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DOI
10.1002/chem.202002367

Publication date
2020

Document Version
Final published version

Published in
Chemistry-A European Journal

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Citation for published version (APA):

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Easy Access to Phosphine-Borane Building Blocks

G. Bas de Jong[a, b] Nuria Ortega,[b] Martin Lutz,[c] Koop Lammertsma,[b, d] and J. Chris Slootweg[a, b]

Abstract: In this paper, we highlight the synthesis of a variety of primary phosphine-boranes (RPH$_2$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$_2$NPH$_2$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-BH$_4$] of which the phenyl-derivative Li$_2$[PhP-BH$_4$] 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 (hydrophosphinatation)[2] or substitution reactions. The latter proceeds typically by in situ mono or double deprotonation affording the reactive phosphane diide M[RP][3] and phosphanediide M$_2$[RP] intermediates.[4] Notable examples include the pyrophoric phenylphosphine (PhPH$_3$) that provides the useful, but poorly characterized, phenylphosphonediide M$_2$[PhP],[5] and the pyrophoric and hazardous 1,2-bis-phosphinobenzene 1,2-(PhP)$_2$C$_6$H$_4$[6] that is required to produce the privileged DuPhos ligand class.[7] A clear drawback of these primary phosphines is their pyrophoric nature, high sensitivity to oxidation and noxious character,[8] which requires experienced chemists with dedicated lab facilities to handle these compounds safely.[9] Furthermore, the appealing primary (dialkylamino)phosphines (R$_2$NPH$_2$) that are suitable for further functionalization (treatment with HCl provides the corresponding chlorophosphines)[10] are, in addition, thermally labile. For example, iPr$_2$NPH$_2$ decomposes upon attempted isolation.[11]

Protecting the phosphorus lone pair with a borane (BH$_3$) moiety offers advantages,[11] as the corresponding primary phosphine-boranes (RPH$_2$BH$_3$) are easier to handle,[12] but also provide access to interesting polyphosphinoborane material [RPH-BH$_3$], 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$_3$·THF or BH$_3$·SMe$_2$.[12, 14] Yet, Noth and later Manners et al. described that the direct synthesis of some selected primary phosphine-boranes is also feasible by using Li[BH$_4$],[11] 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 aryl-phosphine-boranes that are also applicable for primary aminophosphine-boranes (R$_2$NPH$_2$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$_2$BH$_3$), including the bis-borate protected 1,2-bis-phosphinobenzene 1,2-(PhP)$_2$C$_6$H$_4$ and present the first single-crystal structure of the phenylphosphonediide Li$_2$[PhP-BH$_4$].

Results and Discussion

Treatment of dichlorophosphines 1a-c (R=Ph (a), Mes (b), tBu (c)) with 2 equiv of Li[BH$_4$] in diethyl ether afforded after work-up easy access to the colorless primary phosphine-boranes.
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[AlH₄] cf. PhPCl₂ reduction to PhPH₃, max. 55% yield (lit. value)⁴⁶).

Interestingly, treatment of 1,2-bis(dichlorophosphino)benzene (1d; 1,2-(PCl₂)₃C₆H₄) with Li[BH₄] in diethyl ether afforded the novel bis-phosphine-borane 1,2-(PH₂BH₃)₃C₆H₄ (2d, δ¹³P(H) = −52.4 (J(P,B) = 34.4 Hz), δ¹⁰B NMR = −41.5 (J(B,H) = 103.29 Hz, 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⋅⋅⋅H–B and C–H⋅⋅⋅H–B interactions in the solid state as a result of the oppositely charged hydrogen atoms (Table 2), which also explains the low melting point of 1.0–2.0 °C (see Experimental). In the crystal structure of 1,2-(PPh₂BH₃)₃C₆H₄ (1d) 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) Å) bond lengths for an arylphosphine-borane. 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⋅⋅⋅H–B and C–H⋅⋅⋅H–B interactions in the solid state as a result of the oppositely charged hydrogen atoms (Table 2), which also explains the low melting point of 1.0–2.0 °C. 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.²⁵ 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.

