

Synthesis, Structure, and Solution Behavior of a Phosphine–Borane-Stabilized 1,3-Dicarbanion[†]

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Summary: The reaction between the phosphine-borane $\{(Me_3Si)CH_2\}_2P(BH_3)Ph(2) \text{ and } 2 \text{ equiv of } n-BuLi \text{ in } THF \text{ yields the } 1,3-dicarbanion complex (THF)_2Li}\{(Me_3SiCH)_2-P(BH_3)Ph\}Li(THF)_3 (3), which crystallizes as an unusual contact ion pair. In solution 3 is subject to dynamic exchange which interconverts the two lithium environments.$

Phosphine—borane-stabilized carbanions are key intermediates in the synthesis of a range of important phosphorus compounds, including chiral mono- and polyphosphines with applications as ligands in catalytically active transition-metal complexes.¹ However, until recently phosphine borane-stabilized carbanions were almost exclusively prepared and used in situ and the structures of, and bonding in, these species had not been investigated. Indeed, prior to our and other groups' recent efforts,^{2–5} the coordination chemistry of these potentially ambidentate ligands was confined to a single example, [Ph₂P(BH₃)CHPPh₂(BH₃)][Li(tmeda)₂],⁶ which crystallizes as a separated ion pair complex (tmeda = N,N,N',N'-tetramethylethylenediamine).

Over the last 3 years, as part of an ongoing project investigating the coordination chemistry of phosphine– borane-stabilized carbanions, we have shown that these ligands adopt a wide variety of coordination modes in their complexes with the alkali and alkaline-earth metals.² Observed binding modes include terminal BH₃- and C-donor coordination, chelating modes, and various bridging modes; the exact nature of the binding mode depends on the substituents at the P and C centers, the metal ion, and the presence of coligands.

Very recently the groups of Westerhausen and Harder have independently demonstrated that $CH_2\{PPh_2(BH_3)\}_2$ undergoes deprotonation at the central carbon atom to give novel alkali-metal and alkaline-earth-metal derivatives.^{3,4} In the latter case Harder and co-workers have shown that the reaction between $CH_2\{PPh_2(BH_3)\}_2$ and $(4-t-BuC_6H_4CH_2)_2$ - $Ca(THF)_4$ yields the methandiide complex [[C{PPh_2(BH_3)}_2]- $Ca]_2$ (1),⁴ in which two adjacent phosphine—borane groups support a formal 1,1-dicarbanion; this prompted us to investigate whether a *single* phosphine—borane group would support *two* adjacent carbanion centers to give a 1,3-dicarbanion. We describe herein the results of our initial investigations in this area and report the unusual structure and solution behavior of a novel lithium complex of a 1,3-dicarbanion supported by both phosphine—borane and silyl groups.

Treatment of PhPCl₂ with 2 equiv of Me₃SiCH₂MgCl in diethyl ether, followed by 1 equiv of BH₃·SMe₂, yields the air-stable phosphine—borane {(Me₃Si)CH₂}₂P(BH₃)Ph (**2**) as a colorless, crystalline solid (Scheme 1);⁷ single crystals of **2** were obtained from cold methylcyclohexane.⁸ The structure of **2** (Figure 1) is unexceptional; the P–C(7) and P–C-(11) distances are 1.8110(17) and 1.8130(17) Å, respectively, whereas the P–B distance is 1.924(2) Å.

The ¹H, ¹³C{¹H}, ³¹P{¹H}, and ¹¹B{¹H} NMR spectra of **2** are as expected; the ³¹P{¹H} spectrum exhibits a broad quartet at 11.7 ppm, while the ¹¹B{¹H} spectrum exhibits a broad doublet at -38.2 ppm ($J_{PB} = 58.8$ Hz).

The reaction between **2** and 2 equiv of *n*-BuLi in THF proceeds cleanly to give the corresponding 1,3-dicarbanion in good yield as a pale yellow solid, which may be recrystallized from cold THF to give single crystals of the adduct

