

Mono(borane)phosphides as Ligands to Lithium and Aluminum

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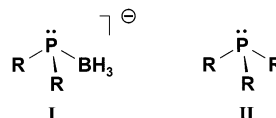
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The complexation potential of mono(borane)diorganophosphides toward lithium and aluminum has been explored in the complexes $[\{(tmeda)Li\}\{P(BH_3)Me_2\}]$ (**1**), $[\{(-)-sparteine\}Li]\{P^*(BH_3)(Ph)tBu\}$ (**2**), $[(tmeda)_2Li]^+[Al\{P(BH_3)Me_2\}_4]^-$ (**3**), and $[(mtbe)Li]^+[Al\{P(BH_3)Me_2\}_4]^-$ (**4**) (*tmeda* = *N,N,N,N*-tetramethylethylenediamine; *mtbe* = methyl-*tert*-butyl ether). In **1** there is competing Li–P and Li–H–B bonding, while in **2** Li–P coordination is absent due to steric hindrance. Compound **2** contains the enantiomerically pure *P*-chiral anion $[P^*(BH_3)(Ph)tBu]^-$, which is a valuable building block for the synthesis of *P*-chirogenic phosphines. The complexes **3** and **4** are the first homoleptic tetraphosphorus aluminates to be structurally characterized.

Introduction

Borane adducts of diorganophosphides **I** are isoelectronic with organophosphines **II** but carry an overall negative charge. Despite the similarity to the excellent transition metal ligands **II**, the metal complexation potential of **I** has not been explored in depth.¹ This is the more surprising as complexes of organophosphides with metals from virtually all parts of the periodic table have been the subject of considerable recent interest.² *P*-chiral phosphide-boranes of type **I** ($R^1 \neq R^2$) have been shown to be valuable building blocks in the synthesis of enantiomerically pure phosphines with chirogenic phosphorus centers.³ The importance of *P*-chiral phosphines, inter alia in homogeneous catalysis, has triggered a burst in pertinent activities including chiral tertiary phosphine-boranes.⁴



We were interested in main group metal complexes of ligands **I** as we and others have been utilizing anionic organophosphines for the synthesis of stable main group metal phosphine complexes.^{2d,5} Anionic phosphines have been shown to be superior in their coordination ability even toward those main group metals which were previously unknown to form stable phosphine complexes.^{2d,5,6} Often they could be shown to induce unusual coordination geometries and bonding modes at the metal center.⁷ More specifically, our aim was to find the first evidence if ligands **I** are able to bind to main group metal cations via coordinative P–M bonding. Here we report the first structural data on lithium compounds of **I** ($R^1 = R^2 = Me$; $R^1 = tBu$, $R^2 = Ph$) as well as on the synthesis and structure of an homoleptic tetraphosphorus aluminate having exclusively substituents **I** ($R^1 = R^2 = Me$).

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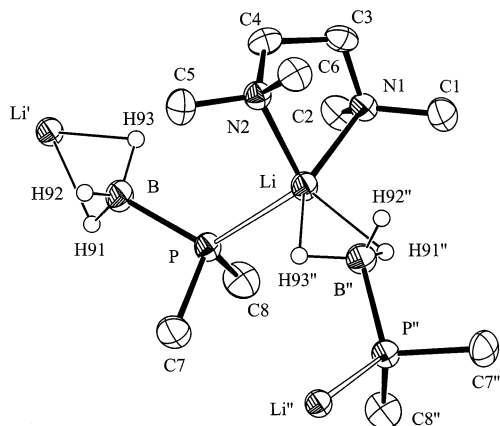


Figure 1. Structure of **1** in the crystal (displacement ellipsoids 50%; H atoms at B with arbitrary radius, all other H atoms omitted for clarity; symmetry operations: primed atoms: $x, 0.5-y, 0.5+z$, double prime: $x, 0.5-y, z-0.5$).

