Synthesis, Crystal Structure, and Solution Behavior of a Sterically Hindered α-Metalated Phosphine-Borane

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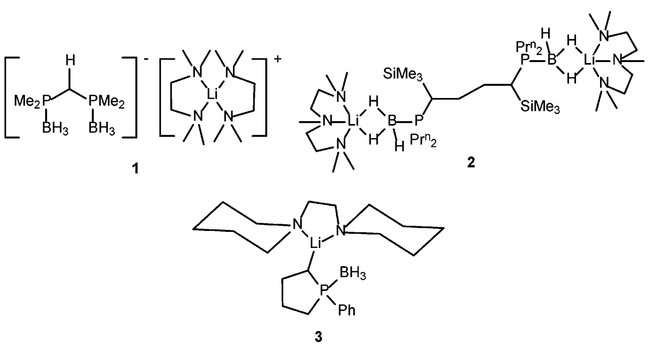
*Summary: Treatment of the phosphine-borane adduct $(Me_3Si)_2CHPMe_2(BH_3)$ (**4**) with n-BuLi in THF, followed by recrystallization from diethyl ether/methylcyclohexane, gives $(THF)_3Li\{(Me_3Si)_2CPMe_2(BH_3)\}_2Li$ (**5**), which crystallizes as a contact ion multiple ate complex. In solution **5** is subject to a dynamic equilibrium between the ate complex and a second, possibly monomeric species.*

Phosphine-borane-stabilized carbanions are key intermediates in the synthesis of polyphosphines,[1] such as the homochiral diphosphine DIPAMP.[2] However, despite their synthetic utility, to date only three such species have been isolated and structurally characterized.[3−5] Each of these compounds adopts a different structural motif in the solid state (Chart 1): $[Me_2P(BH_3)CHPMe_2(BH_3)][Li(tmeda)_2]$ (**1**) crystallizes as a separated ion pair with no contact between the carbanion center and the lithium ion;[3] the unusual dicarbanion complex $[[(Me_3Si)\{n\text{-}Pr_2P(BH_3)\}CCH_2]Li(pmdeta)]_2$ (**2**) crystallizes as a contact ion multiple in which the lithium cations are associated with the BH_3 hydrogens rather than the carbanion centers;[4] and the α-metalated phenylphospholane-borane (**3**) crystallizes as a molecular species with a direct C−Li bond [tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, pmdeta = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine].[5]

Clearly, the structure of these compounds is influenced by the interplay of several factors, including (i) the degree of charge delocalization at the carbanion center, (ii) the nature of the substituents at phosphorus, and (iii) the presence of co-ligands such as tmeda or pmdeta. We have recently observed that the structure adopted by an α-metalated phosphine-borane can have significant consequences for its reactions: protonation of the (−)-sparteine analogue of **2** $[[(Me_3Si)\{n\text{-}Pr_2P(BH_3)\}CCH_2]Li\{(-)\text{-sparteine}\}]_2$ gives a 1:1 mixture of *rac*- and *meso*-diastereomers of the bis(phosphine-borane) $[(Me_3Si)\{n\text{-}Pr_2P(BH_3)\}CHCH_2]_2$. No stereoselectivity is observed in these protonolysis reactions since the Li{(−)-sparteine} moiety is bound to the borane hydrogens rather than the carbanion center at which protonation occurs.

We describe herein the preparation of a new, sterically hindered phosphine-borane, its metalation, and the solid-state structure and solution behavior of the resulting lithium derivative.