We then selected P-phenyl and P-(diisopropylamino) 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 phosphaneide 3a-e with trimethylsilylchloride to afford the bis(trimethylsilyl)phosphine-boranes 4 (Scheme 2). In both cases, phosphine-borane 2c could be readily deprotonated with 2 equiv of n-butylithium in THF at −78 °C (3a; δ¹³P(H) = −166.4, δ¹⁰B = 0.6). Subsequent treatment with Me₂SiCl and work-up afforded PhP(SiMe₃)₂BH₃ (4a; 98%; δ¹³P(H) = −95.6 (J(P,B) = 32.4 Hz), δ¹⁰Si = 6.0 (J(Si,B) = 48.5 Hz), δ¹³B = −40.1 (J(B,H) = 98.3 Hz, J(B,P) = 24.7 Hz)) and 1Pr₂N(SiMe₃)₂BH₃ (4e; 89%; δ¹³P(H) = 1.1 (J(P,B) = 26.6 Hz), δ¹⁰Si = 2.2 (J(Si,B) = 72.2 Hz); δ¹³B = −35.4 ppm (J(B,H) = 98.8 Hz, J(B,P) = 34.7 Hz) as colorless solids. Single crystals of 4e were obtained from a

![Figure 1. Molecular structure of 1,2-(PH₂BH₃)₃C₆H₄ (2d) in the crystal (displacement ellipsoids are set at 50% probability).](image)

### Table 1. δ¹³P(H) and δ¹⁰B NMR chemical shifts including δ¹³P(H) and δ¹⁰B coupling constants of compounds 2a–h, 3a, and 4a–e.

<table>
<thead>
<tr>
<th>δ¹³P(H) [ppm]</th>
<th>δ¹³P(H) [Hz]</th>
<th>δ¹⁰B NMR [ppm]</th>
<th>δ¹⁰B [Hz]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>−47.4</td>
<td>34.8</td>
<td>−42.2</td>
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<tr>
<td>2b</td>
<td>−68.3</td>
<td>40.5</td>
<td>−40.7</td>
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<tr>
<td>2c</td>
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<td>2e</td>
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</tr>
<tr>
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<td>−13.2</td>
<td>45.9</td>
<td>−41.0</td>
</tr>
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<td>48.9</td>
<td>−34.5</td>
</tr>
<tr>
<td>2h</td>
<td>2.1</td>
<td>51.6</td>
<td>−36.7</td>
</tr>
<tr>
<td>3a</td>
<td>−166.4</td>
<td>−</td>
<td>−34.5</td>
</tr>
<tr>
<td>4a</td>
<td>−95.6</td>
<td>32.4</td>
<td>−40.1</td>
</tr>
<tr>
<td>4e</td>
<td>1.1</td>
<td>26.6</td>
<td>−35.4</td>
</tr>
</tbody>
</table>

**Scheme 1.** Synthesis of primary phosphine-boranes RPH₂BH₃, 2. TMP = 2,2,6,6-tetramethylpiperidyl.

**Table 2.** Potential intermolecular dihydrogen bonds with BH₂ as acceptor in the crystal structure of 2d.

<table>
<thead>
<tr>
<th>Bond length</th>
<th>Bond angle</th>
<th>Torsion angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1–H1P–H1B</td>
<td>1.292(18)</td>
<td>2.33(2)</td>
</tr>
<tr>
<td>C4–H4–H4B</td>
<td>0.94(2)</td>
<td>2.38(3)</td>
</tr>
</tbody>
</table>

Symmetry codes: i: x, y, z; ii: x−1/2, y, z−1/2; ii: x+1/2, y, z. D = donor, A = acceptor BH₂.
mixture of diethyl ether and pentane at \(-30^\circ\text{C}\). 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 BH3 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\(^{[16]}\) 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 0.976 g cm\(^{-3}\), and a low melting point (28.7–29.4 °C).