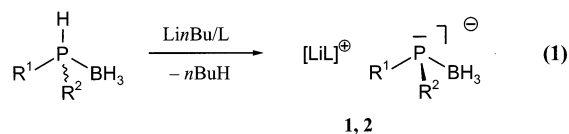
Table 1. Selected Distances (Å) and Angles (deg) for 1 with Estimated Standard Deviations in Units of the Last Significant Figure in Parentheses^a

(a) Distances			
P–B	1.945(3)	Li–N1	2.188(4)
P–C7	1.839(3)	Li–N2	2.117(4)
P–C8	1.838(3)	Li⋯B''	2.372(4)
P–Li	2.620(4)	Li–H91''	2.03(2)
B–H91	1.12(3)	Li⋯H92''	2.80(2)
B–H92	1.09(3)	Li–H93''	2.03(2)
B–H93	1.15(2)		
(b) Angles			
B–P–Li	120.2(1)	P–Li–N1	108.4(2)
B–P–C7	102.9(1)	P–Li–N2	109.5(1)
B–P–C8	103.1(1)	N1–Li–N2	85.0(1)
Li–P–C7	112.7(1)	P–Li–H91''	114.8(8)
Li–P–C8	115.9(1)	P–Li–H93''	98.1(6)
C7–P–C8	99.3(2)	P–Li⋯B''	117.4(1)

^a For symmetry operations see Figure 1.

Results and Discussion

The synthesis of ligands **I** is accomplished by deprotonation of secondary phosphine-boranes with strong bases,⁸ such as lithium organyls.⁹ As depicted in eq 1,



1: $\text{R}^1 = \text{R}^2 = \text{Me}$; L = tmeda

2: $\text{R}^1 = t\text{Bu}$; $\text{R}^2 = \text{Ph}$; L = (–)-sparteine

the lithium complex of mono(borane)dimethylphosphide (**1**) was obtained from dimethylphosphine-borane $\text{Me}_2\text{PH-BH}_3$ and crystallized by addition of tmeda. Its solid state structure (Figure 1, Table 1) shows each ligand to be coordinated by its phosphido and borane groups to two different lithium atoms, which, in addition, carry one molecule of tmeda. The Li–P bond length

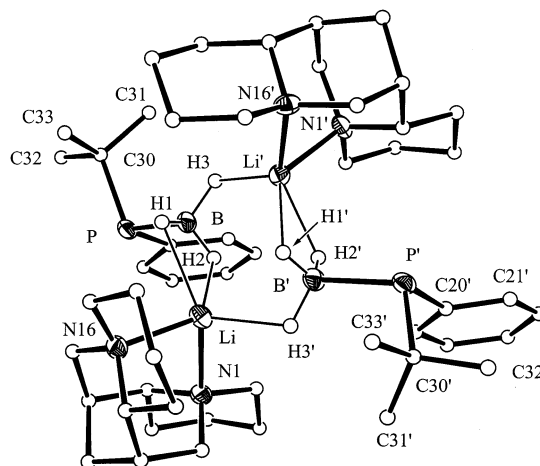


Figure 2. Molecular structure of dimers of **2** in the crystal (displacement ellipsoids 50%; C atoms and H atoms at B with arbitrary radii, all other H atoms omitted for clarity; primed atoms are related to those without a prime by a crystallographic 2-fold axis, symmetry operation: $2-x, y, 2-z$).

(2.620(4) Å) is typical for lithium coordination by anionic organophosphines^{2d} but noticeably longer than in lithium phosphides LiPR_2 .^{2c,d,10} The structural details of the Li–H–B interactions (Li–H91'' 2.03(2), Li–H93'' 2.03(2), nonbonding Li⋯B'' 2.372(4) Å) are comparable to previously described examples. The P–B bond in **1** (1.945(3) Å) is slightly lengthened upon deprotonation of $\text{Me}_2\text{PH-BH}_3$ (P–B 1.898 ± 0.010 Å; by MW spectroscopy)¹¹ and subsequent lithium coordination, which is in accord with the reduced charge separation in the anion $[\text{P}(\text{BH}_3)\text{Me}_2]^-$ as compared to neutral $\text{Me}_2\text{PH-BH}_3$.¹²

The formation of two coordinative interactions of each anion **I** in **1** results in an infinite-strand formation (Figure 1) and suggests that the phosphino coordination of **I** to lithium is comparable in strength to its borane coordination via B–H–Li bonds.