Chart 1

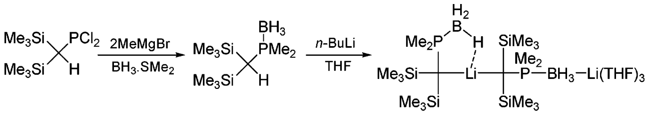


1

2

3

Scheme 1



4

5

Treatment of $(Me_3Si)_2CHPCl_2$[6] with 2 equiv of MeMgBr, followed by 1 equiv of $BH_3{\cdot}SMe_2$, gives the adduct $(Me_3Si)_2CHPMe_2(BH_3)$ (**4**) in essentially quantitative yield.[7] The reaction between **4** and 1 equiv of *n*-BuLi in THF gives the complex $(THF)_3Li\{(Me_3Si)_2CPMe_2(BH_3)\}_2Li$ (**5**), which is obtained as colorless blocks suitable for X-ray crystallography on crystallization from methylcyclohexane/diethyl ether (Scheme 1);[8] the solid-state structure of **5** is shown in Figure 1, along with selected bond lengths and angles.[9]

Compound **5** crystallizes as a discrete molecular species. The two lithium ions lie in very different environments: [Li(2)] is bound by the carbanion centers of two phosphine-borane-stabilized carbanions and has a short contact to one of the H atoms of a BH_3 group from one carbanion ligand. The second lithium ion [Li(1)] is bound in an η^3-fashion by the H atoms of

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(7) **4**: Both **4** and **5** (see ref 8) were synthesized using standard Schlenk techniques under an atmosphere of dry nitrogen, and all solvents were dried and degassed before use. To a cold (−78 °C) solution of $(Me_3Si)_2CHPCl_2$[6] (7.16 g, 27.40 mmol) in diethyl ether (50 mL) was added, dropwise, MeMgBr (18.27 mL of a 3.0 M solution in diethyl ether, 54.81 mmol). The solution was allowed to attain room temperature and was stirred for 16 h. BH_3SMe_2 (13.70 mL of a 2.0 M solution in ether, 27.40 mmol) was added, and the resulting solution was stirred for 3 h. Water (50 mL) was added, and the organic layer was extracted into diethyl ether (3 × 30 mL). The combined organic extracts were dried over sodium sulfate. The solution was filtered and the solvent was removed in vacuo from the filtrate to give **4** as a white solid. Isolated yield: 5.82 g, 91%. $^1H\{^{11}B\}$ NMR (500.16 MHz, $CDCl_3$, 25 °C): δ 0.24 (s, 18H, $SiMe_3$), 0.30 (d, $J_{PH} = 17.7$ Hz, 1H, CH), 0.63 (d, $J_{PH} = 14.7$ Hz, 3H, BH_3), 1.38 (d, $J_{PH} = 9.8$ Hz, 6H, PMe_2). $^{13}C\{^1H\}$ NMR (125.65 MHz, $CDCl_3$, 25 °C): δ 2.98 (d, $^3J_{PC} = 2.5$ Hz, $SiMe_2$), 12.61 (d, $J_{PC} = 5.3$ Hz, CH), 17.38 (d, $J_{PC} = 36.7$ Hz, PMe_2). $^{11}B\{^1H\}$ NMR (160.35 MHz, $CDCl_3$, 25 °C): δ −33.3 (d, $J_{PB} = 59.5$ Hz). $^{31}P\{^1H\}$ NMR (202.35 MHz, $CDCl_3$, 25 °C): δ 6.5 (q, $J_{PB} = 59.5$ Hz).

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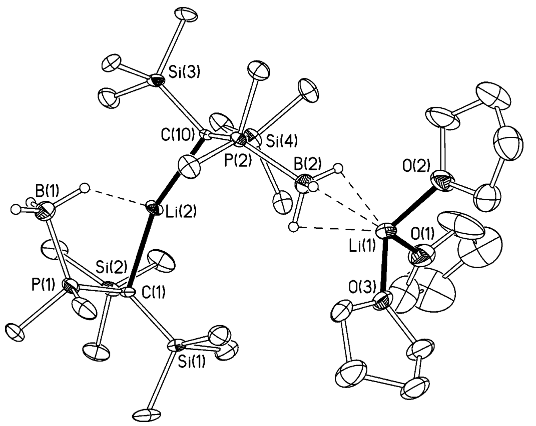

