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FULL PAPER

# Easy Access to Phosphine-Borane Building Blocks

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**Abstract:** In this paper, we highlight the synthesis of a variety of primary phosphine–boranes ($RPH_2{\cdot}BH_3$) from the corresponding dichlorophosphines, simply by using $Li[BH_4]$ as reductant and provider of the $BH_3$ protecting group. The method offers facile access not only to alkyl- and arylphosphine–boranes, but also to aminophosphine–boranes ($R_2NPH_2{\cdot}BH_3$) that are convenient building blocks but without the protecting $BH_3$ moiety thermally labile and notoriously difficult to handle. The borane-protected primary phosphines can be doubly deprotonated using *n*-butyllithium to provide soluble phosphanediides $Li_2[RP{\cdot}BH_3]$ of which the phenyl-derivative $Li_2[PhP{\cdot}BH_3]$ was structurally characterized in the solid state.

## Introduction

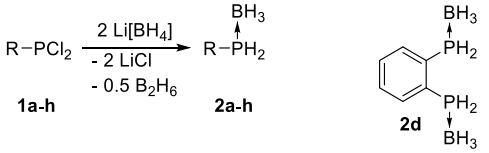
Primary phosphines ($RPH_2$)[1] are the archetypical building blocks that are used for the creation of a plethora of functionalized phosphorus compounds via addition (hydrophosphination)[2] or substitution reactions. The latter proceeds typically by *in situ* mono or double deprotonation affording the reactive phosphanide M[RPH][3] and phosphanediide $M_2[RP]$ intermediates.[4] Notable examples include the pyrophoric phenylphosphine ($PhPH_2$) that provides the useful, but poorly characterized, phenylphosphanediide $M_2[PhP]$,[5] and the pyrophoric and hazardous 1,2-bis-phosphinobenzene 1,2-$(PH_2)_2C_6H_4$[6] that is required to produce the privileged DuPhos ligand class.[7] An obvious drawback of these primary phosphines is their pyrophoric nature, high sensitivity to oxidation and noxious character,[1c] which requires experienced chemists with dedicated lab facilities to handle these compounds safely.[8] Furthermore, the appealing primary (dialkylamino)phosphines ($R_2NPH_2$) that are suitable for further functionalisation (treatment with HCl provides the corresponding chlorophosphines)[9] are, in addition, thermally labile. For example, $iPr_2NPH_2$ decomposes upon attempted isolation.[10]

Protecting the phosphorus lone pair with a borane ($BH_3$) moiety offers advantages,[11] as the corresponding primary phosphine–boranes ($RPH_2{\cdot}BH_3$) are easier to handle,[12] but also provide access to interesting polyphosphinoborane material $[RPH–BH_2]_n$ by catalytic dehydrogenation/dehydrocoupling.[13] Typically, primary phosphine–boranes are prepared in a two-step procedure by $Li[AlH_4]$ reduction of the corresponding dichlorophosphines and subsequent treatment of the resulting primary phosphine with $BH_3{\cdot}THF$ or $BH_3{\cdot}SMe_2$.[12,14] Yet, Nöth and later Manners *et al.* described that the direct synthesis of some selected primary phosphine–boranes is also feasible by using $Li[BH_4]$,[15] which does not require the handling of primary phosphine intermediates.

To further advance this field, we were keen on developing a general protocol for the synthesis of primary alkyl- and arylphosphine–boranes that are also applicable for primary aminophosphine–boranes ($R_2NPH_2{\cdot}BH_3$). We were further curious if the stabilizing $BH_3$ moiety would also offer the possibility for characterizing phosphanediides $M_2[RP]$ in the solid state. Herein, we report on a robust protocol for the synthesis of a range of substituted phosphine–borane building blocks ($RPH_2{\cdot}BH_3$), including the bis-borane protected 1,2-bis-phosphinobenzene 1,2-$(PH_2{\cdot}BH_3)_2C_6H_4$, and present the first single-crystal structure of the phenylphosphanediide $Li_2[PhP{\cdot}BH_3]$.

## Results and Discussion

Treatment of dichlorophosphines **1a**–**c** (R = Ph (**a**), Mes (**b**), *t*Bu (**c**)) with 2 equiv. of $Li[BH_4]$ in diethyl ether afforded after work-up easy access to the colorless primary phosphine–boranes **2a**–**c**[14a-c,15e] on a multigram scale (85–98%; Scheme 1, Table 1). This procedure is not only convenient (max. 60 minutes reaction time), it is also higher yielding than the two-step procedure that requires an excess of $Li[AlH_4]$ (*cf*. $PhPCl_2$ reduction to $PhPH_2$, max. 55% yield (lit. value)[16]).




R = Ph (**a**), Mes (**b**), *t*Bu (**c**), $iPr_2N$ (**e**), $Cy_2N$ (**f**), TMP (**g**), $(Me_3Si)_2N$ (**h**)

**Scheme 1.** Synthesis of primary phosphine-boranes $RPH_2{\cdot}BH_3$ **2**. TMP = 2,2,6,6-tetramethylpiperidyl.

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**Table 1.** $^{31}P\{^{1}H\}$ and $^{11}B$ NMR chemical shifts including $^{1}J(P,B)$ and $^{1}J(B,H)$ coupling constants of compounds **2a-h**, **3a**, and **4a**,**e**.

| | $\delta^{31}P\{^{1}H\}$ (ppm) | $^{1}J(P,B)$ (Hz) | $\delta^{11}B$ NMR (ppm) | $^{1}J(B,H)$ (Hz) |
|---|---|---|---|---|
| **2a** | –47.4 | 34.8 | –42.2 | 101.2 |
| **2b** | –68.3 | 40.5 | –40.7 | 101.3 |
| **2c** | –10.7 | 37.0 | –43.1 | 100.4 |
| **2d** | –52.4 | 34.4 | –41.5 | 103.3 |
| **2e** | –18.6 | 50.8 | –41.4 | 99.9 |
| **2f** | –13.2 | 45.9 | –41.0 | 96.8 |
| **2g** | –15.9 | 48.9 | –34.5 | 99.2 |
| **2h** | 2.1 | 51.6 | –36.7 | 98.2 |
| **3a** | –166.4 | - | –34.5 | 84.5 |
| **4a** | –95.6 | 32.4 | –40.1 | 98.3 |
| **4e** | 1.1 | 26.6 | –35.4 | 98.8 |

Interestingly, treatment of 1,2-bis(dichlorophosphino)benzene (**1d**; 1,2-$(PCl_2)_2C_6H_4$) with $Li[BH_4]$ in diethyl ether afforded the novel bis-phosphine–borane 1,2-$(PH_2{\cdot}BH_3)_2C_6H_4$ (**2d**, $\delta^{31}P\{^{1}H\}$ = –52.4 ($^{1}J(P,B)$ = 34.4 Hz), $\delta^{11}B$ NMR = –41.5 ($^{1}J(B,H)$ = 103.29 Hz, $^{1}J(B,P)$ = 25.0 Hz); Scheme 1) as a colorless crystalline solid in 65% isolated yield. Recrystallization from a mixture of DCM and pentane at –78 °C afforded colorless crystals suitable for an X-ray crystal structure determination. The molecular structure of **2d** (Figure 1) displays typical P–B (P1–B1 1.9182(17), P2–B2 1.9193(18) Å) and P–C (P1–C1 1.8080(14), P2–C2 1.8050(14) Å) bond lengths for an arylphosphine–borane. The molecular structure of **2d** also shows intermolecular $P–H^{\delta+}\cdots^{\delta-}H–B$ and $C–H^{\delta+}\cdots^{\delta-}H–B$ interactions in the solid state as a result of the oppositely charged hydrogen atoms (Table 2),[13b] where the $BH_3$ moiety functions as the acceptor.

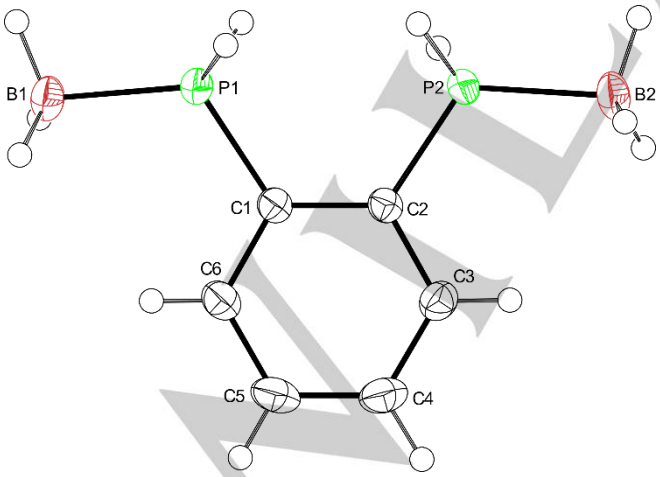



**Figure 1.** Molecular structure of 1,2-$(PH_2{\cdot}BH_3)_2C_6H_4$ (**2d**) in the crystal (displacement ellipsoids are set at 50% probability). Selected bond lengths [Å], angles and torsion angles [°]: P1–B1 1.9182(17), P2–B2 1.9193(18), P1–C1 1.8080(14), P2–C2 1.8050(14), B1–H1B 1.108(19), B1–H2B 1.071(19), B1–H3B 1.062(19), B2–H4B 1.096(19), B2–H5B 1.07(2), B2–H6B 1.05(2), C1–P1–B1 117.53(7), C2–P2–B2 119.03(8), C2–C1–P1 123.44(10), C1–C2–P2 123.51(10), B1–P1–C1–C2 165.66(12), B2–P2–C2–C1 166.77(12).

**Table 2.** Potential intermolecular dihydrogen bonds with $BH_3$ as acceptor in the crystal structure of **2d**.

| | D–H [Å] | H···A [Å] | D···A [Å] | D–H···A [°] |
|---|---|---|---|---|
| P1–H1P···H1B$^{i}$ | 1.292(18) | 2.33(2) | 3.491(18) | 148.1(13) |
| C4–H4···H4B$^{ii}$ | 0.94(2) | 2.38(3) | 3.308(19) | 168.3(17) |

Symmetry codes *i*: x-½, y, ½-z; *ii*: x+½, ½-y, -z. D = donor, A = acceptor $BH_3$

Next, we turned our attention to the primary aminophosphines in the hope that the accessibility of these building blocks can also be improved by the direct reduction of dichloroaminophosphines with $Li[BH_4]$. Indeed, treatment of **1e**–**h** (R = $iPr_2N$ (**e**), $Cy_2N$ (**f**), TMP (**g**), $(Me_3Si)_2N$ (**h**)) with 2 equiv. of $Li[BH_4]$ in diethyl ether at 0 °C afforded after work-up the colorless primary aminophosphine–boranes **2e**–**h** (81–98%; $\delta^{31}P\{^{1}H\}$ = –18.6 (**2e**), –13.2 (**2f**), –15.9 (**2g**), 2.1 (**2h**); Scheme 1). We obtained suitable crystals for $iPr_2NPH_2{\cdot}BH_3$ (**2e**) from diethyl ether at –70 °C of which the molecular structure could be determined by X-ray crystal structure analysis (Figure 2). In the solid state, the molecules **2e** sit on a crystallographic mirror plane with a planar nitrogen N1; the angle sum is 360.0(2)°. Interestingly, in this case there are no intermolecular distances that are shorter than the sum of van-der-Waals radii. This crystal structure therefore belongs to the rare collection of "loosely packed" crystals.[17] The loose packing can also be seen in the low crystal density of only 0.970 g/cm$^3$, which also explains the low melting point of 1.0–2.0 °C.