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⁽⁷⁾ Synthesis of **2**: to a cold (-78 °C) solution of PhPCl₂ (1.28 mL, 9.4 mmol) in diethyl ether (30 mL) was added Me₃SiCH₂MgCl (40 mL of a 0.47 M solution in diethyl ether, 18.8 mmol). The resulting solution was warmed to room temperature and was stirred overnight. BH₃·SMe₂ (4.7 mL, 9.4 mmol) was added, the solution was stirred for 2 h, and then water (40 mL) was added. The organic layer was extracted into diethyl ether (3 × 30 mL), the combined organic extracts were dried over MgSO₄ and filtered, and the solvent was removed in vacuo from the filtrate to yield **2** as a colorless solid which was purified by crystallization from cold (-30 °C) methylcyclohexane (20 mL). Isolated yield: 2.24 g, 80%. Anal. Calcd for C₁₄H₃₀BPSi₂: C, 56.74; H, 10.20. Found: C, 56.88; H, 10.15. ¹H{¹¹B} NMR (*d*₈-toluene, 25 °C): δ -0.18 (d, *J*_{PC} = 1.9 Hz, SiMe₃), 18.62 (d, *J*_{PC} = 23.0 Hz, CH₂), 128.26 (d, *J*_{PC} = 9.6 Hz, *m*-ph), 131.65 (d, *J*_{PC} = 8.6 Hz, *o*-Ph), 134.07 (d, *J*_{PB} = 58.8 Hz). ³¹P{¹H} NMR (*d*₈-toluene, 25 °C): δ -138.2 (d, *J*_{PB} = 58.8 Hz).



Figure 1. Molecular structure of 2 with 40% probability ellipsoids. Selected bond lengths (Å) and angles (deg): P-B = 1.924(2), P-C(1) = 1.8203(18), P-C(7) = 1.8110(17), P-C(11) = 1.8130(17), Si(1)-C(7) = 1.8853(17), Si(2)-C(11) = 1.8852(17); C(7)-P-C(11) = 106.55(8).

Scheme 1. ^{*a*}



^{*a*}Reagents and conditions: (i) 2 Me₃SiCH₂MgCl/Et₂O; (ii) BH₃. SMe₂/Et₂O; (iii) 2 *n*-BuLi/THF.

 $(THF)_2Li\{(Me_3SiCH)_2P(BH_3)Ph\}Li(THF)_3$ (3) (Scheme 1).⁹ Somewhat surprisingly, 3 appears to be formed irrespective of the reaction stoichiometry: treatment of 2 with 1 equiv of *n*-BuLi in THF, followed by removal of the solvent, yields a sticky yellow oil, which we were unable to purify further.

(9) Synthesis of **3**: to a solution of **2** (1.04 g, 3.51 mmol) in THF (30 mL) was added *n*-BuLi (2.81 mL, 7.03 mmol), and the resulting solution was stirred for 1 h. The solution was concentrated to approximately 5 mL and was cooled to -30 °C for 16 h, yielding pale yellow blocks of **3** suitable for X-ray crystallography. Isolated yield: 1.41 g, 60%. Anal. Calcd for C₃₄H₆₈BLi₂O₅PSi₂: C, 61.06; H, 10.25. Found: C, 60.88; H, 10.14. ¹H{¹¹B} NMR (d_8 -toluene, 25 °C): δ –0.25 (d, J_{PH} = 17.4 Hz, 2H, CH), 0.22 (s, 18H, SiMe₃), 1.07 (d, J_{PH} = 12.9 Hz, BH₃), 1.49 (m, 20H, THF), 3.61 (m, 20H, THF), 7.14 (m, 1H, *p*-Ph), 7.27 (m, 2H, *m*-Ph), 8.10 (m, 2H, *o*-Ph). ¹³C{¹H} NMR (d_8 -THF, 25 °C): δ 4.17 (d, J_{PC} = 3.8 Hz, SiMe₃), 14.74 (d, J_{PC} = 18.2 Hz, CH), 25.40 (THF), 67.86 (THF), 126.64 (Ar), 127.05 (d, J_{PC} = 7.7 Hz, Ar), 129.89 (d, J_{PC} = 8.7 Hz, Ar) (ipso carbon not observed). ⁷Li{¹H} NMR (d_8 -toluene, 25 °C): δ -34.4 (d, J_{PB} = 107.9 Hz). ³¹P{¹H} NMR (d_8 -THF, 25 °C): δ 3.4 (q, J_{PB} = 107.9 Hz).



Figure 2. Molecular structure of 3 with 40% probability ellipsoids and with C-bound H atoms and THF minor disorder components omitted for clarity. Selected bond lengths (Å) and angles (deg): Li(1)–C(7) = 2.218(3), Li(1)–C(11) = 2.234(3), Li(1)–O(1) = 1.975(3), Li(1)–O(2) = 2.014(3), Li(2)–H(0A) = 2.01(2), Li(2)–H(0B) = 2.03(2), Li(2)···B = 2.384(4), Li(2)–O(3) = 1.976(3), Li(2)–O(4) = 1.950(3), Li(2)–O(5) = 1.961(3), P–B = 1.943(2), P–C(1) = 1.8685(16), P–C(7) = 1.7571(17), P–C(11) = 1.7620(16), Si(1)–C(7) = 1.8179(18), Si(2)–C(11) = 1.8115(16); C(7)–P–C(11) = 109.51(8), C(7)–Li(1)–C(11) = 80.42(11).