Figure 1. Molecular structure of **5** with 30% probability ellipsoids and with H atoms, except those bound to B atoms, omitted for clarity. Selected bond lengths (Å) and angles (deg): Li(2)−C(1) 2.249(8), Li(2)−C(10) 2.252(8), Li(2)−H(1C) 2.03(8), Li(1)−H(2D) 2.13(5), Li(1)−H(2E) 2.10(5), Li(1)−H(2F) 2.31(6), Li(1)−O(1) 1.924(12), Li(1)−O(2) 1.953(10), Li(1)−O(3) 1.948(9), C(1)−P(1) 1.755(5), P(1)−B(1) 1.944(7), C(10)−P(2) 1.750(5), P(2)−B(2) 1.926(6), C(1)−Li(2)−C(10) 162.3(4), Si(1)−C(1)−Si(2) 113.5(2), Si(1)−C(1)−P(1) 117.1(2), Si(2)−C(1)−P(1) 113.4(2), Si(3)−C(10)−Si(4) 113.2(2), Si(3)−C(10)−P(2) 116.3(2), Si(4)−C(10)−P(2) 112.2(2).

the BH_3 group of the second carbanion ligand. The coordination of Li(1) is completed by three molecules of THF to give a pseudotetrahedral coordination geometry. Thus the solid-state structure of **5** contains both Li−C and $Li-H_3B$ contacts and exhibits features of the structures of both **2** and **3**; the overall structure of **5** may best be described as a contact ion multiple dialkyllithate complex.

Although the existence of dialkyllithate complexes was first proposed many years ago,[10] few such compounds have been isolated in the solid state; crystallographically characterized complexes of this type are limited to the tris(trimethylsilyl)methyl derivatives $[Li(L)_n][\{(Me_3Si)_3C\}_2Li]$ $[Li(L)_n = Li(THF)_4$ (**6**),[11] $Li(tmeda)_2$ (**7**),[12] (pmdeta)LiClLi(pmdeta)[13]], the closely related cyclic species $[Li(tmeda)_2][\{(Me_3Si)_2C(SiMe_2CH_2)\}_2Li]$ (**8**),[14] and the recently reported dibenzyllithate complex $[Li(tmeda)_2][(tmeda)Li(CH_2Ph)_2]$ (**9**).[15]

The charge-stabilizing Me_3Si and Me_2PBH_3 groups in **5** are exactly isoelectronic, and therefore, it is perhaps unsurprising that the dialkyllithate portion of **5** bears a close resemblance to the dialkyllithate anions in the separated ion multiple complexes **6**−**8**. The Li(2)−C(1) and Li(2)−C(10) distances in **5** of 2.249(8) and 2.252(8) Å, respectively, are somewhat longer than the corresponding distances in **6**−**8** [2.16(1)/2.20(1), 2.213(5), and 2.156(4) Å, respectively].[11,12,14] This is consistent with the increased coordination number of Li(2) in **5** due to the short contact with one of the borane hydrogen atoms [Li(2)···H(1C) 2.03(8) Å]; consistent with this, whereas the dialkyllithate anions in **6** and **7** are exactly linear, the C(1)−Li(2)−C(10) angle in **5** is 162.3(4)° [for comparison, the C−Li−C angle in the somewhat constrained cyclic dialkyllithate anion in **8** is 171.4(7)°]. The carbanion centers in **5** are distinctly pyramidal [sum of angles within the ligand at C(1) 344.0°, C(10) 341.7°].