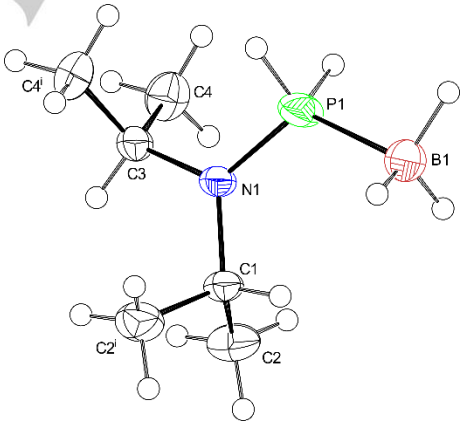


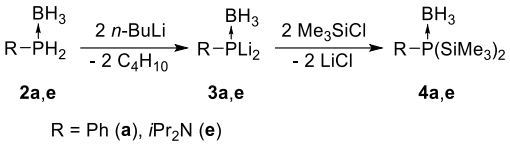

**Figure 2.** Molecular structure of $iPr_2NPH_2{\cdot}BH_3$ in the crystal (**2e**; symmetry code *i*: x, 1-y, z. Displacement ellipsoids are set at 50% probability). Selected bond lengths [Å] and angles [°]: P1–B1 1.898(2), P1–N1 1.6297(15), N1–C1 1.482(2), N1–C3 1.489(2), B1–H1A 1.15(3), B1–H1B 1.055(19); N1–P1–B1 120.03(9), C1–N1–C3 118.49(14), C1–N1–P1 120.34(12), C3–N1–P1 121.17(11).

We then selected *P*-phenyl and *P*-(diisopropyl)amino substituted **2a**,**e** to investigate their applicability as synthons in organophosphorus chemistry, in particular by studying the double deprotonation and subsequent quenching of the intermediate phosphanediide **3a**,**e** with trimethylsilylchloride to afford the bis(trimethylsilyl)phosphine-boranes **4** (Scheme 2). In both cases, phosphine–borane **2** could be readily deprotonated with 2 equiv. of *n*-butyllithium in THF at –78 °C (**3a**: $\delta^{31}P\{^{1}H\}$ = –166.4, $\delta^{7}Li$ = 0.6). Subsequent treatment with $Me_3SiCl$ and work-up afforded $PhP(SiMe_3)_2{\cdot}BH_3$ (**4a**; 98%; $\delta^{31}P\{^{1}H\}$ = –95.6 ($^{1}J(P,B)$ = 32.4 Hz), $\delta^{29}Si$ = 6.0 ($^{1}J(Si,P)$ = 48.5 Hz), $\delta^{11}B$ = –40.1 ($^{1}J(B,H)$ = 98.3 Hz,

10.1002/chem.202002367




$^1J$(B,P) = 24.7 Hz)) and *i*Pr$_2$NP(SiMe$_3$)$_2$·BH$_3$ (**4e**; 89%; $\delta^{31}$P{$^1$H} = 1.1 ($^1J$(P,B) = 26.6 Hz), $\delta^{29}$Si = 2.2 ($^1J$(Si,P) = 72.2 Hz); $\delta^{11}$B = –35.4 ($^1J$(B,H) = 98.8 Hz, $^1J$(B,P) = 34.7 Hz) as colorless solids. Single crystals of **4e** were obtained from a mixture of diethyl ether and pentane at –30 °C. The crystal structure of **4e** (Figure 3) contains two independent molecules in the asymmetric unit of which one was well ordered, while the other was refined with a disorder model. The structure of **4e** contains intramolecular C–H···H dihydrogen bonds where the BH$_3$ groups function as acceptors (Table 3). The packing of the molecules, however, does not contain intermolecular distances that are shorter than the sum of van-der-Waals radii, as is the case for **2e**. In addition, a PLATON calculation[18] detects the presence of four small, symmetry related voids in the unit cell with a volume of 21 Å$^3$ each (minor disorder component ignored). This loose packing results in a low crystal density of only 0.976 g/cm$^3$, and a low melting point (28.7–29.4 °C).




**Scheme 2.** Synthesis of phosphanediides **3** and bis(trimethylsilyl)phosphine-boranes **4**.

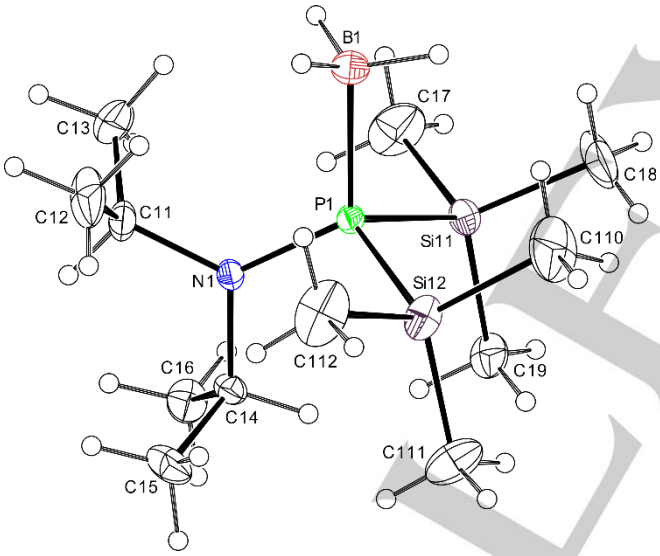



**Figure 3.** Molecular structure of *i*Pr$_2$NP(SiMe$_3$)$_2$·BH$_3$ in the crystal (**4e**; displacement ellipsoids were drawn at the 30% probability level, only one of two independent molecules is shown). Selected bond lengths [Å] and angles [°] (the values of only one of two independent molecules are given): P1–B1 1.9685(16), P1–N1 1.6987(10), P1–Si11 2.2853(4), P1–Si12 2.2905(5), N1–C11 1.4797(15), N1–C14 1.4763(14), B1–H1A 1.113(19), B1–H1B 1.07(2), B1–H1C 1.07(2); N1–P1–B1 118.52(6), N1–P1–Si11 107.29(4), N1–P1–Si12 110.41(4), Si11–P1–Si12 111.523(18), B1–P1–Si11 104.89(6), B1–P1–Si12 104.12(7), P1–N1–C11 125.17(8), P1–N1–C14 118.24(8), C11–N1–C14 116.37(9).

**Table 3.** Potential intramolecular dihydrogen bonds with BH$_3$ as acceptor in crystal structure of **4e**. The asymmetric unit contains two independent molecules. The minor disorder component is ignored.

| | D–H [Å] | H···A [Å] | D···A [Å] | D–H···A [°] |
|---|---|---|---|---|
| C12–H12C···H1C[*] | 0.98 | 2.23 | 3.131(19) | 152 |
| C13–H13A···H1B[*] | 0.98 | 2.17 | 3.065(19) | 151 |
| C22–H22C···H2A[**] | 0.98 | 2.22 | 3.098(16) | 148 |
| C23–H23A···H2C[**] | 0.98 | 2.20 | 3.090(18) | 151 |

[*] Molecule 1; [**] Molecule 2. D = donor, A = acceptor BH$_3$

During our investigations,[19] Oulyadi, Gaumont, Harrison-Marchanda *et al*. reported on the characterization of the gem-dilithium phosphido-borane Li$_2$[PhP·BH$_3$] intermediate **3a** in THF solution, which matches with our findings, but they did not provide structural characterization in the solid state.[20] We anticipated that the BH$_3$ moiety might assist the crystallization of this unique dianion and indeed found it to be possible to obtain the highly reactive phosphanediide **3a** as a colorless solid (91%), which can be recrystallized from a mixture of THF, DME and hexanes at –78 °C to provide colorless crystals suitable for X-ray analysis. The molecular structure of **3a** features the dianionic [PhP·BH$_3$] fragment, of which the phosphorus atom connects to four lithium ions in the polymeric chain in the direction of the crystallographic *b*-axis (P1–Li1 2.550(3), P1–Li2 2.524(4), P1–Li1$^{ii}$ 2.540(4), P1–Li2$^{ii}$ 2.561(4) Å; Figure 4). The polymeric chain is supported by the BH$_3$ moiety which also interacts with the lithium ions (Li1–H2B$^{i}$ 1.83(3), Li2–H3B 1.96(3) Å), and by the DME molecule which is also bridging the lithium centers (O1–Li1 2.307(4), O1–Li2$^{ii}$ 1.995(4), O2–Li1 2.015(4), O2–Li2$^{ii}$ 2.520(4) Å), with no short intermolecular contacts between the two chains. **3a** was twinned in the crystal structure and a twofold rotation about *hkl*=(1,0,-1) was used in its crystal structure analysis (see Experimental Section). In the monoclinic system this is equivalent to a twofold rotation about the *a,c*-diagonal in direct space (for a view along the *a,c*-diagonal, see Figure 5).[21] Overall, the asymmetric unit contains two independent Li centers, one [PhP·BH$_3$] dianion, and one DME molecule. The presence of H$_2$B–H···Li interactions has been reported for related lithium borane phosphanides Li[R$_2$P·BH$_3$],[22,23] but the crystal structure of **3a** represents, in fact, the first structural characterization of an arylphosphanediide M$_2$[ArP] in the solid state.