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 \(-78^\circ\text{C}\) 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\(^{iv}\) 2.540(4), P1–Li2\(^{iv}\) 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 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\(^{iv}\) 1.995(4), O2–Li1 2.015(4), O2–Li2\(^{iv}\) 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 the 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 H8–H–Li interactions has been reported for related lithium borane phosphanides Li[R,P-BH\(_3\)]\(^{22,23}\) but the crystal structure of 3a represents, in fact, the first structural characterization of an arylphosphane- diide M\(_2\)(ArP) in the solid state.
Furthermore, we showed that the use in THF, 100.0 mmol) in Et₂O 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 PhH₃-BH₃ (2a) as colorless crystals (5.29 g, 42.7 mmol, 85.3%). ¹H NMR (400.1 MHz, CDCl₃): δ = 0.90 (br. q, J(H,B) = 10.6 Hz; J(H,H) = 7.8 Hz, 2H; PH₃); 7.43–7.59 (m, 3H; m-pPh₂H); 7.65–7.77 (m, 2H; o-PH₂H); ¹³C(NMR (128.4 MHz, CDCl₃): δ = −42.2 (dt, J(H,B) = 101.2 Hz, J(B,P) = 36.2 Hz); ¹¹B NMR (100.0 MHz, CDCl₃): δ = 119.9 (d, J(B,C) = 57.7 Hz; ipso-PHC); 129.2 (d, J(C,P) = 10.6 Hz; m-PHC); 132.0 (d, J(C,P) =

Conclusion

We herein provide a facile protocol that gives easy access to a range of substituted primary phosphine-boranes (RP₃H₂BH₃). 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 (RN₃H₂BH₃) offer new opportunities as versatile building block in the synthesis of organophosphorus compounds, which can be easily deprotected using common procedures. Furthermore, we showed that the use of BH₃ also offers increased solubility and stability of reactive intermediates, which allowed the first structural characterization of an arylphosphonediide 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 subdued sodium mirror. ¹H and ¹³C(¹H) NMR spectra were recorded on a Bruker Avance 250, Bruker Avance 400 or Bruker Avance 500 and internally referenced to the residual solvent resonances (CDCl₃: ¹H = 7.26, ¹³C(¹H) = 77.2; THF-δ₈: ¹H = 3.58, 1.72, ¹³C(¹H) = 67.2, 5.3 ppm or TMS; ¹⁹F(¹H), ¹⁹B(¹H), ¹¹B, Li and ²⁵Si NMR spectra were recorded on a Bruker Avance 250 or Bruker Avance 400 and externally referenced (85% H₃PO₄, BF₃·OEt₂ and LiCl, respectively). Chemical shifts are reported in ppm. High resolution mass spectra were recorded on a Bruker MicroTOF with ESI nebulizer (ESI). Melt- ing points were measured in sealed capillaries and are uncorrected. PhPCl₃, BuPCl₃, PhP·BH₃·ClCl (DME) (R = Mes,[²⁶] iPr₂N,[²⁵] Cy₂N,[²⁶] TMP[²⁷] and (Me₂Si)₃N)[³⁸] were prepared according to known literature procedures.

Synthesis and characterization

**PhH₃-BH₃ (2a):** A solution of PhPCl₃ (6.8 mL, 50.0 mmol) in Et₂O (100 mL) was added dropwise in about 30 minutes to a solution of Li[BH₄] (50.0 mL, 2.0 m in THF, 100.0 mmol) in Et₂O (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 PhH₃-BH₃ (2a) as colorless crystals (5.29 g, 42.7 mmol, 85.3%). ¹H NMR (400.1 MHz, CDCl₃): δ = 0.90 (br. q, J(H,B) = 10.6 Hz; J(H,H) = 7.8 Hz, 2H; PH₃); 7.43–7.59 (m, 3H; m-pPh₂H); 7.65–7.77 (m, 2H; o-PH₂H); ¹³C(NMR (128.4 MHz, CDCl₃): δ = −42.2 (dt, J(H,B) = 101.2 Hz, J(B,P) = 36.2 Hz); ¹¹B NMR (100.0 MHz, CDCl₃): δ = 119.9 (d, J(B,C) = 57.7 Hz; ipso-PHC); 129.2 (d, J(C,P) = 10.6 Hz; m-PHC); 132.0 (d, J(C,P) =