Crude ${}^{31}P{}^{1}H$, ${}^{11}B{}^{1}H$, and ${}^{7}Li{}^{1}H$ NMR spectra of this oil are consistent with the presence of equal amounts of **3** and unreacted **2**, rather than formation of the expected monolithiated species.

To our knowledge, with the exception of the dilithium complex (THF)Li[C(SiMe₃)₂[SiMe₂CH(PPh₂){Li(THF)₂}]],¹⁰ isolated serendipitously from the reaction between HC-(SiMe₃)₂(SiMe₂CH₂PPh₂) and MeLi, compound **3** is the first example of a formal 1,3-dicarbanion with an $E-C^-$ - $E'-C^--E$ skeleton. The molecular structure of **3** is shown in Figure 2, along with selected bond lengths and angles.

Compound **3** crystallizes as a contact ion pair ate complex in which one lithium ion is bound by the two carbanion centers and by the oxygen atoms of two molecules of THF, affording a four-coordinate, distorted-tetrahedral geometry at lithium; the second lithium ion is coordinated by three molecules of THF and in an η^2 manner by the BH₃ group of the dicarbanion, affording a pseudotetrahedral geometry at this lithium center. Thus, the carbanion ligand acts as a bidentate C,C'-donor to one lithium ion, generating a dialkyllithate "anion", while simultaneously bridging via its borane hydrogen atoms to the lithium "counterion". The SiMe₃ groups of the ligand are arranged in a cis configuration with respect to the PC₂Li ring, positioning them on the opposite face of the ring to the phenyl group.

The Li(1)–C(7) and Li(1)–C(11) distances in **3** (2.218(3) and 2.234(3) Å, respectively) compare with Li–C distances of 2.249(8) and 2.252(8) Å in the related ate complex (THF)₃Li{(Me₃Si)₂CPMe₂(BH₃)}₂Li (**4**),^{2b} which contains a monodentate, sterically hindered phosphine–borane-stabilized carbanion, and with the Li–C distance of 2.213(5) Å in the anion of [{(Me₃Si)₃C}₂Li][Li(tmeda)₂] (tmeda = N,N, N',N'-tetramethylethylenediamine);¹¹ the C(7)–Li(1)–C(11)

⁽⁸⁾ Crystallographic data for **2** and **3** are as follows. Data were collected on a Nonius KappaCCD diffractometer ($\lambda = 0.71073$ Å) at 150 K, and structures were solved by direct methods; H atoms of the BH₃ groups were refined freely, while others were constrained as riding atoms. Disorder was satisfactorily resolved for some THF ligands of **3**, with the aid of displacement parameter restraints. **2**: C₁₄H₃₀BPSi₂, fw = 296.34, monoclinic, space group $P2_1/c$, a = 13.792(3) Å, b = 10.686(3) Å, c = 13.1277(15) Å, $\beta = 92.447(10)^\circ$, V = 1933.0(7) Å³, $Z = 4, \mu = 0.252$ mm⁻¹, crystal size 0.18 × 0.10 × 0.05 mm, $R_{int} = 0.058$ (27151 measured and 4411 unique data), R = 0.039 on F values of 3322 reflections with $F^2 > 2\sigma$, $R_w = 0.095$ on all F^2 values, goodness of fit 1.062, final difference synthesis within ± 0.36 eÅ⁻³. **3**: C₃₄H₆₈BL₁₂O₃P-Si₂, fw = 668.72, triclinic, space group PI, a = 10.193(4) Å, b = 11.3220(14) Å, c = 19.021(4) Å, $\alpha = 86.058(13)^\circ$, $\beta = 82.76(2)^\circ$, $\gamma = 75.133(12)^\circ$, V = 2103.2(9) Å³, $Z = 2, \mu = 0.156$ mm⁻¹, crystal size 0.34 × 0.30 × 0.30 mm, $R_{int} = 0.036$ (32 091 measured and 9453 unique data), R = 0.045 on F values of 7164 reflections with $F^2 > 2\sigma$, $R_w = 0.125$ on all F^2 values, goodness of fit 1.030, final difference synthesis within ± 0.306 eÅ⁻³.