The deprotonation of racemic *tert*-butylphenylphosphine-borane with Li-*n*Bu in diethyl ether in the presence of (–)-sparteine leads to **2**, which contains the enantiomerically pure *P*-chiral anion $[\text{P}^*(\text{BH}_3)(\text{Ph})t\text{Bu}]^-$ (eq 1).^{3c} In the crystal the molecules of **2** are arranged into dimers with crystallographic 2 (C_2) symmetry (Figure 2, Table 2). Dimer formation is brought about exclusively by Li–H–B bonds; that is, the phosphino groups are not lithium-coordinated at all. As shown in Figure 2, the coordination of each BH_3 group to two lithium cations by two (2.00(9)/2.25(7) Å) and one Li–H–B interaction (2.03(6) Å), respectively, leads to a central Li–H–B–H–Li–H–B–H eight-membered ring of the dimer. The coordination sphere of lithium is completed by one molecule of (–)-sparteine. As compared to **1**, the increased steric bulk of the substituents at phosphorus and of the donor (–)-sparteine at lithium apparently renders any Li–P coordination impossible while Li–H–B interactions are still maintained in the

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(12) $\text{Me}_2\text{PH-BH}_3$ is zwitterionic (positive charge at P, negative charge at B), which leads to a large molecular dipole moment and should shorten the P–B bond due to ionic contributions. In $[\text{P}(\text{BH}_3)\text{Me}_2]^-$ there is only a negative charge at B.

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Table 2. Selected Distances (Å) and Angles (deg) for 2^a

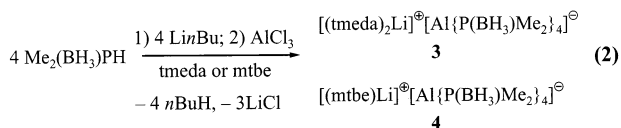
(a) Distances			
P–B	1.966(6)	Li–N1	2.08(1)
P–C20	1.840(6)	Li–N16	2.085(9)
P–C30	1.879(8)	Li···B	2.47(1)
B–H1	1.16(5)	Li···B'	2.68(1)
B–H2	1.02(8)	Li–H1	2.25(7)
B–H3	1.13(7)	Li–H2	2.00(9)
		Li–H3'	2.03(6)
(b) Angles			
B–P–C20	104.6(2)	N1–Li–N16	88.3(4)
B–P–C30	106.4(3)	H1–Li–N1	137(1)
C20–P–C30	102.1(3)	H1–Li–N16	91(1)
B–H1–Li	87(2)	H2–Li–N1	99(2)
B–H2–Li	106(2)	H2–Li–N16	130(2)
B–H3–Li'	112(2)	H3'–Li–N1	96(2)
		H3'–Li–N16	127(2)

^a For symmetry operations see Figure 2.

crystal. Although no structural data are at hand for *t*Bu(Ph)PH–BH₃, the long P–B bond in **2** (1.966(6) Å) nicely reflects the increased steric bulk at phosphorus.

As **2** crystallizes in the enantiomorphous space group *C*₂ (No. 5) and the absolute structure is given by the known configuration of (–)-sparteine, the structure determination of **2** is fully independent proof of the absolute configuration of chiral anions [P*(BH₃)(Ph)*t*Bu][–] obtained by this synthesis.^{3c} Although the structure of **2** does not allow immediate clues as to the transition state leading to the enantioselective deprotonation of *t*Bu(Ph)PH–BH₃ with Li-*n*Bu in the presence of (–)-sparteine, it nicely reflects the optimal sterical fitting of the chiral anions [P*(BH₃)(Ph)*t*Bu][–], and especially its bulky Ph and *t*Bu substituents, with the peripheral six-membered rings of (–)-sparteine (Figure 2). It should also be noted that no enantioselectivity is observed when Me(Ph)PH–BH₃ is deprotonated with Li-*n*Bu/(–)-sparteine.^{3a}

Reaction of AlCl₃ with 4 equiv of Li[P(BH₃)Me₂][–] yields a lithium aluminate which could be crystallized depending upon the donor present as **3** or **4** containing the counterions [(tmeda)₂Li]⁺ and [(mtbe)Li]⁺, respectively (eq 2).



Both compounds contain the aluminate anion [Al{P(BH₃)Me₂}₄][–], which exhibits a characteristic quintet in its ²⁷Al NMR spectrum in solution (δ(²⁷Al) = 142.2 ppm; ¹J_{AlP} = 130.9 Hz). To our knowledge, the anion [Al{P(BH₃)Me₂}₄][–] is the first homoleptic tetraphosphorus aluminate to be structurally characterized.^{13,14} In the solid state it is almost perfectly tetrahedral. In **3**, which contains discrete anions and [(tmeda)₂Li]⁺ cations, the ions have crystallographic $\bar{4}$ (*S*₄) symmetry,