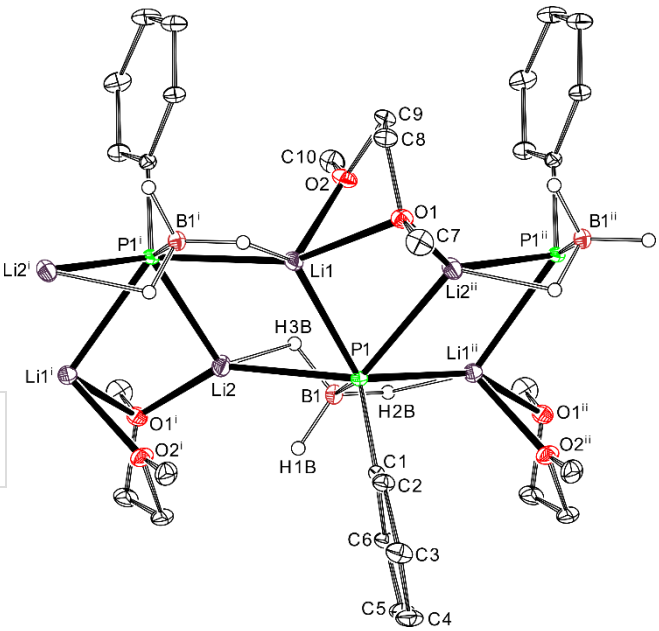


**Figure 4.** Part of the polymeric chain in the crystal structure of $Li_2[PhP{\cdot}BH_3](DME)$ (**3a**). Displacement ellipsoids were drawn at the 30% probability level. C–H hydrogen atoms are omitted for clarity. Symmetry codes *i*: 3/2-x, y-1/2, 1/2-z; *ii*: 3/2-x, y+1/2, 1/2-z. Selected bond lengths [Å] and angles [°] in the crystal structure of **3a**: P1–B1 1.996(2), P1–Li1 2.550(3), P1–Li2 2.524(4), P1–Li1ii 2.540(4), P1–Li2ii 2.561(4), B1–H1B 1.13(3), B1–H2B 1.17(3), B1–H3B 1.16(3), O1–Li1 2.307(4), O1–Li2ii 1.995(4), O2–Li1 2.015(4), O2–Li2ii 2.520(4), Li1–H2Bi 1.83(3), Li2–H3B 1.96(3); B1–P1–Li1 113.61(11), B1–P1–Li2 60.62(11), B1–P1–Li1ii 64.42(10), B1–P1–Li2ii 117.10(11), P1i–Li1–P1 111.56(13), O1–Li1–P1 94.92(13), O2–Li1–P1 98.87(15), O1–Li1–P1i 153.28(16), O2–Li1–P1i 106.45(16), P1–Li2–P1i 111.71(13), O1i–Li2–P1 144.57(18), O2i–Li2–P1 107.13(15), O1i–Li2–P1i 102.97(15), O2i–Li2–P1i 86.60(12).

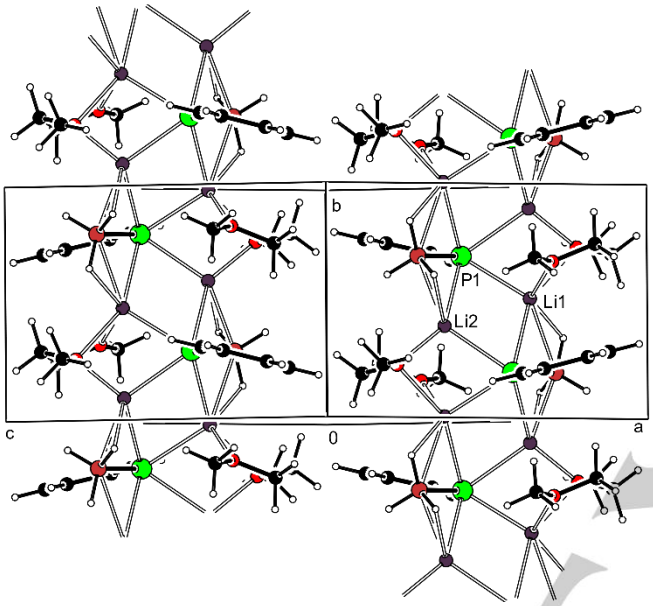



**Figure 5.** One-dimensional coordination chains in *b*-direction in the crystal structure of $Li_2[PhP{\cdot}BH_3](DME)$ (**3a**). View approximately along the *a,c*-diagonal. Shown are two of the one-dimensional coordination chains which are related by the inversion center of the space group.

## Conclusion

We herein provide a facile protocol that gives easy access to a range of substituted primary phosphine-boranes ($RPH_2{\cdot}BH_3$). These stable borane protected phosphines are well behaved in contrast to the free unprotected ones that are difficult to handle or even unstable. In particular, the readily accessible aminophosphine-boranes ($R_2NPH_2{\cdot}BH_3$) offer new opportunities as versatile building block in the synthesis of organophosphorus compounds, which can be easily deprotected using common procedures.[12] Furthermore, we showed that the use of $BH_3$ also offers increased solubility and stability of reactive intermediates, which allowed the first structural characterization of an arylphosphanediide in the solid state.

## Experimental Section

### General methods and materials

All manipulations were carried out under an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures and stored under 3 Å molecular sieves or a sublimed sodium mirror. $^1$H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance 400 or Bruker Avance 500 and internally referenced to the residual solvent resonances ($CDCl_3$: $^1$H δ = 7.26, $^{13}C\{^1H\}$ δ =77.2; THF-*D8*: $^1$H δ = 3.58, 1.72, $^{13}C\{^1H\}$ δ = 67.2, 5.3 or TMS; $^{31}P\{^1H\}$, $^{31}$P, $^{11}B\{^1H\}$, $^{11}$B, $^7$Li and $^{29}$Si NMR spectra were recorded on a Bruker Avance 400 and externally referenced (85% $H_3PO_4$, $BF_3{\cdot}OEt_2$ and LiCl, respectively). Chemical shifts are reported in ppm. High resolution mass spectra were recorded on a Bruker MicroTOF with ESI nebulizer (ESI). Melting points were measured in sealed capillaries and are uncorrected. $PhPCl_2$, *t*$BuPCl_2$, $PCl_3$, *i*$Pr_2NH$, $Cy_2NH$, TMP, $(Me_3Si)_2NNa$ (1.0 M in THF), $Li[BH_4]$ (2M in THF) and *n*BuLi (1.6M in hexanes) were purchased from Sigma and used as received. $Me_3SiCl$ was bought from Sigma and freshly distilled before use. The various dichlorophosphines $RPCl_2$ (R = Mes,[24] *i*$Pr_2N$,[25] $Cy_2N$,[26] TMP,[27] and $(Me_3Si)_2N$)[28] were prepared according to known literature procedures.

### Synthesis and characterization

**$PhPH_2{\cdot}BH_3$ (2a)**: A solution of $PhPCl_2$ (6.8 mL, 50.0 mmol) in $Et_2O$ (100 mL) was added dropwise in about 30 minutes to a solution of $Li[BH_4]$ (50.0 mL, 2.0 M in THF, 100.0 mmol) in $Et_2O$ (200 mL) at 0 °C. A colorless precipitate was formed and the reaction mixture was stirred for another 30 minutes during which the temperature was allowed to warm to room temperature. The solvent was removed *in vacuo*, the product was extracted into pentane (3 x 100 mL) and then filtered over Celite. Removal of pentane *in vacuo* afforded a colorless solid. Recrystallization from pentane at –30 °C yielded $PhPH_2{\cdot}BH_3$ (**2a**)[13b, 14b] as colorless crystals (5.29 g, 42.7 mmol, 85.3%). $^1$H NMR (400.1 MHz, $CDCl_3$): *δ* 0.90 (br. q, $^1J$(H,B) = 100.2 Hz, 3H; B*H*$_3$), 5.52 (dq, $^1J$(H,P) = 371.5 Hz, $^3J$(H,H) = 7.8 Hz, 2H; P*H*$_2$), 7.43–7.59 (m, 3H; *m,p*-Ph*H),* 7.65–7.77 (m, 2H; *o*-Ph*H*); $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$): *δ* 0.90 (dt, $^2J$(H,P) = 16.1, $^3J$(H,H) = 8.0 Hz, 3H; B*H*$_3$), 5.52 (dq, $^1J$(H,P) = 371.5 Hz, $^3J$(H,H) = 7.8 Hz, 2H; P*H*$_2$), 7.43–7.59 (m, 3H; *m,p*-Ph*H),* 7.65–7.77 (m, 2H; *o*-Ph*H*); $^{11}$B NMR (128.4 MHz, $CDCl_3$ ): *δ* –42.2 (dq, $^1J$(B,H) = 101.2 Hz, $^1J$(B,P) = 36.2 Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$): *δ* 119.9 (d, $^1J$(C,P) = 57.7 Hz; *ipso*-Ph*C*), 129.2 (d, $^3J$(C,P) = 10.6 Hz; *m*-Ph*C*), 132.0 (d, $^4J$(C,P) = 2.7 Hz; *p*-Ph*C*), 133.7 (d, $^2J$(C,P) = 9.1 Hz; *o*-Ph*C*); $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): *δ* –47.4 (q, $^1J$(P,B) = 34.8 Hz).

**$MesPH_2{\cdot}BH_3$ (2b)**: A solution of $MesPCl_2$ (1.10 g, 4.98 mmol) in $Et_2O$ (10 mL) was added dropwise in about 30 minutes to a solution of $Li[BH_4]$ (5.0 mL, 2.0 M in THF, 10.0 mmol) in $Et_2O$ (20 mL) at 0 °C. A colorless precipitate was formed and the reaction mixture was stirred for another 30 minutes during which the temperature was slowly warmed to room temperature. The solvent was removed *in vacuo*, the product was extracted into pentane (3 x 10 mL) and then filtered over Celite. Removal of pentane *in vacuo* afforded $MesPH_2{\cdot}BH_3$ (**2b**)[14a] as a colorless solid (0.81 g, 4.88 mmol, 97.6%). Colorless crystals were obtained by crystallization from pentane at –30 °C. H NMR (250.1 MHz, $CDCl_3$): *δ* 0.85 (br. q, $^1J$(H,B) = 98.2 Hz, 3H; B*H*$_3$), 2.30 (s, 3H; *p*-PhC*H*$_3$), 2.45 (s, 6H; *o*-PhC*H*$_3$), 5.46 (dq, $^1J$(H,P) = 370.4 Hz, $^3J$(H,H) = 7.6 Hz, 2H; P*H*$_2$), 6.94 (d, $^4J$(H,P) = 3 Hz, 2H; *m*-Ph*H*); $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$): *δ* 0.84 (dt, $^2J$(H,P) = 15.6, $^3J$(H,H) = 7.8 Hz, 3H; B*H*$_3$), 2.30 (s, 3H; *p*-PhC*H*$_3$), 2.45 (s, 6H; *o*-PhC*H*$_3$), 5.46 (dq, $^1J$(H,P) = 370.4 Hz, $^3J$(H,H) = 7.6 Hz, 2H; P*H*$_2$), 6.94 (d, $^4J$(H,P) = 3 Hz, 2H; *m*-Ph*H*); $^{11}$B NMR (128.4 MHz, $CDCl_3$): *δ* –40.7 (dq, $^1J$(B,H) = 101.3 Hz, $^1J$(B,P) = 34.8 Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$): *δ* 21.1 (d, $^5J$(C,P) = 1.0 Hz; *p*-PhC*H*$_3$), 21.6 (d, $^3J$(C,P) = 8.5 Hz; *o*-PhC*H*$_3$), 116.8 (d, $^1J$(C,P) = 57.9 Hz; *ipso*-Ph*C*), 129.4 (d, $^3J$(C,P) = 8.3 Hz; *m*-Ph*C*), 141.0 (d, $^2J$(C,P) = 8.0 Hz; *o*-Ph*C*), 141.3 (d, $^4J$(C,P) = 2.3 Hz; *p*-Ph*C*); $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$): *δ* –68.3 (br. d, $^1J$(P,B) = 40.5 Hz).