2.7 Hz; p-PhCl, 133.7 (d, J(C,P) = 9.1 Hz; o-PhCl); 31P{1H} NMR (101.3 MHz, CDC13); δ = −47.4 ppm (q, J(P,B) = 34.8 Hz).

**MesPh-BH2 (2b):** A solution of MesPCl3 (1.10 g, 4.98 mmol) in Et2O (10 mL) was added dropwise in about 30 minutes to a solution of Li[BH4] (5.0 mL, 2.0 M in THF, 10.0 mmol) in Et2O (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 then removed in vacuo, the product was extracted into pentane (3 × 10 mL) and then filtered over Celite. Removal of pentane in vacuo afforded MesPh-BH2 (2b) 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, CDCl3); δ = 0.85 (br, q, J(H,B) = 98.2 Hz, 3H; BH3); 2.30 (s, 3H; p-PhCH3); 2.45 (s, 6H; o-PhCH3); 5.46 (dd, J(P,H) = 370.4 Hz, J(H,J) = 7.6 Hz, 2H; PH3); 6.94 (d, J(J,H) = 3 Hz, 2H; m-PhH); 1H{13C} NMR (400.1 MHz, CDCl3); δ = 0.84 (dt, J(H,J) = 15.6, J(J,H) = 7.8 Hz, 3H; BH3); 2.30 (s, 3H; p-PhCH3); 2.45 (s, 6H; o-PhCH3); 5.46 (dq, J(J,H) = 370.4 Hz, J(H,J) = 7.6 Hz, 2H; PH3); 6.94 (d, J(J,H) = 3 Hz, 2H; m-PhH). 13C NMR (100.6 MHz, CDCl3); δ = 21.1 (d, J(J,C) = 1.0 Hz; p-PhCH3); 21.6 (d, J(J,C) = 8.5 Hz; o-PhCH3); 65.8 (d, J(J,C) = 57.9 Hz; ipso-Ph3); 129.4 (d, J(J,C) = 8.3 Hz; m-PhC); 141.0 (d, J(J,C) = 6.0 Hz; o-PhC); 141.5 (d, J(J,C) = 2.3 Hz; p-PhC); 31P{1H} NMR (101.3 MHz, CDCl3); δ = −68.3 ppm (br, d, J(P,B) = 40.5 Hz).

**BuPPh-BH2 (2c):** A solution of BuP(Cl3) (31.5 g, 19.8 mmol) in Et2O (40 mL) was added dropwise in about 30 minutes to a solution of Li[BH4] (20 mL, 2.0 M in THF, 20.0 mmol) in Et2O (80 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 then removed in vacuo, the product was extracted into pentane (3 × 20 mL) and then filtered over Celite. After removal of all volatiles, subsequent distillation (89–91°C, 10 mbar) yielded BuPPh-BH2 (2c). The resulting yellow oil (22.38 g, 79.98 mmol, 53.3%) was separated from the Ph3P by fractional distillation (81–84°C, 3×10–2 mbar) yielding 1,2-(P(Cl)3)2CH3 as a pale yellow oil (39.39 g, 140.7 mmol, 93.8%), 85% pure according to 31P{1H} NMR spectroscopy. Further purification of 1,2-(P(Cl)3)2CH3 can be achieved by fractional distillation using a spinning band (60 × 2.5 cm, 4 bladed), yielding 1,2-(P(Cl)3)2CH3 as a colorless oil (22.38 g, 79.98 mmol, 53.3%).

1H NMR (500.2 MHz, CDCl3); δ = 7.70–7.77 (m, 2H; m-PhH); 8.20–8.27 (m, 2H; o-PhH); 13C NMR (125.8 MHz, CDCl3); δ = 130.6 (t, J(J,C) = 6.4 Hz; m-PhC); 133.4 (s, o-PhC); 144.3 (t, J(J,C) = 12.7 Hz; ipso-Ph3); 31P{1H} NMR (101.3 MHz, CDCl3); δ = 151.6 ppm.