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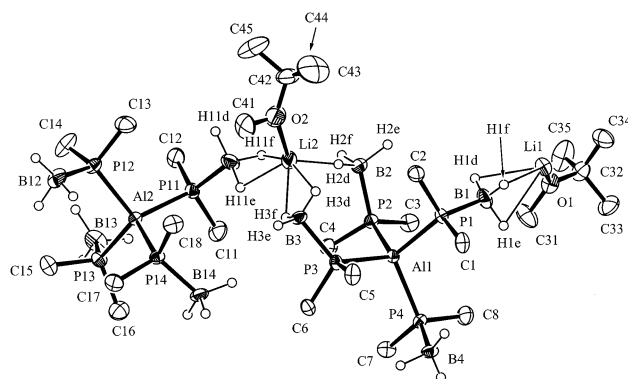


Figure 3. Crystallographically independent part of the crystal structure of **4** (displacement ellipsoids 50%; H atoms at B with arbitrary radius, all others omitted for clarity).

Table 3. Selected Distances (Å) and Angles (deg) for 4^a

(a) Distances			
Al1–P1	2.375(2)	Al2–P11	2.382(2)
Al1–P2	2.367(2)	Al2–P12	2.374(2)
Al1–P3	2.371(2)	Al2–P13	2.378(2)
Al1–P4	2.375(2)	Al2–P14	2.372(2)
P1–B1	1.918(7)	P11–B11	1.942(7)
P2–B2	1.945(6)	P12–B12	1.924(8)
P3–B3	1.942(6)	P13–B13	1.925(6)
P4–B4	1.927(6)	P14–B14	1.927(6)
Li1–O1	2.04(1)	Li2–O2	1.93(1)
Li1···B1	2.46(1)	Li2···B2	2.65(1)
Li1···B4''	2.61(1)	Li2···B3	2.62(1)
Li1···B14'	2.62(1)	Li2···B11	2.54(1)
Li1–H1d	2.33 ^b	Li2–H2d	1.70 ^b
Li1–H1e	2.48 ^b	Li2–H3d	1.32 ^b
Li1–H1f	2.25 ^b	Li2–H3f	1.99 ^b
Li1–H4d''	2.22 ^b	Li2–H11e	2.09 ^b
Li1–H4f''	2.43 ^b	Li2–H11f	2.35 ^b
Li1–H14d'	2.34 ^b		
Li1–H14e'	2.24 ^b		
(b) Angles			
P1–Al1–P2	107.10(8)	P11–Al2–P12	108.97(8)
P1–Al1–P3	109.25(8)	P11–Al2–P13	110.45(8)
P1–Al1–P4	110.09(8)	P11–Al2–P14	108.34(8)
P2–Al1–P3	106.18(8)	P12–Al2–P13	109.23(8)
P2–Al1–P4	114.23(8)	P12–Al2–P14	109.97(8)
P3–Al1–P4	109.82(8)	P13–Al2–P14	109.85(8)
Al1–P1–B1	115.1(2)	Al2–P11–B11	117.2(2)
Al1–P2–B2	112.4(2)	Al2–P12–B12	116.8(3)
Al1–P3–B3	116.7(2)	Al2–P13–B13	116.6(2)
Al1–P4–B4	112.4(2)	Al2–P14–B14	115.0(2)

^a Symmetry operations: primed atoms: *x*, *y*–1, *z*, double prime: 1–*x*, –*y*, 2–*z*. ^b H atoms at B found but not refined.

but extensive disorder of the P-methyl and BH₃ groups does not allow the extraction of accurate structural data with the exception of the Al–P bond length (2.377(1) Å). In **4** the cation [(mtbe)Li]⁺ is tightly associated with BH₃ groups by an extensive set of Li–H–B bonds (Table 3). Thereby the individual anions are linked to an infinite three-dimensional polymer (Figure 3). More specifically, in addition to the coordinated ether oxygen atom one of the two crystallographically independent lithium atoms (Li1) makes contacts to seven B–H hydrogen atoms shorter than 2.5 Å, while the second one (Li2) has only five such contacts (Table 3). This association between anions and cations leads to less symmetrical aluminate anions, as manifested especially in the conformation of the P(BH₃)Me₂ groups (Figure 4). The structure of **4** yields precise bond distances and angles, however, as there is no appreciable disorder