***t*$BuPH_2{\cdot}BH_3$ (2c)**: A solution of *t*$BuPCl_2$ (3.15 g, 19.8 mmol) in $Et_2O$ (40 mL) was added dropwise in about 30 minutes to a solution of $Li[BH_4]$ (20 mL, 2.0 M in THF, 20.0 mmol) in $Et_2O$ (80 mL) at 0 °C. A colorless precipitate was formed and the reaction mixture was stirred for another 30 min. during which the temperature was allowed to warm to room

temperature. The solvent was removed *in vacuo*, the product was extracted into pentane (3 x 20 mL) and then filtered over Celite. After removal of all volatiles, subsequent distillation (89–91 °C, 10 mbar) yielded *t*BuPH$_2$·BH$_3$ (**2c**)[14c, 15e] as a colorless oil (1.82 g, 17.5 mmol, 88.4%). $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ 0.51 (br. q, $^1J$(H,B) = 100.1 Hz, 3H; B*H*$_3$), 1.25 (d, $^3J$(H,P) = 15.5 Hz, 9H; C(C*H*$_3$)$_3$), 4.38 (dq, $^1J$(H,P) = 353.1 Hz, $^3J$(H,H) = 7.6 Hz, 2H; P*H*$_2$); $^1$H{$^{11}$B} NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.51 (dt, $^2J$(H,P) = 15.7, $^3J$(H,H) = 7.8 Hz, 3H; B*H*$_3$), 1.25 (d, $^3J$(H,P) = 15.5 Hz, 9H; C(C*H*$_3$)$_3$), 4.38 (dq, $^1J$(H,P) = 353.1 Hz, $^3J$(H,H) = 7.6 Hz, 2H; P*H*$_2$); $^{11}$B NMR (128.4 MHz, $CDCl_3$): $\delta$ –43.1 (dq, $^1J$(B,H) = 100.4 Hz, $^1J$(B,P) = 35.5 Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 24.9 (d, $^1J$(C,P) = 36.2 Hz; *C*(CH$_3$)$_3$), 27.7 (d, $^2J$(C,P) = 2.8 Hz; C(*C*H$_3$)$_3$); $^{31}$P{$^1$H} NMR (101.3 MHz, $CDCl_3$): $\delta$ –10.7 (q, $^1J$(P,B) = 37.0 Hz).

**1,2-(PH$_2$·BH$_3$)$_2$C$_6$H$_4$ (2d)**: **Step 1. Synthesis of 1,2-(P[O]Cl$_2$)$_2$C$_6$H$_4$**: A mixture of 1,2-(P[O]OMe$_2$)$_2$C$_6$H$_4$ (5.88 g, 20.0 mmol) and $PCl_5$ (16.66 g, 80.0 mmol) was heated for 16 hours at 120 °C in a three-necked flask with reflux condenser under a nitrogen atmosphere. *Caution: this is a very exothermic reaction.* The mixture liquefied and slowly turned from pale yellow to dark yellow. Upon cooling to room temperature, the mixture solidified. Subsequently, all volatiles were removed *in vacuo* and the remaining pale brown solid was distilled (140 °C at 5.1 x 10$^{-2}$ mbar) yielding 1,2-(P[O]Cl$_2$)$_2$C$_6$H$_4$[29] as a colorless solid (5.55 g, 17.8 mmol, 89.0%), 98% pure according to $^{31}$P {$^1$H} NMR spectroscopy, which was used without further purification. $^1$H NMR (500.2 MHz, $CDCl_3$): $\delta$ 7.89–7.95 (m, 2H; *m*-Ph*H*), 8.33–8.45 (m, 2H; *o*-Ph*H*); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 134.1–134.4 (m; *m*-Ph*C*), 134.6 (t, $^{2,3}J$(C,P) = 13.6 Hz; *o*-Ph*C*), 136.1 (dd, $^1J$(C,P) = 156.2 Hz, $^2J$(C,P) = 11.4 Hz; *ipso*-Ph*C*); $^{31}$P{$^1$H} NMR (101.3 MHz, $CDCl_3$): $\delta$ 31.2 (s). **Step 2. Synthesis of 1,2-(PCl$_2$)$_2$C$_6$H$_4$**: A mixture of 1,2-(P[O]Cl$_2$)$_2$C$_6$H$_4$ (5.31 g, 98% pure, 17.0 mmol) and $Ph_3P$ (9.83 g, 37.5 mmol) was heated for 16 hours at 230 °C in a three-necked flask with reflux condenser under a nitrogen atmosphere. The mixture liquefied and slowly turned from pale yellow to brown. Upon cooling to room temperature, the mixture solidified. All volatiles were removed *in vacuo* and the product was separated from the $Ph_3PO$ byproduct using a Schlenk to Schlenk distillation (100 °C at 4.0 x 10$^{-2}$ mbar). Subsequently, the resulting yellow oil was purified by fractional distillation (81–84 °C at 2.9 x 10$^{-2}$ mbar) yielding 1,2-(PCl$_2$)$_2$C$_6$H$_4$ as a pale yellow oil (1.80 g, 6.43 mmol, 37.7%), 96% pure according to $^{31}$P{$^1$H} NMR spectroscopy. Alternatively, 1,2-(PCl$_2$)$_2$C$_6$H$_4$ can be synthesized on large scale in a one-pot protocol, without purification of the intermediate 1,2-(P[O]Cl$_2$)$_2$C$_6$H$_4$ as follows: A mixture of 1,2-(P[O]Cl$_2$)$_2$C$_6$H$_4$ (44.13 g, 150.0 mmol) and $PCl_5$ (124.93 g, 600 mmol) was heated for 16 hours at 120 °C in a three-necked flask with reflux condenser under a nitrogen atmosphere. *Caution: this is a very exothermic reaction.* All volatiles were removed *in vacuo* and immediately $Ph_3P$ (78.69 g, 300.0 mmol) was added. The mixture was heated for another 16 hours at 230 °C. Upon cooling to room temperature, all volatiles were removed *in vacuo* and the resulting mixture was purified by Schlenk to Schlenk distillation (140 °C, 4.0 x 10$^{-2}$ mbar) yielding 1,2-(PCl$_2$)$_2$C$_6$H$_4$ as a yellow oil (39.38 g, 140.7 mmol, 93.8%), 85% pure according to $^{31}$P {$^1$H} NMR spectroscopy. Further purification of 1,2-(PCl$_2$)$_2$C$_6$H$_4$ can be achieved by fractional distillation using a spinning band (60 x 2.5 cm, 4 bladed), yielding 1,2-(PCl$_2$)$_2$C$_6$H$_4$[30] as a colorless oil (22.38 g, 79.98 mmol, 53.3%). $^1$H NMR (500.2 MHz, $CDCl_3$): $\delta$ 7.70–7.77 (m, 2H; *m*-Ph*H*), 8.20–8.27 (m, 2H; *o*-Ph*H*); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 130.6 (t, $^{3,4}J$(C,P) = 6.4 Hz; *m*-Ph*C*), 133.4 (s, *o*-Ph*C*), 144.3 (t, $^{1,2}J$(C,P) = 12.7 Hz; *ipso*-Ph*C*); $^{31}$P{$^1$H} NMR (101.3 MHz, $CDCl_3$): $\delta$ 151.6 (s). **Step 3. Synthesis of 1,2-(PH$_2$·BH$_3$)$_2$C$_6$H$_4$ (2d)**: A solution of Li[$BH_4$] (1.81 mL, 2.0 M in THF, 3.62 mmol) in $Et_2O$ (5 mL) was added dropwise in about 30 minutes to a solution of 1,2-(PCl$_2$)$_2$C$_6$H$_4$ (0.29 g, 1.04 mmol) in $Et_2O$ (5 mL) at 0 °C. A colorless precipitate was formed and the reaction mixture was stirred for another 30 minutes at 0 °C. The reaction mixture was concentrated at 0 °C and filtered over a glass filter. The remaining solvents where removed *in vacuo* at 0 °C, the product was extracted into $Et_2O$ (3 x 10 mL) followed by a second filtration. Removal of $Et_2O$ at 0 °C *in vacuo* yielded 1,2-(PH$_2$·BH$_3$)$_2$C$_6$H$_4$ (**2d**) as small colorless needles, 99% pure according to $^{31}$P NMR spectroscopy (0.11 g, 0.65 mmol, 64.7%). Recrystallization from a mixture of DCM and pentane at –78 °C yielded colorless crystals suitable for X-ray analysis. M.p. 81.7–82.8 °C; $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.96 (br. q, $^1J$(H,B) = 99.44 Hz, 6H; B*H*$_3$), 5.73 (dq, $^1J$(H,P) = 373.9 Hz, $^3J$(H,H) = 8.1 Hz, 4H; P*H*$_2$), 7.66–7.73 (m, 2H; *m*-Ph*H*), 7.92–8.01 (m, 2H; *o*-Ph*H*); $^1$H{$^{11}$B} NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.96 (dt, $^2J$(H,P) = 15.65 Hz, $^3J$(H,H) = 7.83, 6H; B*H*$_3$), 5.73 (dq, $^1J$(H,P) = 373.9 Hz, $^3J$(H,H) = 8.1 Hz, 4H; P*H*$_2$), 7.66–7.73 (m, 2H; *m*-Ph*H*), 7.92–8.01 (m, 2H; *o*-Ph*H*); $^{11}$B NMR (128.4 MHz, $CDCl_3$): $\delta$ –41.5 (dq, $^1J$(B,H) = 103.29 Hz, $^1J$(B,P) = 25.0 Hz); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ 125.8 (dd, $^1J$(C,P) = 52.7 Hz, $^2J$(C,P) = 3.6 Hz; *ipso*-Ph*C*), 132.6 (dd, $^3J$(C,P) = 11.8 Hz, $^4J$(C,P) = 2.7 Hz; *m*-Ph*C*), 136.1 (dd, $^3J$(C,P) = 15.4 Hz, $^2J$(C,P) = 7.3 Hz; *o*-Ph*C*); $^{31}$P{$^1$H} NMR (101.3 MHz, $CDCl_3$): $\delta$ –52.4 (br. d, $^1J$(P,B) = 34.4 Hz); HR ESI-MS: m/z (%): 169.07 (2.8) [M –H]$^-$, 167.05 (2.2) [M –H$_2$ –H]$^-$, 155.04 (2.0) [M –BH$_3$ –H]$^-$; calcd for C$_6$H$_{13}$B$_2$P$_2$ (M –H): 169.0686, found 169.0684.