**Step 3. Synthesis of 1,2-(P(Cl)3)2CH3 (2d):** A solution of Li[BH4] (1.81 g, 20 ml in THF, 3.62 mmol) in Et2O (5 ml) was added dropwise in about 30 minutes to a solution of 1,2-(P(Cl)3)2CH3 (0.29 g, 1.04 mmol) in Et2O (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 Et2O (3 × 10 mL) followed by a second filtration. Removal of Et2O at 0°C in vacuo yielded 1,2-(P(Cl)3)2CH3 (2d) as small colorless needles, 99% pure according to 31P NMR spectroscopy (0.11 g, 0.65 mmol, 64%). Recrystallization from a mixture of DCM and pentane at −78°C yielded colorless crystals suitable for X-ray analysis. Mp: 81.7–82.8°C. 1H NMR (400.1 MHz, CDCl3); δ = 0.96 (br, q, J(H,J) = 99.44 Hz, 6H; BH3); 5.73 (dq, J(J,H) = 373.9 Hz, J(H,J) = 8.1 Hz, 4H; PH3); 7.66–7.73 (m, 2H; m-PhH); 7.92–8.01 (m, 2H; o-PhH); 13C NMR (400.1 MHz, CDCl3); δ = 96.0 (dt, J(J,C) = 15.66 Hz, 6.65 Hz, 7.83 Hz, 6H; BH3); 5.73 (dq, J(J,H) = 373.9 Hz, J(H,J) = 8.1 Hz, 4H; PH3); 7.66–7.73 (m, 2H; m-PhH); 7.92–8.01 (m, 2H; o-PhH); 13C NMR (128.4 MHz, CDCl3); δ = −41.5 (dq, J(J,H) = 103.29 Hz, J(H,J) = 25.0 Hz); 31P{1H} NMR (128.4 MHz, CDCl3); δ = −3.05 (dd, J(J,C) = 25.7 Hz, J(J,P) = 3.6 Hz; ipso-Ph3); 13C NMR (125.8 MHz, CDCl3); δ = −128.5 (dd, J(J,C) = 11.8 Hz, J(J,P) = 2.7 Hz; m-PhC); 136.1 (dd, J(J,P) = 15.4 Hz, J(J,C) = 7.3 Hz; o-PhC); 31P{1H} NMR (101.3 MHz, CDCl3); δ = −52.4 ppm (br, d, J(P,B) = 34.4 Hz); HR ESI-MS: m/z (%): 391 [M–H]−, 167.05 (2.2) [M−BH3, H]+; 155.04 (2.0) [M−BH3, H2]+; Elemental analysis calcd (%) for C15H23P3: C, 68.06; H, 9.68; Found: C, 68.06; H, 9.68.

** Parr NH2P-Cl3 (2e):** A solution of ParrNPCl3 (4.6 mL, 25.0 mmol) in Et2O (50 mL) was added dropwise in about 30 minutes to a solution of Li[BH4] (25.0 mL, 2.0 M in THF, 50.0 mmol) in Et2O (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 then removed in vacuo, the product was extracted into pentane (3 × 100 mL) and then filtered over Celite. Removal of pentane in vacuo.
afforded iPr$_2$NH$_2$BH$_2$ (2e) as a colorless oil (3.35 g, 22.8 mmol, 91.3%). Crystals suitable for X-ray analysis were obtained from di-ethyl ether at –70 °C. M.p. 1.0–2.0 °C; 1H NMR (250.1 MHz, CDCl$_3$): δ = 1.12 (d, J(H,H) = 6.8 Hz, 12H; CH$_2$), 3.57 (sept, J(H,H) = 6.8 Hz, 2H; CH$_2$), 5.93 (dq, J(H,P) = 379.4 Hz, J(H,H) = 6.8 Hz, 2H; PH$_3$), signals for BH$_2$ were unresolved; 1H[15]B NMR (400.1 MHz, CDCl$_3$): δ = 0.67 (dt, J(H,P) = 15.2, J(H,H) = 6.4 Hz, 3H; BH$_3$), 1.12 (d, J(H,H) = 6.8 Hz, 12H; CH$_2$), 3.57 (sept, J(H,H) = 6.8 Hz, 2H; CH$_2$), 5.93 (dq, J(H,P) = 379.4 Hz, J(H,H) = 6.3 Hz, 2H; CH$_2$); 1B NMR (128.4 MHz, CDCl$_3$): δ = –41.4 (dq, J(B,P) = 99.9 Hz, J(B,H) = 30.9 Hz); 13C NMR (100.6 MHz, CDCl$_3$): δ = 21.5 (d, J(C,P) = 3.2 Hz; CH$_2$); 47.2 (d, J(P,C) = 3.7 Hz; CH$_2$); 1H[15]P NMR (101.3 MHz, CDCl$_3$): δ = –16.8 ppm (q, J(P,B) = 50.8 Hz); HR ESI-MS: m/z (%) = 146.13 (0.2) [M–H]–, 144.11 (0.3) [M–H$_2$], Elemental analysis calcd (%) for C$_5$H$_8$BNP (M–H): 146.1277, found 146.1274.