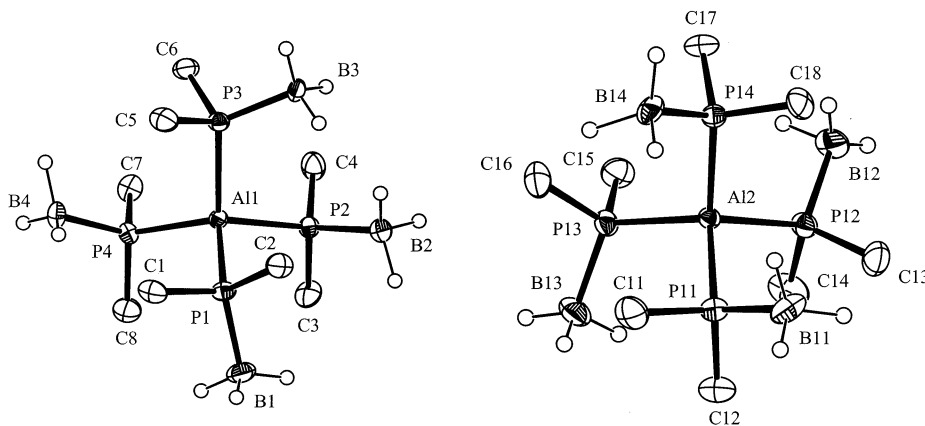


Figure 4. Molecular structure of the two crystallographically independent anions in **4** (displacement ellipsoids 50%; H atoms at B with arbitrary radius, all others omitted for clarity).

(Table 3). The Al–P distances in the two crystallographically independent anions of **4** range between 2.367(2) and 2.382(2) Å and are virtually identical to those in **3**. They are at the lower limit of previously determined Al–P bonds, although strictly comparable compounds and bonding situations are not available.

In summary, our results show already clearly that diorganophosphide-monoboranes **I** are similar as ligands to other anionic phosphines and may be used to prepare stable main group element complexes. The coordinative P–M bonds formed to lithium, and probably also to other electronically highly unsaturated, hard metal centers, are directly comparable to those formed by other anionic phosphines but longer (and presumably weaker) than metal phosphide bonds. At least in their lithium compounds the P–M bonds of ligands **I** effectively have to compete with metal borane interactions.

Experimental Section

All experiments were carried out with rigorous exclusion of air and moisture under purified dry argon in standard Schlenk tube glassware. Solvents were dried under argon over sodium or sodium–potassium alloy and were freshly distilled prior to use. Reagents: Li-*n*Bu (Aldrich), AlCl₃ (99.99%, Aldrich), (–)-sparteine (Aldrich, distilled from CaH₂), tmeda (Aldrich, distilled from CaH₂), Me₂PH–BH₃: from 109 mmol HPM₂¹⁵ and 109 mL of a 1 M solution of BH₃·THF/THF in 50 mL of THF at –78 °C, *rac*-*t*Bu(Ph)PH–BH₃:^{3a,h} from 625.8 mmol of *rac*-*t*Bu(Ph)PH and 313 mL of a 2 M solution of BH₃·SMe₂/THF in 250 mL of THF at –78 °C. Instruments: NMR spectra: JEOL JMN-GX-400, Bruker AMX-600. Standards: ¹H/¹³C NMR: internal THF-*d*₈ or external tetramethylsilane, TMS; ³¹P NMR: external 85% H₃PO₄/H₂O; ²⁷Al NMR: external 1 M Al³⁺/D₂O; ¹¹B NMR: external BF₃·Et₂O; ⁷Li NMR: external 1 M LiCl/D₂O. Chemical shifts are in ppm with negative signs referring to high field. ¹H and ¹³C chemical shifts are reported relative to TMS, while those of ³¹P, ²⁷Al, ¹¹B, and ⁷Li are reported relative to the standards mentioned above. IR spectra: Perkin-Elmer 1760 X FT-IR. The elemental analyses were performed by the microanalytical laboratory of the University of Konstanz on a Heraeus CHN-O-Rapid instrument. Melting points were determined in sealed capillaries in a Büchi 530 apparatus and are uncorrected.

[[tmeda]Li]{P(BH₃)Me₂} (1). A 2.5 M solution of Li-*n*Bu in hexane (11.9 mL, 29.8 mmol) was added to a solution of