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bite angle for **3** is 80.42(11)°. The Li(2)···H distances of 2.01(2) and 2.03(2) Å are similar to the Li···H distances of 1.94(3) and 2.05(3) Å in the 1,4-dicarbanion complex $[(Me_3Si)\{n-Pr_2P(BH_3)\}C(CH_2)]_2Li_2(THF)_4$,^{2a} in which the Li cations are also bound by the BH₃ groups in an η^2 manner.



Metalation of **2** leads to a significant shortening of the P-C(7) and P-C(11) distances from 1.8110(17) and 1.8130(17) Å, respectively, in **2** to 1.7571(17) and 1.7620(16) Å in **3**; similarly, the Si(1)-C(7) and Si(2)-C(11) distances decrease from 1.8853(17) and 1.8852(17) Å, respectively, in **2** to 1.8179(18) and 1.8115(16) Å in **3**. This is consistent with significant delocalization of the carbanion charges onto the phosphorus and silicon atoms. In contrast, the P-B distance increases from 1.924(2) Å in **2** to 1.943(2) Å in **3**.

The ${}^{31}P{}^{1}H$ and ${}^{11}B{}^{1}H$ NMR spectra of **3** consist of a broad quartet at 3.4 ppm and a broad doublet at -34.4 ppm, respectively ($J_{PB} = 107.9 \text{ Hz}$). We have previously observed that α -deprotonation of phosphine-borane adducts results in a significant increase in the ${}^{31}P^{-11}B$ coupling constant in the corresponding anion;² for example, the ${}^{31}P$ - ${}^{11}B$ coupling constant in (Me₃Si)₂{Me₂P(BH₃)}CH is 59.4 Hz, whereas the corresponding coupling constant in 4 is 89.4 Hz. The magnitude of the increase in J_{PB} upon α -metalation appears to be a function of the degree of charge delocalization in the metalated form. In 4 the highly charge-localizing lithium ion inhibits the delocalization of charge onto phosphorus and the ${}^{31}P^{-11}B$ coupling constant is 89.4 Hz;^{2b} in the heavier alkali-metal derivatives $[[(Me_3Si)_2{Me_2P(BH_3)}C]M]_n (M =$ Na, K, Rb, $n = \infty$; M = Cs, n = 2), in which charge localization is less pronounced, the corresponding coupling constants lie between 95.2 and 101.6 Hz.^{2c} Similarly, in $[(Me_3Si)_2{Me_2P(BH_3)}C]_2Mg$, in which the pyramidal carbanion centers of the ligands are coordinated to the charge-localizing Mg^{2+} ion, the ${}^{31}P^{-11}B$ coupling constant (88.9 Hz) is significantly less than in [(Me₃Si)₂{Me₂P(BH₃)}C]₂- $M(THF)_n$ (M = Ca, n = 4; M = Sr, Ba, n = 5; $J_{PB} = 95.6 -$ 105.2 Hz), in which there is no direct contact between the metals and the essentially planar carbanion centers.^{2d} The change in the magnitude of the ${}^{31}P-{}^{11}B$ coupling constant observed on metalation of 2 (49.1 Hz) represents the largest such increase reported to date and may be attributed to increased charge delocalization onto phosphorus due to the stabilization of two adjacent negative charges by the single phosphorus center in 3. Unfortunately, the ${}^{31}P-{}^{11}B$ coupling constant for 1 was not reported, and so we are unable to compare the effect of a single phosphine-borane center supporting two adjacent negative charges with the effect of two phosphine-borane groups supporting an adjacent methanediide center.

The ³¹P{¹H} and ¹¹B{¹H} NMR spectra of **3** do not change significantly with temperature: the signal at 3.4 ppm in the ³¹P{¹H} spectrum merely broadens slightly as the temperature is reduced to -60 °C, before sharpening again to a broad quartet centered at 5.4 ppm ($J_{PB} = 108.3$ Hz) at -90 °C, while the signal at -34.4 ppm in the ¹¹B{¹H} spectrum also broadens as the temperature is reduced to -60 °C before



Figure 3. Variable-temperature ⁷Li NMR spectra of **3** in d_8 -toluene (referenced to external 1.0 M LiCl in D₂O).