In contrast to the separated ion multiple complexes **6**−**8**, compound **5** crystallizes as a contact ion multiple by virtue of the coordination of the second borane group to the lithium cation. The Li(1)−H distances in **5** [2.10(5), 2.13(5), and 2.31(6) Å] compare with Li−H distances of 2.02(4)−2.12(4) Å in $(THF)_3Li(\eta^3\text{-}BH_4)$ (**10**),[16] and the Li···B distance of 2.279(11) Å in **5** compares with Li···B distances of 2.319(7) Å in **10** and 2.223(7) Å in $\{HC(3,5\text{-}Me_2pz)_3\}Li(\eta^3\text{-}BH_4)$.[17]

Variable-temperature NMR spectroscopy reveals that compound **5** exhibits dynamic behavior in solution. In d_8-THF the ^1H, $^{31}P\{^1H\}$, and $^{11}B\{^1H\}$ NMR spectra of **5** exhibit a single set of ligand resonances and the ^7Li spectrum consists of a single signal; these spectra are invariant over the temperature range 20 to −80 °C. This is consistent with either rapid exchange between the two types of alkyl ligand or the presence of a molecular, mononuclear, or symmetrical oligonuclear complex, $[(THF)_nLi\{(Me_3Si)_2CPMe_2(BH_3)\}]_m$ (**A**), in this solvent.

At room temperature the ^1H NMR spectrum of **5** in d_8-toluene once again exhibits a single set of ligand resonances, and these merely broaden slightly as the temperature is reduced. In contrast, the $^{31}P\{^1H\}$ and ^7Li NMR spectra of **5** in d_8-toluene change significantly with temperature. At room temperature the $^{31}P\{^1H\}$ spectrum consists of a well-resolved quartet at −1.64 ppm ($J_{PB} = 89.4$ Hz). However, as the temperature is reduced, this signal broadens considerably and begins to decoalesce until, below −70 °C, the spectrum consists of two broad multiplets at −1.32 and −2.98 ppm (Figure 2). By −90 °C this second multiplet has decoalesced into two peaks and the spectrum consists of three broad, poorly resolved multiplets at −0.67, −3.22, and −3.80 ppm in the approximate ratio 5:2:2. The ^7Li spectrum is also consistent with dynamic behavior in solution. As the temperature is reduced below ambient, the singlet observed at room temperature broadens and begins to decoalesce until, at −90 °C, the spectrum consists of a major signal at 0.9 ppm and two smaller signals at 0.5 and 2.5 ppm.

A recent $^{13}C\{^1H\}$, ^6Li, and ^7Li NMR investigation suggests that in many cases organolithium compounds are subject to

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(8) **5**: To a solution of **4** (1.46 g, 6.23 mmol) in THF (20 mL) was added *n*-BuLi (2.5 mL of a 2.5 M solution in hexanes, 6.25 mmol), and the solution was stirred for 5 h. The solvent was removed in vacuo, and the resulting sticky solid was washed with light petroleum to give **5** as a white solid. Recrystallization of this solid from cold (5 °C) methylcyclohexane/diethyl ether gave single crystals of **5** suitable for X-ray crystallography. Isolated yield: 0.93 g, 43%. Calcd for $C_{30}H_{78}B_2Li_2O_3P_2Si_4$ (696.72): C 51.72, H 11.28; found C 51.89, H 11.38. ^1H NMR (500.16 MHz, d_8-toluene, 25 °C): δ 0.26 (s, 18H, $SiMe_3$), 1.24 (m, 6H, THF), 1.31 (d, $J_{PH} = 12.6$ Hz, 6H, PMe_2), 3.39 (m, 6H, THF). $^{13}C\{^1H\}$ NMR (125.65 MHz, d_8-toluene, 25 °C): δ 6.83 ($SiMe_3$), 19.48 (PMe_2), 24.97 (THF), 68.03 (THF) [quaternary carbon not observed]. ^7Li NMR (194.25 MHz, d_8-toluene, 25 °C): δ 0.6. $^{11}B\{^1H\}$ NMR (160.35 MHz, d_8-toluene, 25 °C): δ −28.3 (d, $J_{PB} = 89.4$ Hz). $^{31}P\{^1H\}$ NMR (202.35 MHz, d_8-toluene, 25 °C): δ −1.6 (q, $J_{PB} = 89.4$ Hz).