2.26 g (29.8 mmol) of Me₂PH–BH₃ in 40 mL of Et₂O at room temperature under stirring, resulting in a clear solution. After addition of 4.5 mL (3.5 g, 29.8 mmol) of tmeda a vigorous reaction set in. After reducing the solvent in vacuo to 20 mL, colorless crystals formed, which proved suitable for X-ray structure determination. Yield: 4.3 g (21.6 mmol, 73%); mp 122.5 °C. Anal. Calcd for C₈H₂₅BLiN₂P (%): C, 48.52; H, 12.73; N, 14.15. Found: C, 47.41; H, 12.45; N, 16.44, indicating slight excess of tmeda. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ 2.30 (s, 4 H, CH₂), 2.15 (s, 12 H, NCH₃), 0.77 (d, ²J_{HP} = 3.5 Hz, 6 H, PCH₃), 0.26 (br q, ¹J_{HB} = 85.5 Hz, 3 H, BH₃). ¹³C{¹H} NMR (101 MHz, THF-*d*₈, 25 °C): δ 58.75 (s, CH₂), 46.27 (s, NCH₃), 16.78 (d, ¹J_{CP} = 12.9 Hz, PCH₃). ³¹P{¹H} NMR (162 MHz, THF-*d*₈, 25 °C): δ –96.12 (q, ¹J_{PB} = 41.5 Hz). ¹¹B{¹H} (128 MHz, THF-*d*₈, 25 °C): δ –24.22 (d, ¹J_{BP} = 41.5 Hz). ⁷Li{¹H} NMR (155.5 MHz, THF-*d*₈, 25 °C): δ 5.16 (s). IR (Nujol, cm^{–1}): ν(BH) 2322 (s), 2230 (s), 2158 (s).

[[(-)-Sparteine]Li]{P*(BH₃)(Ph)*t*Bu} (2).^{3c} A 2.5 M solution of Li-*n*Bu in hexane (4.0 mL, 10.1 mmol) was added to a solution of 2 mL (1.8 g, 10.1 mmol) of *rac*-*t*Bu(Ph)PH–BH₃ and 2.3 mL (2.4 g, 10.1 mmol) of (–)-sparteine in 50 mL of Et₂O at –90 °C. A white precipitate formed immediately. The suspension was warmed to 30 °C, and stirring was continued for 1 h. The precipitate was separated by centrifugation and washed twice with 10 mL portions of Et₂O. Single crystals suitable for X-ray diffraction were grown from the supernatant clear solution, which was cooled slowly to –80 °C. The enantiomeric homogeneity of **2** was checked by alkylation with 2-MeOC₆H₄CH₂Cl^{3c} and subsequent chiral HPLC using a CHIRALPAK AD (250 × 4.6 mm) column which indicated ee's higher than 98%. Yield: 3.4 g (9.4 mmol, 94%); mp 187–192 °C (dec). Anal. Calcd for C₂₅H₄₃BLiN₂P (%): C, 71.43; H, 10.31; N, 6.66. Found: C, 70.93; H, 9.46; N, 6.70. ¹H NMR (600 MHz, THF-*d*₈, 25 °C, TMS): sparteine signals: δ 2.68 (d), 2.63 (d), 2.59 (t), 2.49 (d), 2.33 (d), 2.10 (d), 1.97 (d), 1.91 (d), 1.90 (t), 1.89 (t), 1.76 (d), 1.70 (d), 1.67 (t), 1.65 (d), 1.45 (d), 1.40 (q), 1.38 (br s), 1.25 (m), 1.23 (d), 1.21 (d), 1.20 (t), 0.98 (d); anion signals: δ 7.66–7.64 (dd, ³J_{HH} ≈ ³J_{PH} ≈ 5–7 Hz, 2 H, *o*-H), 7.05–7.03 (t, ³J_{HH} ≈ 7 Hz, 2 H, *m*-H), 7.00–6.98 (t, ³J_{HH} = 7.3 Hz, 1 H, *p*-H), 0.94 (d, ³J_{HP} = 10.1 Hz, 9 H, CH₃), 0.36 (br. q, ¹J_{HB} = 85.8 Hz, 3 H, BH₃). ¹³C{¹H} NMR (151 MHz, THF-*d*₈, 25 °C, TMS): sparteine signals: δ 67.40, 64.98, 62.81, 57.03, 56.24, 54.51, 37.65, 35.69, 34.43, 30.13, 28.37, 27.12, 26.76, 25.98, 25.63; anion signals: δ 146.39 (d, ¹J_{CP} = 25.4 Hz, *ipso*-C), 137.57 (d, ²J_{CP} = 12.7 Hz, *o*-C), 126.5 (d, ³J_{CP} = 4 Hz, *m*-C), 125.9 (br. s, *p*-C), 30.35 (d, ²J_{CP} = 12.1 Hz, CH₃), 27.69 (d, ¹J_{CP} = 13.3 Hz, CCH₃). ³¹P{¹H} NMR (162 MHz, THF-*d*₈, 25 °C): δ –7.29 (q, ¹J_{PB} = 38.5 Hz). ¹¹B{¹H} (152.5 MHz, THF-*d*₈, 25 °C): δ –31.36 (d, ¹J_{BP} = 39.1 Hz). ⁷Li{¹H} NMR (233 MHz, THF-*d*₈, 25 °C): δ 5.04 (br s). IR (Nujol, cm^{–1}): ν(BH) 2389 (vs), 2272 (vs).