***i*Pr$_2$NPH$_2$·BH$_3$ (2e)**: A solution of *i*Pr$_2$NPCl$_2$ (4.6 mL, 25.0 mmol) in $Et_2O$ (50 mL) was added dropwise in about 30 minutes to a solution of Li[$BH_4$] (25 mL, 2.0 M in THF, 50.0 mmol) in $Et_2O$ (100 mL) at 0 °C. A colorless precipitate was formed and the reaction mixture was stirred for another 30 minutes during which the temperature was allowed to warm to room temperature. The solvent was removed *in vacuo*, the product was extracted into pentane (3 x 100 mL) and then filtered over Celite. Removal of pentane *in vacuo* afforded *i*Pr$_2$NPH$_2$·BH$_3$ (**2e**) as a colorless oil (3.35 g, 22.8 mmol, 91.3%). Crystals suitable for X-ray analysis were obtained from diethyl ether at –70 °C. M.p. 1.0–2.0 °C; $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ 1.12 (d, $^3J$(H,H) = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$), 3.57 (sept, $^3J$(H,H) = 6.8 Hz, 2H; C*H*(CH$_3$)$_2$), 5.93 (dq, $^1J$(H,P) = 379.4 Hz, $^3J$(H,H) = 6.3 Hz, 2H; P*H*$_2$), signals for B*H*$_3$ were unresolved; $^1$H{$^{11}$B} NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.67 (dt, $^2J$(H,P) = 15.2, $^3J$(H,H) = 6.4 Hz, 3H; B*H*$_3$), 1.12 (d, $^3J$(H,H) = 6.8 Hz, 12H; CH(C*H*$_3$)$_2$), 3.57 (sept, $^3J$(H,H) = 6.8 Hz, 2H; C*H*(CH$_3$)$_2$), 5.93 (dq, $^1J$(H,P) = 379.4 Hz, $^3J$(H,H) = 6.3 Hz, 2H; P*H*$_2$); $^{11}$B NMR (128.4 MHz, $CDCl_3$): $\delta$ –41.4 (dq, $^1J$(B,H) = 99.9 Hz, $^1J$(B,P) = 50.9 Hz); $^{13}$C NMR (100.6 MHz, $CDCl_3$): $\delta$ 21.5 (d, $^3J$(C,P) = 3.2 Hz; CH(*C*H$_3$)$_2$), 47.2 (d, $^2J$(C,P) = 3.7 Hz; *C*H(CH$_3$)$_2$); $^{31}$P{$^1$H} NMR (101.3 MHz, $CDCl_3$): $\delta$ –18.6 (q, $^1J$(P,B) = 50.8 Hz); HR ESI-MS: m/z (%): 146.13 (0.2) [M –H]$^-$, 144.11 (0.3) [M –H$_2$ –H]$^-$; calcd for C$_6$H$_{18}$BNP (M –H)$^-$: 146.1277, found 146.1274.

**Cy$_2$NPH$_2$·BH$_3$ (2f)**: A solution of Cy$_2$NPCl$_2$ (1.41 g, 5.0 mmol) in $Et_2O$ (50 mL) was slowly added to a solution of Li[$BH_4$] (5.0 mL, 2.0 M in THF, 10.0 mmol) in $Et_2O$ (20 mL) at 0 °C. A colorless precipitate was formed and the reaction mixture was stirred for another 30 minutes during which the temperature was allowed to warm to room temperature. The solvent was removed *in vacuo*, the product was extracted into pentane (3 x 30 mL) and then filtered over Celite. Removal of pentane *in vacuo* yielded a colorless solid, which after recrystallization from a mixture of diethyl ether and pentane at –70 °C yielded Cy$_2$NPH$_2$·BH$_3$ (**2f**) as colorless crystals (0.87 g, 4.1 mmol, 81.6%). M.p. 48.2–49.9 °C; $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.71 (br. q, $^1J$(H,B) = 94.7 Hz, 3H; B*H*$_3$), 0.97–1.11 (m, 2H; Cy*H*), 1.22–1.36 (m, 4H; Cy*H*), 1.42–1.54 (m, 4H; Cy*H*), 1.57–1.67 (m, 6H; Cy*H*), 1.74–1.82 (m, 4H; Cy*H*), 2.99–3.13 (m, 2H; Cy*H*N), 6.02 (dq, $^1J$(H,P) = 379.8 Hz, $^3J$(H,H) = 6.3 Hz, 2H; P*H*$_2$); $^1$H{$^{11}$B} NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.71 (dt, $^2J$(H,P) = 15.2 Hz, $^3J$(H,H) = 6.3 Hz, 3H; B*H*$_3$), 0.97–1.11 (m, 2H; Cy*H*), 1.22–1.36 (m, 4H; Cy*H*), 1.42–1.54 (m, 4H; Cy*H*), 1.57–1.67 (m, 6H; Cy*H*), 1.74–1.82 (m, 4H; Cy*H*), 2.99–3.13 (m, 2H; Cy*H*N), 6.02 (dq, $^1J$(H,P) = 379.8 Hz, $^3J$(H,H) = 6.3 Hz, 2H; P*H*$_2$); $^{11}$B NMR (128.4 MHz, $CDCl_3$): $\delta$ –41.0 (dq, $^1J$(B,H) = 96.8 Hz, $^1J$(B,P) = 54.9 Hz); $^{13}$C NMR (68.9 MHz, $CDCl_3$): $\delta$ 25.3 (s, NCHCH$_2$CH$_2$*C*H$_2$), 25.9 (s, NCHCH$_2$*C*H$_2$CH$_2$), 32.3 (d, $^3J$(C,P) = 3.0 Hz; NCH*C*H$_2$CH$_2$CH$_2$), 56.5 (d, $^2J$(C,P) = 3.2 Hz; N*C*HCH$_2$CH$_2$CH$_2$); $^{31}$P{$^1$H} NMR (162.0 MHz, $CDCl_3$): $\delta$ –13.2 (br. q, $^1J$(P,B) = 45.9 Hz); HR ESI-MS: m/z (%): 242.18 (64.0) [M –H +O]$^-$, 226.19 (100.0) [M –H]$^-$; calcd for C$_{12}$H$_{26}$BNP (M –H)$^-$: 226.1904, found 226.1901.

**(CH$_2$)$_3$(CMe$_2$)$_2$NPH$_2$·BH$_3$ (2g)**: A solution of TMPPCl$_2$ (1.21 g, 5.0 mmol; TMP = 2,2,6,6-tetramethylpiperidine) in $Et_2O$ (10 mL) was added slowly to a solution of Li[$BH_4$] (5.0 mL, 2.0 M in THF, 10.0 mmol) in $Et_2O$ (20 mL) at 0 °C. The reaction mixture was stirred for 30 minutes at 0 °C and another 30 minutes during which the mixture was allowed to warm to room temperature. All volatiles were removed *in vacuo*, the product was extracted into $Et_2O$ (3 x 30 mL) and then filtered over Celite. Removal of $Et_2O$ *in vacuo* afforded TMPPH$_2$·BH$_3$ (**2g**) as a colorless powder (0.92 g,

4.9 mmol, 98.4%). Recrystallization from a mixture of $Et_2O$ and pentanes at –70 °C yielded colorless needles. M.p. >20 °C (decomp); $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ 1.14 (s, 12H; NC($CH_3$)$_2$C$H_2$C$H_2$), 1.13–1.21 (m, 4H; NC(CH$_3$)$_2$C$H_2$CH$_2$), 1.23–1.31 (m, 2H; NC(CH$_3$)$_2$CH$_2$C$H_2$), 1.82 (br. q, $^1J$(H,B) = 99.3 Hz, 3H; B$H_3$), 5.79 (dq, $^1J$(H,P) = 369.6 Hz, $^1J$(H,H) = 6.8 Hz, 2H; P$H_2$); $^1$H{$^{11}$B} NMR (400.1 MHz, $CDCl_3$): $\delta$ 1.14 (s, 12H; NC($CH_3$)$_2$CH$_2$CH$_2$), 1.13–1.21 (m, 4H; NC(CH$_3$)$_2$C$H_2$CH$_2$), 1.23–1.31 (m, 2H; NC(CH$_3$)$_2$CH$_2$C$H_2$), 1.82 (dt, $^1J$(H,P) = 13.6 Hz, $^3J$(H,H) = 6.9 Hz, 3H; B$H_3$), 5.79 (dq, $^1J$(H,P) = 369.6 Hz, $^1J$(H,H) = 6.8 Hz, 2H; P$H_2$); $^{11}$B NMR (128.4 MHz, $CDCl_3$): $\delta$ –34.5 (dq, $^1J$(B,H) = 99.2 Hz, $^1J$(B,P) = 52.7 Hz); $^{13}$C NMR (125.8 MHz, $C_6D_6$): $\delta$ 17.0 (s; NC(CH$_3$)$_2$CH$_2$C$H_2$), 29.0 (d, $^3J$(C,P) = 4.3 Hz; NC($CH_3$)$_2$CH$_2$CH$_2$), 40.9 (d, $^3J$(C,P) = 4.9 Hz; NC(CH$_3$)$_2$C$H_2$CH$_2$), 55.6 (s, NC(CH$_3$)$_2$CH$_2$CH$_2$); $^{31}$P{$^1$H} NMR (162.0 MHz, $CDCl_3$): $\delta$ –15.9 (br. q, $^1J$(P,B) = 48.9 Hz); HR ESI-MS: m/z (%): 202.15 (22.0) [M –H +O]$^-$, 186.16 (36.0) [M –H]$^-$; calcd for $C_9H_{22}BNP$ (M –H)$^-$: 186.1590, found 186.1587.

