per equivalent of siloxy−alkyl dianion. The greater reactivity toward siloxanes of **4** and **5** in comparison to the alkali metal derivatives of the silicon- and phosphine−borane-stabilized carbanion $[(Me_3Si)_2\{Me_2P(BH_3)\}]^-$ may be attributed to the greater degree of negative charge at the carbanion center in the former, due to decreased opportunities for negative hyperconjugation and a consequent increase in nucleophilicity of the carbanion.

Experimental Section

All manipulations were carried out using standard Schlenk techniques under an atmosphere of dry nitrogen. THF and diethyl ether were distilled under nitrogen from potassium or sodium/potassium alloy, respectively. THF was stored over activated 4 Å molecular sieves; diethyl ether was stored over a potassium film. Deuterated toluene and THF were distilled from potassium and were deoxygenated by three freeze−pump−thaw cycles and stored over activated 4 Å molecular sieves. The compounds MeNa[24] and $Me_3P(BH_3)$[25] were prepared by previously published procedures. All other compounds were used as supplied; *n*-BuLi was supplied by Aldrich as a 2.5 M solution in hexane.

^1H, ^7Li, $^{11}B\{^1H\}$, $^{13}C\{^1H\}$, ^{29}Si INEPT, and $^{31}P\{^1H\}$ spectra were recorded on a JEOL Lambda500 spectrometer operating at 500.16,

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194.25, 160.35, 125.65, 99.25, and 202.35 MHz, respectively; ^{1}H, ^{13}C, and ^{29}Si chemical shifts are quoted in ppm relative to tetramethylsilane, ^{11}B, ^{7}Li, and ^{31}P chemical shifts are quoted in ppm relative to external $BF_3(OEt_2)$, 1.0 M LiCl, and 85% H_3PO_4, respectively. Elemental analyses were obtained by the Elemental Analysis Service of London Metropolitan University.

$[\{Me_2P(BH_3)CH_2\}Na(THF)]_\infty$ (5a). A solution of $Me_3P(BH_3)$ (1.81 g, 20.13 mmol) in cold (−10 °C) diethyl ether (30 mL) was added to solid MeNa (0.81 g, 21.30 mmol). The mixture was allowed to attain room temperature and was stirred for 16 h. The solvent was removed *in vacuo*, the product was extracted into THF (10 mL) and filtered, and the filtrate was cooled to −30 °C. After several hours colorless crystals of **5a** suitable for X-ray crystallography deposited. Isolated yield: 1.18 g, 52.5%. Anal. Calcd for $C_3H_{11}BNaP$ (111.9) (coordinated THF lost under vacuum): C 32.20, H 9.91. Found: C 32.11, H 9.82. ^{1}H NMR (d_8-THF, 25 °C): δ −0.92 (d, $J_{PH} = 10.7$ Hz, 2H, PCH_2), 0.32 (q of d, $J_{PH} = 13.2$ Hz, $J_{BH} = 89.4$ Hz, 3H, BH_3), 0.99 (d, $J_{PH} = 9.8$ Hz, 6H, PMe_2). ^{13}C{^{1}H} NMR (d_8-THF, 25 °C): δ 0.50 (br, PCH_2), 20.74 (d, $J_{PC} = 30.4$ Hz, PMe_2). ^{11}B{^{1}H} NMR (d_8-THF, 25 °C): δ −32.5 (d, $J_{PB} = 89.7$ Hz). ^{31}P{^{1}H} NMR (d_8-THF, 25 °C): δ −4.2 (q, $J_{PB} = 89.7$ Hz).

$\{Me_2P(BH_3)CHSiMe_2OLi\}_4Li_4(Et_2O)_{2.75}(THF)_{1.25}$ (6). To a solution of $Me_3P(BH_3)$ (0.38 g, 4.28 mmol) in THF (20 mL) was added *n*-BuLi (1.71 mL, 4.28 mmol), and the resulting solution was stirred for 2 h. The solvent was removed *in vacuo* to yield an off-white oil. This was dissolved in diethyl ether (20 mL), and an excess of hexamethylcyclotrisiloxane (1.56 g, 7.01 mmol) was added. Upon standing for 2 h at room temperature, colorless block crystals of **6** deposited. Isolated yield: 0.29 g, 54.2%. Anal. Calcd for $C_{36}H_{101.5}B_4Li_8O_8P_4Si_4$ (997.7): C 43.34, H 10.25. Found: C 43.13, H 10.12. ^{1}H{^{11}B} NMR (d_8-THF, 25 °C): δ −0.72 (d, $J_{PH} = 18.3$ Hz, 4H, PSiCH), −0.05 (s, 24H, $SiMe_2$), 0.42 (d, $J_{PH} = 13.7$ Hz, 12H, BH_3), 1.03 (d, $J_{PH} = 9.8$ Hz, 24H, PMe_2), 1.10 (t, $^{3}J_{HH} = 7.0$ Hz, 15H, Et_2O), 1.77 (m, 6H, THF), 3.37 (q, $^{3}J_{HH} = 7.0$ Hz, 10H, Et_2O), 3.61 (m, 6H, THF). ^{13}C{^{1}H} NMR (d_8-THF, 25 °C): δ 6.43 (br, $SiMe_2$), 14.79 (Et_2O), 18.15 (d, $J_{PC} = 23.02$ Hz, CH), 21.40 (d, $J_{PH} = 29.7$ Hz, PCH_3), 25.47 (THF), 65.41 (Et_2O), 67.33 (THF). ^{7}Li NMR (d_8-THF, 25 °C): δ 1.6. ^{11}B{^{1}H} NMR (d_8-THF, 25 °C): δ −32.7 (d, $J_{PB} = 84.8$ Hz). ^{31}P{^{1}H} NMR (d_8-THF, 50 °C): δ −9.9 (q, $J_{PB} = 84.8$ Hz). ^{29}Si NMR (THF, 25 °C): δ −10.48.

Crystal Structure Determinations of 5a and 6. Measurements for **5a** were made at 150 K on a Nonius KappaCCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å), whereas measurements for **6** were made at 120 K on a Bruker APEX2 diffractometer using silicon-monochromated synchrotron radiation ($\lambda = 0.6712$ 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 were constrained with a riding model, except those bound to boron, which were freely refined; U(H) was set at 1.2 (1.5 for methyl groups) times U_{eq} for the parent atom. Disorder was successfully resolved and modeled for the THF/diethyl ether combination described above. Programs were Bruker APEX2 (control) and SAINT (integration), Nonius COLLECT and associated programs, and SIR97 and SHELXTL for structure solution, refinement, and molecular graphics.[26]

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Supporting Information Available: For **5a** and **6** details of structure determination, atomic coordinates, bond lengths and angles, and displacement parameters in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org. Observed and calculated structure factor details are available from the authors upon request.

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