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Table 4. Crystal Structure Data for 1–4

	1	2	3	4
formula	C ₈ H ₂₅ BLiN ₂ P	C ₅₀ H ₈₆ B ₂ Li ₂ N ₄ P ₂ (dimer)	C ₃₀ H ₆₈ AlB ₄ LiN ₄ P ₄	C ₁₃ H ₄₈ AlB ₄ LiOP ₄
<i>M_r</i>	198.02	840.76	565.82	421.55
cryst size, mm ³	0.1 × 0.15 × 0.2	0.2 × 0.3 × 0.4	0.5 × 0.5 × 0.5	0.2 × 0.2 × 0.2
cryst syst	monoclinic	monoclinic	tetragonal	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (No. 14)	<i>C</i> 2 (No. 5)	<i>P</i> 4 <i>b</i> 2 (No. 117)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> , Å	9.458(3)	20.337(7)	12.622(1)	14.958(2)
<i>b</i> , Å	14.815(3)	10.688(2)	12.622(1)	13.150(1)
<i>c</i> , Å	10.724(3)	14.484(5)	12.179(2)	30.129(3)
β, deg	113.68(3)	126.67(2)	90	108.12(1)
<i>V</i> , Å ³	1376.1(7)	2525(1)	1940.3(4)	5633(1)
<i>Z</i>	4	2	2	8
<i>D</i> _{calcd} , g cm ⁻³	0.956	1.106	0.969	0.994
μ(Mo Kα), cm ⁻¹	1.64	1.22	2.32	3.00
<i>F</i> (000), e	440	920	624	1840
<i>hkl</i> range	±11, +18, +13	±24, +13, +17 plus Friedel opp.	+16, +16, +15 plus Friedel opp.	+17, -15, ±35
(<i>sin</i> θ)/λ _{max} , Å ⁻¹	0.617	0.617	0.650	0.595
no. of reflns measd	2862	5180	5588	10 286
no. of unique reflns	2713	4716	2242	9879
<i>R</i> _{int}	0.034	0.072	0.073	0.069
no. of params refined	218	284	75	433
<i>R</i> (<i>F</i>)/ <i>wR</i> (<i>F</i> ²) ^a	0.043/0.098	0.065/0.185	0.062/0.147	0.066/0.157
<i>x</i> (Flack)		0.2(2)	0.6(3)	
GoF (<i>F</i> ²)	1.00	1.02	1.25	1.01
Δρ _{fin} (max./min.), e Å ⁻³	0.26/−0.21	0.27/−0.35	0.47/−0.33	1.34/−0.61

^a Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (XP)^2 + YP]$, $P = [\max(F_o^2, 0) + 2F_c^2]/3$. **1**: $X = 0.0392$, $Y = 0.1756$; **2**: $X = 0.0948$, $Y = 0.8829$; **3**: $X = 0.0$, $Y = 3.1245$; **4**: $X = 0.0525$, $Y = 2.43$.