sharpening somewhat to a broad doublet centered at -33.4ppm. The room-temperature ¹H NMR spectrum of **3** in d_8 toluene is consistent with the solid-state structure, although a single pair of signals is observed for the THF protons, suggesting rapid dynamic exchange of these ligands on the NMR time scale. In addition to these signals and signals due to the phenyl ring, the spectrum exhibits a broad doublet at -0.25 ppm ($J_{\rm PH} = 17.4$ Hz), due to the methine protons at the carbanion centers, and a singlet at 0.22 ppm, due to the trimethylsilyl protons; the BH₃ protons give rise to a very broad signal at 1.07 ppm, which collapses to a doublet $(J_{\rm PH} =$ 12.9 Hz) on decoupling of the ¹¹B nucleus. As the temperature is reduced, the signal due to the SiMe₃ protons broadens and shifts to lower field, before sharpening at -90 °C to a singlet at 0.87 ppm. Concurrently, the signal at 8.10 ppm, due to the ortho protons of the phenyl ring, broadens and shifts to lower field, until at -90 °C this signal sharpens to a poorly resolved multiplet centered at 8.80 ppm. The remaining signals change little with temperature.

The room-temperature ⁷Li NMR spectrum of **3** consists of a singlet at 1.6 ppm (Figure 3), consistent with rapid exchange between the two lithium environments on the NMR time scale. However, as the temperature is reduced this signal broadens and begins to decoalesce, until at -90 °C the spectrum consists of two relatively sharp singlets of approximately equal intensity at -0.6 and 1.9 ppm.

Previous variable-temperature, multielement NMR studies of the sterically hindered organolithium compounds $[{(Me_3Si)_3C}_2Li][LiL_n]$ ($L_n = (THF)_4$, (tmeda)₂) have revealed that these may be subject to dynamic equilibria between a range of species in solution, including ate complexes and both contact and separated ion pairs.^{11,12} The variable-temperature ⁷Li NMR data for **3** indicate that there



is rapid exchange between the two lithium environments at room temperature, while the variable-temperature ¹H, ³¹P- $\{^{1}H\}$, and $\{^{11}B\}^{1}H\}$ NMR spectra suggest that the species present at low temperature are different from the species present at high temperatures, although not dramatically so. This behavior may be attributed to the operation of a dynamic equilibrium between the contact ion pair form observed in the solid state (3) and either a solvent-separated ion pair (3a) and/or solvent-separated ion triple form (3b) or an alternative molecular species in which both lithium ions are each bound to a carbanion center (3c) (Scheme 2). At higher temperatures this equilibrium is rapid on the NMR time scale and so a time-averaged spectrum is observed; as the temperature is reduced the rate of exchange between these forms decreases, leading to broadening of some of the NMR signals, while concurrently the equilibrium increasingly favors the contact ion pair form 3. Thus, although the rate of exchange is reduced with decreasing temperature, individual signals due to 3a, 3b, and/or 3c are not observed, since at low temperatures the contact ion pair form 3 predominates. Unfortunately, with the present data, it is not possible to distinguish unambiguously between these processes; however, we tentatively favor an equilibrium involving 3c, since the ionic compounds 3a and 3b are likely to be less favored in the nondonor solvent toluene used in this study.

The ⁷Li signal for the cationic component of ate complexes typically lies to higher field than that of the anionic component, and so we attribute the signal at -0.6 ppm in the low-temperature ⁷Li NMR spectrum of **3** to the formally cationic

component and the signal at 1.6 ppm to the formally anionic dialkyllithate component. For comparison, the solid-state ⁷Li NMR spectrum of the dialkyllithate complex [{(Me₃-Si)₃C}₂Li][Li(THF)₄] exhibits signals at 1.7 and 2.8 ppm, assigned to the cation and dialkyllithate anion, respectively.¹¹ It is informative to compare the low-temperature ⁷Li NMR spectrum of 3 with that of 4, which adopts a closely related dialkyllithate contact ion multiple structure in the solid state.^{2b} Whereas for 4 signals due to both the ate complex (for which ⁷Li signals are observed at 0.5 and 2.5 ppm for the cationic and anionic components, respectively) and a mononuclear (or symmetrical oligonuclear) complex (which has a ⁷Li signal at 0.9 ppm) may be observed at low temperature, for 3 only the ate complex is observed, reflecting stability of this species due to the bidentate, dianionic nature of the ligand.

In summary, we have shown that a single phosphine—borane center, in conjunction with silyl groups, is able to support two adjacent carbanion centers. The reported dilithium derivative crystallizes as a contact ion pair ate complex, which is subject to dynamic exchange which inter-converts the two lithium environments.

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Supporting Information Available: CIF files giving details of the structure determination, atomic coordinates, bond lengths and angles, and displacement parameters for **2** and **3**. 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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