**(Me$_3$Si)$_2$NPH$_2$·BH$_3$ (2h)**: **Step 1. Synthesis of (Me$_3$Si)$_2$NPCl$_2$**: (Me$_3$Si)$_2$NNa (25.0 mL, 1.0 M in THF, 25.0 mmol) was added slowly to a solution of $PCl_3$ (2.18 mL, 25.0 mmol) in THF (74 mL) at 0 °C. The reaction mixture was stirred for 30 minutes at 0 °C and subsequently 30 minutes at room temperature after which the solvent was removed *in vacuo*, the product extracted into diethyl ether (3 x 30 mL) and then filtered. Removal of diethyl ether yielded (Me$_3$Si)$_2$NPCl$_2$ as a colorless oil. **Step 2. Synthesis of (Me$_3$Si)$_2$NPH$_2$·BH$_3$**: The resulting (Me$_3$Si)$_2$NPCl$_2$ was dissolved in $Et_2O$ (50 mL) and added slowly to a solution of Li[$BH_4$] (25.0 mL, 2.0 M in THF, 50.0 mmol) in $Et_2O$ at 0 °C and subsequently stirred for 60 minutes at the same temperature. The following purification steps where all carried out at 0 °C. The solvent was removed *in vacuo*, the product was extracted into $Et_2O$ (3 x 30 mL) and then filtered over Celite. Removal of $Et_2O$ *in vacuo* yielded (Me$_3$Si)$_2$NPH$_2$·BH$_3$ (**2h**) as a pale yellow solid (4.36 g, 21.2 mmol, 84.6%; 92.3% pure according to $^{31}$P NMR spectroscopy). Recrystallization from a mixture of diethyl ether and pentane at –70 °C afforded (Me$_3$Si)$_2$NPH$_2$·BH$_3$ (**2h**) as small needless (3.28 g, 15.9 mmol, 63.6%). M.p. 5–7 °C; $^1$H NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.26 (br. s, 18H; (C$H_3$)$_3$Si), 0.67 (br. q, $^1J$(H,B) = 94.3 Hz, 3H; B$H_3$), 6.06 (dq, $^1J$(H,P) = 371.7 Hz, $^3J$(H,H) = 6.7 Hz, 2H; P$H_2$); $^1$H{$^{11}$B} NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.26 (br. s, 18H; (C$H_3$)$_3$Si), 0.67 (dt, $^2J$(H,P) = 15.3 Hz, $^3J$(H,H) = 6.7 Hz, 3H; B$H_3$), 6.06 (dq, $^1J$(H,P) = 371.6, $^3J$(H,H) = 6.7 Hz, 2H; P$H_2$); $^{11}$B NMR (128.4 MHz, $CDCl_3$): $\delta$ –36.7 (dq, $^1J$(B,H) = 98.2, $^1J$(B,P) = 54.4 Hz); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ 2.1 (d, $^3J$(C,P) = 3.4 Hz; (C$H_3$)$_3$Si); $^{29}$Si NMR (79.5 MHz, $CDCl_3$): $\delta$ 12.9 (br. s); $^{31}$P{$^1$H} NMR (162.0 MHz, $CDCl_3$): $\delta$ 2.1 (q, $^1J$(P,B) = 51.6 Hz); HR ESI-MS: m/z (%): 206.11 (1.0) [M –H]$^-$, 160.10 (100.0) [M –PH$_2$BH$_3$]$^-$; calcd for $C_6H_{22}BNPSi_2$ (M –H): 206.1129, found 206.1124.

**Li$_2$[PhP·BH$_3$] (3a)**: A stock solution of PhPH$_2$·BH$_3$ (**2a**; 14.6 mL, 0.25 M in THF, 5.0 mmol) was cooled to –78 °C, subsequently 2 equiv of *n*-BuLi (6.25 mL, 1.6 M in hexanes, 10.0 mmol) was slowly added and the mixture was stirred for 30 minutes, after which the mixture was slowly warmed to room temperature and stirred for another 30 minutes. The reaction mixture was concentrated to 10% of its volume and washed with hexanes (2x 20 mL). Evaporation of the residue to dryness at 0 °C yielded Li$_2$[PhP·BH$_3$] (**3a**) as a (thermally unstable) colorless powder (1.1 g, 4.6 mmol, 91%). Recrystallization from a mixture of THF, DME and hexanes at –78 °C provided colorless crystals suitable for X-ray analysis. $^1$H NMR (400.1 MHz, THF-$D_8$): $\delta$ 0.68 (br. q, $^1J$(H,B) = 84.9 Hz, 3H; B$H_3$), 0.87 (m, 12H; Hex), 1.30 (m, 16H; Hex), 1.72 (br. s, 2H; THF-$D_8$), 1.78 (m, 3H; THF), 3.56 (br. s, 2H; THF-$D_8$), 3.61 (m, 3H; THF), 6.24–6.28 (m, 1H; *p*-Ph*H*), 6.53–6.57 (m, 2H; *m*-Ph*H*), 7.28–7.31 (m, 2H; *o*-Ph*H*); $^1$H{$^{11}$B} NMR (400.1 MHz, THF-$D_8$): $\delta$ 0.68 (d, $^2J$(H,P) = 6.8 Hz, 3H; B$H_3$), 0.87 (m, 12H; Hex), 1.30 (m, 16H; Hex), 1.72 (br. s, 2H; THF-$D_8$), 1.78 (m, 3H; THF), 3.56 (br. s, 2H; THF-$D_8$), 3.61 (m, 3H; THF), 6.24–6.28 (m, 1H; *p*-Ph*H*), 6.53–6.57 (m, 2H; *m*-Ph*H*), 7.28–7.31 (m, 2H; *o*-Ph*H*); $^7$Li NMR (155.5 MHz, THF-$D_8$): $\delta$ 0.62 (s); $^{11}$B NMR (128.4 MHz, THF-$D_8$): $\delta$ –34.0 (br. q, $^1J$(B,H) = 84.5 Hz); $^{13}$C NMR (100.6 MHz, THF-$D_8$): $\delta$ 15.3 (s; $C_{1,6}$-Hex), 24.41 (s; $C_{2,5}$-Hex), 26.2 (m; $C_{3,4}$-THF), 27.3 (s; $C_{3,4}$-THF-complex), 33.4 (s; $C_{3,4}$-Hex), 68.3 (m; $C_{2,5}$-THF), 69.1 (s; $C_{2,5}$-THF-complex), 117.1 (s; *p*-Ph*C*), 126.7 (d, $^3J$(C,P) = 4.6 Hz; *m*-Ph*C*), 133.6 (d, $^2J$(C,P) = 12.1 Hz; *o*-Ph*C*), 165.9 (d, $^1J$(C,P) = 43.9 Hz; *ipso*-Ph*C*); $^{31}$P{$^1$H} NMR (101.3 MHz, THF-$D_8$): $\delta$ –166.4 (br. m).

**PhP(SiMe$_3$)$_2$·BH$_3$ (4a)**: 2 equiv of *n*BuLi (6.88 mL, 1.6 M in hexanes, 11.0 mmol) was added dropwise to a solution of PhPH$_2$·BH$_3$ (**2a**; 0.62 g, 5.0 mmol) in THF (25 mL) at –78 °C. The reaction mixture was stirred for 30 minutes at the same temperature followed by the slow addition of freshly distilled Me$_3$SiCl (1.40 mL, 11.0 mmol). Subsequently, the reaction mixture was stirred for another 60 minutes during which the temperature was slowly warmed to room temperature. The solvent was removed *in vacuo* and the residue was extracted into pentanes (3 x 20 mL). Removal of pentane *in vacuo* yielded PhP(SiMe$_3$)$_2$·BH$_3$ (**4a**) as a colorless solid (1.25 g, 4.7 mmol, 98.2%). M.p. 65.8–66.9 °C. $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ 0.34 (d, $^3J$(H,P) = 5.7 Hz, 18H; Si(C$H_3$)$_3$), 7.32–7.41 (m, 3H; *m*,*p*-Ph*H*), 7.56–7.67 (m, 2H; *o*-Ph*H*), signals for B$H_3$ were unresolved; $^1$H{$^{11}$B} NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.34 (d, $^3J$(H,P) = 5.7 Hz, 18H; Si(C$H_3$)$_3$), 0.88 (d, $^2J$(H,P) = 10.4 Hz; 3H, B$H_3$), 7.32–7.41 (m, 3H; *m*,*p*-Ph*H*), 7.56–7.67 (m, 2H; *o*-Ph*H*); $^{11}$B NMR (128.4 MHz, $CDCl_3$): $\delta$ –40.1 (dq, $^1J$(B,H) = 98.3 Hz, $^1J$(B,P) = 24.7 Hz); $^{13}$C NMR (62.9 MHz, $CDCl_3$): $\delta$ –1.3 (d, $^2J$(C,P) = 8.6 Hz; Si(C$H_3$)$_3$), 126.5 (d, $^1J$(C,P) = 31.3 Hz; *ipso*-Ph*C*), 128.6 (d, $^3J$(C,P) = 8.9 Hz; *m*-Ph*C*), 129.3 (d, $^4J$(C,P = 2.5 Hz; *p*-Ph*C*), 134.3 (d, $^2J$(C,P) = 6.7 Hz; *o*-Ph*C*); $^{29}$Si NMR (79.5 MHz, $CDCl_3$): $\delta$ 6.0 (d, $^1J$(Si,P) = 48.5 Hz); $^{31}$P{$^1$H} NMR (162.0 MHz, $CDCl_3$): $\delta$ –95.6 (br. d, $^1J$(P,B) = 32.4 Hz).

***i*Pr$_2$NP(SiMe$_3$)$_2$·BH$_3$ (4e)**: 2 equiv of *n*BuLi (10.46 mL, 1.6 M in hexanes, 19.74 mmol) was added slowly to a solution of *i*Pr$_2$NPH$_2$·BH$_3$ (**2e**; 1.23 g, 8.37 mmol) in THF (40 mL) at –78 °C. The reaction mixture was stirred for 30 minutes at the same temperature followed by the slow addition of freshly distilled Me$_3$SiCl (2.12 mL, 16.74 mmol). Subsequently, the reaction mixture was stirred for another 60 minutes during which the temperature was slowly warmed to room temperature. The solvent was removed *in vacuo* and the residue was extracted into pentanes (3 x 30 mL). Removal of pentane *in vacuo* yielded *i*Pr$_2$NP(SiMe$_3$)$_2$·BH$_3$ (**4e**) as a colorless solid (2.18 g, 7.48 mmol, 89.3%). Colorless crystals were obtained by crystallization from a mixture of diethyl ether and pentane at –30 °C. M.p. 28.7–29.4 °C; $^1$H NMR (250.1 MHz, $CDCl_3$): $\delta$ 0.39 (d, $^3J$(H,P) = 5.3 Hz, 18H; Si(C$H_3$)$_3$), 1.29 (d, $^3J$(H,H) = 6.8 Hz, 12H; CH(C$H_3$)$_2$), 3.29 (d. sept, $^3J$(H,P) = 14.7 Hz, $^3J$(H,H) = 6.8 Hz, 2H; C$H$(CH$_3$)$_2$), signals for B$H_3$ were unresolved; $^1$H{$^{11}$B} NMR (400.1 MHz, $CDCl_3$): $\delta$ 0.39 (d, $^3J$(H,P) = 5.3 Hz, 18H; Si(C$H_3$)$_3$), 1.03 (d, $^2J$(H,P) = 7.9 Hz, 3H; B$H_3$), 1.29 (d, $^3J$(H,H) = 6.8 Hz, 12H; CH(C$H_3$)$_2$), 3.29 (d. sept, $^3J$(H,P) = 14.7 Hz, $^3J$(H,H) = 6.8 Hz, 2H; C$H$(CH$_3$)$_2$); $^{11}$B NMR (128.4 MHz, $CDCl_3$): $\delta$ –35.4 (dq, $^1J$(B,H) = 98.8 Hz, $^1J$(B,P) = 34.7 Hz); $^{13}$C NMR (125.8 MHz, $CDCl_3$): $\delta$ –0.3 (d, $^2J$(C,P) = 8.6 Hz; Si(C$H_3$)$_3$), 24.1 (d, $^3J$(C,P) = 1.3 Hz; CH(C$H_3$)$_2$), 51.6 (d, $^2J$(C,P) = 0.9 Hz; C$H$(CH$_3$)$_2$); $^{29}$Si NMR (79.5 MHz, $CDCl_3$): $\delta$ 2.2 (d, $^1J$(Si,P) = 72.2 Hz); $^{31}$P{$^1$H} NMR (162.0 MHz, $CDCl_3$): $\delta$ 1.1 (br. d, $^1J$(P,B) = 26.6 Hz).