[(**tmeda**)₂Li]⁺[Al{P(BH₃)Me₂}₄][−] (**3**). A 2.5 M solution of Li-*n*Bu in hexane (4.0 mL, 10.1 mmol) was added to a solution of 0.76 g (10.1 mmol) of Me₂PH–BH₃ in 10 mL of Et₂O at −80 °C. Warming to room temperature under stirring resulted in a clear yellowish solution. After addition of 0.33 g (2.5 mmol) of AlCl₃ in 5 mL of Et₂O the solution warmed slightly and LiCl started to precipitate. Stirring was continued for 1 h, and LiCl was separated by centrifugation. A 0.38 mL (2.5 mmol) portion of **tmeda** was added to the two-phase liquid, whereupon colorless crystals of **3** formed. Recrystallization in 10 mL of hot toluene gave crystals suitable for X-ray crystallography. Yield: 1.33 g (2.35 mmol, 94%); mp 131.5–133.5 °C. Anal. Calcd for C₂₀H₆₈AlB₄LiN₄ (%) : C, 42.45; H, 12.11; N, 9.90. Found: C, 42.30; H, 11.43; N, 9.80. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ 2.30 (s, 8 H, CH₂), 2.15 (s, 24 H, NCH₃), 1.26 (br s, 24 H, PCH₃), 1.0–0.31 (br q, ¹J_{HB} ≈ 94 Hz, 12 H, BH₃). ¹³C{¹H} NMR (101 MHz, THF-*d*₈, 25 °C): δ 58.8 (s, CH₂), 46.25 (s, CH₃), 12.06 (br. m). ³¹P{¹H} NMR (162 MHz, THF-*d*₈, 25 °C): δ −72.9 to −68.7 (br m). ²⁷Al{¹H} NMR (104 MHz, THF-*d*₈, 25 °C): δ 142.24 (q, ¹J_{AlP} = 130.9 Hz). ¹¹B{¹H} (128 MHz, THF-*d*₈, 25 °C): δ −28.02 (br d, ¹J_{BP} = 26.9 Hz). ⁷Li{¹H} NMR (155.5 MHz, THF-*d*₈, 25 °C): δ 4.96/4.90 (s), the appearance of two signals is attributed to **tmeda**- and THF-coordinated lithium. IR (Nujol, cm^{−1}): ν(BH) 2362 (m), 2345 (m), 2303 (m), 2236 (s).

Crystalline [(**mtbe**)Li]⁺[Al{P(BH₃)Me₂}₄][−] (**4**) was obtained by removing the solvents in the above synthesis in vacuo before the addition of **tmeda**. After dissolving the residue in hot **mtbe** and cooling to room temperature single crystals formed, which proved suitable for X-ray diffraction. Mp: 186.5–188.0 °C (dec). Anal. Calcd for C₁₃H₄₈AlB₄LiOP₄ (%) : C, 37.04; H, 11.48. Found: C, 33.05; H, 10.55. ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ 3.09 (s, 3 H, OCH₃), 1.26 (br s, 24 H, PCH₃), 1.1–0.2 (br q, ¹J_{HB} ≈ 94 Hz, 12 H, BH₃), 1.09 (s, 9 H, CCH₃). ¹³C{¹H} NMR (101 MHz, THF-*d*₈, 25 °C): δ 72.62 (s, CCH₃), 49.32 (s, OCH₃), 27.24 (s, CCH₃), 12.00 (br m). ³¹P{¹H} NMR (162 MHz, THF-*d*₈, 25 °C): δ −69.9 to −65.5 (br m). ²⁷Al{¹H} NMR (104 MHz, THF-*d*₈, 25 °C): δ 142.33 (q, ¹J_{AlP} = 130.3 Hz). ¹¹B{¹H} (128 MHz, THF-*d*₈, 25 °C): δ −27.95 (br d, ¹J_{BP} = 29.3 Hz).

⁷Li{¹H} NMR (155.5 MHz, THF-*d*₈, 25 °C): δ 4.89 (br s). IR (Nujol, cm^{−1}): ν(BH) 2364 (vb).

Structure Determinations. Enraf-Nonius CAD4, *T* = 153–(2) K. Graphite-monochromatized Mo Kα radiation, λ = 0.71069 Å, θ/2θ scans, *Lp* but no absorption corrections; decay corrected for linearly (**1**: −7.7%, **2**: −27%, **4**: −7.6%). Full-matrix least-squares refinement on all unique *F*². Non-hydrogen atoms refined with anisotropic displacement parameters. Further crystal structure data are summarized in Table 4. Programs used included SHELXS-97,¹⁶ SHELXL-97,¹⁶ PLATON,¹⁷ and ORTEP-III.¹⁸

Considerations for **1**: All H atoms found and refined freely with isotropic displacement parameters. **2**: H atoms at boron found and refined freely with isotropic displacement parameters. Absolute structure given by configuration of (−)-sparteine. **3**: The disorder of the BH₃, PCH₃, and CH₂ groups (of one of the **tmeda** molecules) was treated with a split atom model (50/50) and isotropic refinement of the split atom positions. The respective H atoms were calculated also in split positions and included as riding model. **4**: H atoms at boron found and included as fixed-atom contributions into structure factor calculation (*U*_{iso} = 0.05 Å²).

Supporting Information Available: Tables of crystal data, atomic coordinates, anisotropic displacement parameters, hydrogen atom coordinates, and bond lengths and angles for **1–4**. NMR spectra for **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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