(9) Crystal data for **5**: $C_{30}H_{78}B_2Li_2O_3P_2Si_4$, fw = 696.72, orthorhombic, space group $P2_12_12_1$, $a = 13.682(3)$ Å, $b = 16.960(3)$ Å, $c = 19.612(3)$ Å, $V = 4450.9(14)$ Å^3, $Z = 4$, $D_{calcd} = 1.017$ g cm^{-3}, $\mu = 0.226$ mm^{-1}, $T = 150$ K, crystal size 0.54 × 0.42 × 0.10 mm. Bruker SMART CCD diffractometer, structure solution by direct methods, refinement on F^2 ($2\theta < 22.5°$); $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2} = 0.140$ (all 5958 unique data), conventional $R = 0.060$ on F values of 5551 reflections with $F_o^2 > 2\sigma(F_o^2)$, goodness of fit = 1.210, final difference synthesis within ±0.63 e Å^{-3}. H atoms of the BH_3 groups were refined freely, while others were constrained as riding atoms.

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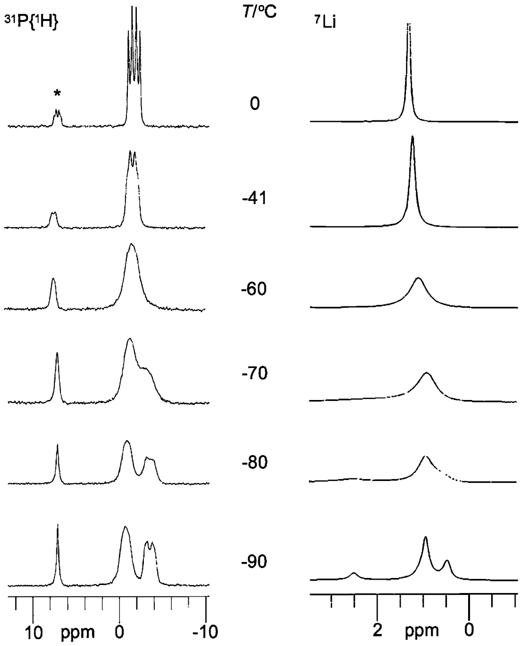

Figure 2. Variable-temperature $^{31}P\{^1H\}$ and ^7Li NMR spectra of **5** in d_8-toluene [* free phosphine-borane **4**].

dynamic equilibria between molecular species and *ate* complexes in solution. In general, the ^7Li signal for the cationic component of an *ate* complex appears to higher field with respect to the corresponding neutral molecular species and the signal for the anionic component appears to lower field than the neutral species.[18]

This suggests that the dynamic behavior exhibited by **5** may be ascribed to the presence of two species at low temperature; the major species corresponds to a mononuclear or symmetrical oligonuclear species of type **A**, whereas the minor species corresponds to an *ate* complex **B**, similar to that observed in the solid state. At higher temperatures these two species are in rapid equilibrium.

$$\underset{\mathbf{A}}{[\mathrm{RLi(THF)}_n]_m} \rightleftharpoons \underset{\mathbf{B}}{[\mathrm{R_2Li}][\mathrm{Li(THF)}_n]}$$

The solid-state ^7Li spectrum of the closely related separated ion multiple *ate* complex **6** exhibits signals at 1.7 ppm, assigned to the cation, and at 2.8 ppm, assigned to the anion.[12] This suggests that the peak at 0.5 ppm in the low-temperature ^7Li spectrum of **5** may be assigned to the cation of an *ate* complex **B**, whereas the signal at 2.5 ppm may be assigned to the anion of this complex.

In summary, the sterically hindered α-metalated phosphine-borane complex **5** adopts a unique structure in the solid state which exhibits both C−Li and BH_3−Li contacts and which may best be described as a contact ion multiple *ate* complex; in solution the *ate* complex is in dynamic equilibrium with a molecular, mononuclear or symmetrical oligonuclear species.

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Supporting Information Available: For **5** 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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