**X-ray crystal structure determinations**

**2d**: $C_6H_{14}B_2P_2$, Fw = 169.73, colourless needle, 0.60 × 0.18 × 0.18 mm$^3$, orthorhombic, Pbca (no. 61), a = 9.2604(4), b = 8.0989(2), c = 26.4819(7) Å, V = 1986.12(11) Å$^3$, Z = 8, $D_x$ = 1.135 g/cm$^3$, $\mu$ = 0.37 mm$^{-1}$. The diffraction experiment was performed on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator ($\lambda$ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å$^{-1}$. The intensity integration was performed with the EvalCCD software.[31] A multi-scan absorption correction and scaling was performed with SADABS[32] (correction range 0.73-0.94). A total of 22295 reflections was measured, 2274 reflections were unique ($R_{int}$ = 0.028), 1921 reflections were observed [I>2$\sigma$(I)]. The structure was solved with direct methods using SHELXS-97.[33] Structure refinement was performed with SHELXL-2018[34] on F$^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps and refined freely with isotropic displacement parameters. 147 Parameters were refined with no restraints. R1/wR2 [I > 2$\sigma$(I)]: 0.0293 / 0.0714. R1/wR2 [all refl.]: 0.0395 / 0.0771. S = 1.051. Residual electron density between -0.22 and 0.32 e/Å$^3$. Geometry

calculations and checking for higher symmetry was performed with the PLATON program.[18]

**2e**: $C_6H_{19}BNP$, Fw = 147.00, colourless block, 0.60 × 0.50 × 0.50 mm$^3$, monoclinic, C2/m (no. 12), a = 11.7959(3), b = 9.8864(2), c = 8.6272(2) Å, β = 90.1828(10) °, V = 1006.09(4) Å$^3$, Z = 4, $D_x$ = 0.970 g/cm$^3$, μ = 0.21 mm$^{-1}$. The diffraction experiment was performed on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å$^{-1}$. The intensity integration was performed with the HKL2000 software.[35] A multi-scan absorption correction and scaling was performed with SADABS[32] (correction range 0.65-0.90). A total of 8401 reflections was measured, 1203 reflections were unique ($R_{int}$ = 0.033), 1030 reflections were observed [I>2σ(I)]. The structure was solved with direct methods using SHELXS-97.[33] Structure refinement was performed with SHELXL-2018[34] on $F^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. The P-H hydrogen atom was kept fixed at the located position. All other hydrogen atoms were refined freely with isotropic displacement parameters. 86 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0371 / 0.0971. R1/wR2 [all refl.]: 0.0454 / 0.1027. S = 1.090. Residual electron density between -0.42 and 0.28 e/Å$^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[18]

**3a**: $C_{10}H_{18}BLi_2O_2P$, Fw = 225.90, yellow needle, 0.60 × 0.24 × 0.09 mm$^3$, monoclinic, $P2_1/n$ (no. 14), a = 12.4001(9), b = 7.2198(7), c = 14.7720(8) Å, β = 94.983(3) °, V = 1317.47(17) Å$^3$, Z = 4, $D_x$ = 1.139 g/cm$^3$, μ = 0.19 mm$^{-1}$. The diffraction experiment was performed on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 125(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å$^{-1}$. The crystal appeared to be twinned with a twofold rotation about *hkl* = (1,0,-1) as twin operation. Consequently, two orientation matrices were used for the integration with the Eval15 software.[36] A multi-scan absorption correction and scaling was performed with TWINABS[32] (correction range 0.64-1.00). A total of 16125 reflections was measured, 3014 reflections were unique ($R_{int}$ = 0.068), 2693 reflections were observed [I>2σ(I)]. The structure was solved with direct methods using SIR97.[37] Structure refinement was performed with SHELXL-2018[34] on $F^2$ of all reflections based on an HKLF-5 file.[38] Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. The B-H hydrogen atoms were refined freely with isotropic displacement parameters. C-H hydrogen atoms were refined with a riding model. 160 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0447 / 0.1255. R1/wR2 [all refl.]: 0.0524 / 0.1313. S = 1.264. Twin fraction BASF = 0.507(3). Residual electron density between -0.29 and 0.45 e/Å$^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[18]

**4e**: $C_{12}H_{35}BNPSi_2$, Fw = 291.37, colourless block, 0.60 × 0.60 × 0.42 mm$^3$, monoclinic, $P2_1/c$ (no. 14), a = 17.1577(4), b = 12.5115(3), c = 18.7430(6) Å, β = 99.706(1) °, V = 3965.94(18) Å$^3$, Z = 8, $D_x$ = 0.976 g/cm$^3$, μ = 0.25 mm$^{-1}$. The diffraction experiment was performed on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin\theta/\lambda)_{max}$ = 0.65 Å$^{-1}$. The intensity integration was performed with the Eval15 software.[36] A multi-scan absorption correction and scaling was performed with SADABS[32] (correction range 0.74-0.90). A total of 103227 reflections was measured, 9124 reflections were unique ($R_{int}$ = 0.032), 7809 reflections were observed [I>2σ(I)]. The structure was solved with direct methods using SHELXS-97.[33] Structure refinement was performed with SHELXL-2018[34] on $F^2$ of all reflections. The asymmetric unit contains two independent molecules. Non-hydrogen atoms of the first molecule were refined freely with anisotropic displacement parameters. The second molecule was refined with a disorder model (ratio 0.87:0.13 between the components). The major disorder form was refined anisotropically, the minor form isotropically. The B-H hydrogen atoms were located in difference Fourier maps and refined freely with isotropic displacement parameters. The C-H hydrogen atoms were introduced in calculated positions and refined with a riding model. 395 Parameters were refined with 455 restraints (distances and angles for handling the disorder). R1/wR2 [I > 2σ(I)]: 0.0321 / 0.0832. R1/wR2 [all refl.]: 0.0396 / 0.0885. S = 1.041. Residual electron density between -0.19 and 0.35 e/Å$^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.[18]

CCDC 2001504 (**2d**), 2001505 (**2e**), 2001507 (**3a**), and 2001506 (**4e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

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[1] a) R. M. Hiney, L. J. Higham, H. Müller-Bunz, D. G. Gilheany, *Angew. Chem. Int. Ed*. **2006**, *45*, 7248–7251; b) B. Stewart, A. Harriman, L. J. Higham, *Organometallics* **2011**, *30*, 5338–5343; c) J. T. Fleming, L. J. Higham, *Coord. Chem. Rev*. **2015**, *297-298*, 127–145.

[2] C. A. Bange, R. Waterman, *Chem. Eur. J*. **2016**, *22*, 12598–12605.

[3] a) M. Driess, G. Huttner, N. Knopf. H. Pritzkow, L. Zsolnai, *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 316–318; b) G. W. Rabe, S. Kheradmandan, L. M. Liable-Sands, I. A. Guzei, A. L. Rheingold, *Angew. Chem. Int. Ed*. **1998**, *37*, 1404–1407; c) G. W. Rabe, H. Heise, G. P. A. Yap, L. M. Liable-Sands, I. A. Guzei, A. L. Rheingold, *Inorg. Chem*. **1998**, *37*, 4235–4245; d) M. Driess, *Acc. Chem. Res*. **1999**, *32*, 1017–1025; e) V. L. Rudzevich, H. Gornitzka, K. Miqueu, J.-M. Sotiropoulos, G. Pfister-Guillouzo, V. D. Romanenko, G. Bertrand, Angew. Chem. Int. Ed. 2002, 41, 1193–1195; f) S. Gómez-Ruiz, E. Hey-Hawkins, *Coord. Chem. Rev*. **2011**, *255* (11-12), 1360–1386.

[4] a) M. Driess, H. Pritzkow, S. Martin, S. Rell, D. Fenske, G. Baum, *Angew. Chem. Int. Ed. Engl*. **1996**, *34*, 986–988; b) M. Driess, U. Hoffmanns, S. Martin, K. Merz, H. Pritzkow, *Angew. Chem. Int. Ed*. **1999**, *38*, 2733–2736; c) N. Wiberg, A. Wörner, D. Fenske, H. Nöth, J. Knizek, K. Polborn, *Angew. Chem. Int. Ed*. **2000**, *39*, 1838–1842; d) J. Geier, J. Harmer, H. Grützmacher, *Angew. Chem. Int. Ed*. **2004**, *43*, 4093–4097; e) R. Wolf, A. Schisler, P. Lönnecke, C. Jones, E. Hey-Hawkins, *Eur. J. Inorg. Chem*. **2004**, 3277–3286; f) S. Tschirschwitz, P. Lönnecke, J. Reinhold, E. Hey-Hawkins, *Angew. Chem. Int. Ed*. **2005**, *44*, 2965–2969; g) M. McPartlin, R. L. Melen, V. Naseri, D. S. Wright, *Chem. Eur. J*. **2010**, *16*, 8854–8860.

[5] a) J. Geier, H. Rüegger, M. Wörle, H. Grützmacher, *Angew. Chem. Int. Ed*. **2003**, *42*, 3951–3954, and references therein; b) D. Stein, A. Dransfeld, M. Flock, H. Rüegger, H. Grützmacher, *Eur. J. Inorg. Chem*. **2006**, *20*, 4157–4167.

[6] a) P. B. Hitchcock, M. F. Lappert, P. Yin, *J. Chem. Soc., Chem. Commun*. **1992**, 1598–1599; b) P. B. Hitchcock, M. F. Lappert, W.-P. Leung, P. Yin, *J. Chem. Soc., Dalton Trans*. **1995**, 3925–3932.

[7] a) M. J. Burk, *Acc. Chem. Res*. **2000**, *33*, 363–372; b) T. P. Yoon, E. N. Jacobsen, *Science* **2003**, *299* (5613), 1691–1693; c) G. Hoge, *J. Am. Chem. Soc*. **2003**, *125*, 10219–10227.

[8] https://schlenklinesurvivalguide.com.

[9] S. G. A. van Assema, P. B. Kraikivskii, S. N. Zelinskii, V. V. Saraev, G. B. de Jong, F. J. J. de Kanter, M. Schakel, J. C. Slootweg, K. Lammertsma, *J. Organomet. Chem*. **2007**, *692*, 2314–2323.

[10] R. B. King, N. D. Sadanani, *Inorg. Chem*. **1985**, *24*, 3136–3139.
[11] a) P. Pellon, *Tetrahedron Lett*. **1992**, *33*, 4451–4452; b) M. Shimizu, K. Tamura, T. Wada, K. Saigo, *Tetrahedron Lett*. **2004**, *45*, 371–374; c) T. Imamoto, T. Oshiki, T. Onozawa, T. Kusumoto, K. Sato, *J. Am. Chem. Soc.* **1990**, *112*, 5244–5252.
[12] a) J. M. Brunel, B. Faure, M. Maffei, *Coord. Chem. Rev*. **1998**, *178–180*, 665–698; b) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev*. **2010**, *110*, 4023–4078; for the synthesis of the corresponding amine-boranes, see e.g.: c) P. V. Ramachandran, A. S. Kulkarni, Y. Zhao, J. Mei, *Chem. Commun*. **2016**, *52*, 11885–11888.
[13] a) H. Dorn, R. A. Singh, J. A. Massey, A. J. Lough, I. Manners, *Angew. Chem. Int. Ed.* **1999**, *38*, 3321–3323; b) H. Dorn, R. A. Singh, J. A. Massey, J. M. Nelson, C. A. Jaska, A. J. Lough, I. Manners, *J. Am. Chem. Soc.* **2000**, *122*, 6669–6678; c) J.-M. Denis, H. Forintos, H. Szelke, L. Toupet, T.-N. Pham, P.-J. Madec, A.-C. Gaumont, *Chem. Commun*. **2003**, 54–55; d) T. J. Clark, J. M. Rodezno, S. B. Clendenning, S. Aouba, P. M. Brodersen, A. J. Lough, H. E. Ruda, I. Manners, *Chem. Eur. J.* **2005**, *11*, 4526–4534; e) A. Schäfer, T. Jurca, J. Turner, J. R. Vance, K. Lee, V. A. Du, M. F. Haddow, G. R. Whittell, I. Manners, *Angew. Chem. Int. Ed*. **2015**, *54*, 4836–4841, and references therein; f) N. L. Oldroyd, S. S. Chitnis, V. T. Annibale, M. I. Arz, H. A. Sparkes, I. Manners, *Nature Commun*. **2019**, *10*, 1370; g) D. Han, F. Anke, M. Trose, T. Beweries, *Coord. Chem. Rev*. **2019**, *380*, 260–286.
[14] For example, for $MesPH_2{\cdot}BH_3$, see: a) I. V. Kourkine, S. V. Maslennikov, R. Ditchfield, D. S. Glueck, G. P. A. Yap, L. M. Liable-Sands, A. L. Rheingold, *Inorg. Chem*. **1996**, *35*, 6708–6716; for $PhPH_2{\cdot}BH_3$ and $MePH_2{\cdot}BH_3$, see: b) K. Bourumeau, A.-C. Gaumont, J.-M. Denis, *J. Organomet. Chem*. **1997**, *529*, 205–213; for $t$BuPH$_2{\cdot}$BH$_3$, see: c) N. Oohara, T. Imamoto, *Bull. Soc. Chem. Jpn*. **2002**, *75*, 1359–1365; for $MenPH_2{\cdot}BH_3$, see: d) N. F. Blank, K. C. McBroom, D. S. Glueck, W. S. Kassel, A. L. Rheingold, *Organometallics* **2006**, *25*, 1742–1748; for $MePH_2{\cdot}BH_3$, see: e) R. Noble-Eddy, S. L. Masters, D. W. H. Rankin, D. A. Wann, B. Khater, J.-C. Guillemin, *Dalton Trans*. **2008**, 5041–5047; for cyclopropyl- and $ClCH_2PH_2{\cdot}BH_3$, see: f) M. Hurtado, M. Yánez, R. Herrero, A. Guerrero, J. Z. Dávalos, J.-L. M. Abboud, B. Khater, J.-C. Guillemin, *Chem. Eur. J.* **2009**, *15*, 4622–4629; for $FcCH_2PH_2{\cdot}BH_3$, see: g) M. A. Pet, M. F. Cain, R. P. Hughes, D. S. Glueck, J. A. Golen, A. L. Rheingold, *J. Organomet. Chem*. **2009**, *694*, 2279–2289; for primary ferrocenylphosphine–boranes, see: h) S. Pandey, P. Lönnecke, E. Hey-Hawkins, *Eur. J. Inorg. Chem*. **2014**, 2456–2465; for $p$-TolPH$_2{\cdot}$BH$_3$, see: i) U. S. D. Paul, H. Braunschweig, U. Radius, *Chem. Commun*. **2016**, *52*, 8573–8576; for $PhPH_2{\cdot}BH_3$, see: j) T. N. Hooper, A. S. Weller, N. A. Beattie, S. A. Macgregor, *Chem. Sci*. **2016**, *7*, 2414–2426.
[15] For $PhPH_2{\cdot}BH_3$, see: a) E. Wiberg, H. Nöth, *Z. Naturforsch*. **1957**, *12b*, 125–126; for $(Mes^*O)PH_2{\cdot}BH_3$, see: b) E. Rivard, A. J. Lough, I. Manners, *J. Chem. Soc., Dalton Trans*. **2002**, 2966–2972; for ($p$-$n$BuC$_6$H$_4$)PH$_2{\cdot}$BH$_3$ and ($p$-dodecylC$_6$H$_4$)PH$_2{\cdot}$BH$_3$, see: c) H. Dorn, J. M. Rodezno, B. Brunnhöfer, E. Rivard, J. A. Massey, I. Manners, *Macromolecules* **2003**, *36*, 291–297; for ($p$-CF$_3$C$_6$H$_4$)PH$_2{\cdot}$BH$_3$, see: d) T. J. Clark, J. M. Rodezno, S. B. Clendenning, S. Aouba, P. M. Brodersen, A. J. Lough, H. E. Ruda, I. Manners, *Chem. Eur. J.* **2005**, *11*, 4526–4534; for $t$BuPH$_2{\cdot}$BH$_3$, see: e) C. Marquardt, T. Jurca, K.-C. Schwan, A. Stauber, A. V. Virovets, G. R. Whittell, I. Manners, M. Scheer, *Angew. Chem. Int. Ed*. **2015**, *54*, 13782–13786.
[16] a) L. D. Freedman, G. O. Doak, *J. Am. Chem. Soc*. **1952**, *74*, 3414–3415; b) L. Maier, *Progress in Inorganic Chemistry*, **1963**, *5*, 27–210.
[17] M. Kaźmierczak, A. Katrusiak, *J. Phys. Chem. C* **2013**, *117*, 1441–1446.
[18] A. L. Spek, *Acta Cryst.* **2009**, *D65*, 148–155.
[19] The SARS-CoV-2 coronavirus that is resonsible for the respiratory disease COVID-19 provided global challenges and opportunities. It provided us some time for writing up our results that we generated more than a decade ago. We appologise for not sharing these results any sooner.
[20] J. Guang, R. Duwald, J. Maddaluno, H. Oulyadi, S. Lakhdar, A.-C. Gaumont, A. Harrison-Marchand, *Chem. Eur. J*. **2018**, *24*, 6717–6721.
[21] Applying the twofold twin rotation on a chain will change the direction from *up* to *down* but will not create clashes with neighboring chains (additional translations are allowed). We conclude that the energy cost of this operation will be low. It is potentially the structural basis for the occurrence of twinning, here.
[22] a) V. L. Rudzevich, H. Gornitzka, V. D. Romanenko, G. Bertrand, *Chem. Commun*. **2001**, 1634–1635; b) G. Müller, J. Brand, *Organometallics* **2003**, *22*, 1463–1467; c) K. Izod, J. M. Watson, W. Clegg, R. W. Harrington, *Eur. J. Inorg. Chem*. **2012**, 1696–1701.
[23] For related systems, see: a) K. Izod, L. J. Bowman, C. Wills, W. Clegg, R. W. Harrington, *Dalton Trans*. **2009**, 3340–3347; b) K. Izod, C. Wills, E. Anderson, R. W. Harrington, M. R. Probert, *Organometallics* **2014**, *33*, 5283−5294; c) K. Izod, A. M. Madlool, P. G. Waddell, *Organometallics* **2019**, *38*, 2654−2663.
[24] S. Freeman, M. J. P. Harger. *J. Chem. Soc. Perkin Trans.* I **1987**, 1399−1406.
[25] S. J. Conway, J. C. Miller, A. D. Bond, B. P. Clark, D. E. Jane. *J. Chem. Soc. Perkin Trans.* I, **2002**, *14*, 1625–1627.
[26] G. Maerkl, B. Alig. *J. Org. Met. Chem.* **1984**, *273*, 1–30.
[27] R. Appel, D. Gudat, E. Niecke, M. Nieger, C. Porz, H. Westermann. *Z. Naturforsch. B.* **1991**, *46*, 865–883.
[28] O. J. Scherer, N. Kuhn, *J. Org. Chem.* **1974**, *82*, 3–6.
[29] M. Shi, Y. Inoue, *J. Chem. Soc., Perkin Trans.* **1998**, *2*, 2421–2427.
[30] H.-J. Kleiner, US patent 4,632,995, December 30, **1986**.
[31] A. J. M. Duisenberg, L. M. J. Kroon Batenburg, A. M. M. Schreurs, *J. Appl. Cryst.* **2003**, *36*, 220–229.
[32] G. M. Sheldrick, **2014**. SADABS and TWINABS. Universität Göttingen, Germany.
[33] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112–122.
[34] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3–8.
[35] Z. Otwinowski, W. Minor, **1997**. *Methods in Enzymology*, Vol. *276*, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
[36] A. M. M. Schreurs, X. Xian, L. M. J. Kroon-Batenburg, *J. Appl. Cryst.* **2010**, *43*, 70–82.
[37] A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* **1999**, *32*, 115–119.
[38] R. Herbst-Irmer, G. M. Sheldrick, *Acta Cryst.* **1998**, *B54*, 443–449.

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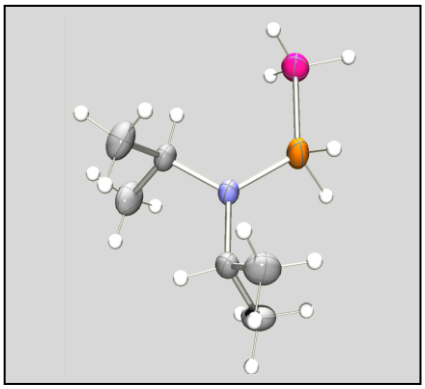

A range of differently substituted primary phosphine-boranes ($RPH_2{\cdot}BH_3$) are now accessible that as unprotected phosphines difficult to handle or even unstable. In particular, the synthesis of the aminophosphane-boranes ($R_2NPH_2{\cdot}BH_3$) offers new opportunities to use as versatile building blocks in the syntheses of organophosphorus compounds.

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