Cy$_2$NPH$_2$BH$_2$ (2f): A solution of Cy$_2$NPCI$_2$ (1.41 g, 5.0 mmol) in Et$_2$O (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$_2$O (20 mL) at 0 °C. A colorless precipitate formed and the reaction mixture was stirred for 30 minutes during which the temperature was allowed to warm to room temperature. The solvent was removed in vacuo, the product was extracted into pentanes (3 × 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$_2$ (2f) as colorless crystals (0.87 g, 4.1 mmol, 81.6%). M.p. 48.2–49.9 °C; 1H NMR (400.1 MHz, CDCl$_3$): δ = 0.71 (br. q, J(H,P) = 94.7 Hz, 3H; BH$_3$), 0.97–1.11 (m, 2H; CyH), 1.22–1.36 (m, 4H; CyH), 1.42–1.54 (m, 4H; CyH), 1.57–1.67 (m, 6H; CyH), 1.74–1.82 (m, 4H; CyH), 2.99–3.13 (m, 2H; CyH), 3.06 (dq, J(H,P) = 379.8 Hz, J(H,H) = 6.3 Hz, 2H; PH$_3$); 1H[15]B NMR (400.1 MHz, CDCl$_3$): δ = 0.71 (dt, J(H,P) = 15.2 Hz, J(H,H) = 6.3 Hz, 3H; BH$_3$); 13C NMR (100.6 MHz, CDCl$_3$): δ = 3.07 (m, 12 H; Hex), 1.30 (m, 16 H; Hex), 1.72 (br. s, 2H; THF-$d_8$); 1H[15]P NMR (128.4 MHz, CDCl$_3$): δ = –41.0 (dq, J(P,B) = 96.8 Hz, J(P,H) = 54.9 Hz); 13C NMR (68.9 MHz, CDCl$_3$): δ = 25.3 (s, NCH$_2$CH$_2$), 25.9 (s, NCH$_2$CH$_2$), 32.3 (d, J(C,P) = 3.0 Hz; NCH$_2$CH$_2$), 56.5 (d, J(C,P) = 3.2 Hz; NCH$_2$CH$_2$); 1P[15]H NMR (162.0 MHz, CDCl$_3$): δ = –12.1 ppm (br. q, J(P,B) = 45.9 Hz); HR ESI-MS: m/z (%) = 242.18 (65.0) [M–P+H]–, 226.19 (100.0) [M–P]; Elemental analysis calcd (%) for Cy$_2$H$_8$BNP (M–P): 226.1904, found 226.1901.

(Me$_2$S$_2$N)$_2$PH$_2$BH$_2$ (2h): 1.23–1.31 (m, J(H,H) = 6.8 Hz, 2H; PH$_3$); 1H[15]B NMR (400.1 MHz, CDCl$_3$): δ = 0.68 (br. q, J(H,P) = 84.9 Hz, 3H; BH$_3$), 0.87 (m, 12H; Hex), 1.30 (m, 16 H, 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-PhH$_3$), 6.53–6.57 (m, 2H; m-PhH$_3$), 7.28–7.31 (m, 2H; o-PhH$_3$); 13C NMR (128.4 MHz, THF–$d_8$): δ = –15.9 ppm (br. q, J(H,P) = 84.5 Hz); 1H[15]P NMR (100.6 MHz, THF–$d_8$): δ = –15.3 (s, Cy$_2$H$_8$); 13C NMR (128.4 MHz, THF–$d_8$): δ = –0.62 (s); 18B NMR (128.4 MHz, THF–$d_8$): δ = –34.0 (br. q, J(B,P) = 84.5 Hz); 18C NMR (100.6 MHz, THF–$d_8$): δ = 153.8 (s, Cy$_2$H$_8$), 24.41 (s; Cy$_2$H$_8$), 68.3 (m; Cy$_2$TBF–complex), 33.4 (s; Cy$_2$H$_8$), 68.3 (m; Cy$_2$TBF–complex), 69.1 (s; Cy$_2$TBF–complex), 117.1 (s; p-PhH$_3$), 126.7 (d, J(C,P) = 4.6 Hz; m-PhH$_3$), 133.6 (d, J(C,P) = 12.1 Hz; o-PhH$_3$), 165.9 (d,
PhSi(SMe)₂B₂H₆ (4a): 2 equiv of nBuLi (6.88 mL, 1.6 M in hexanes, 11.0 mmol) was added dropwise to a solution of PhH₂B₂H₆ (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 Me₅SiCl (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 PhSi(SMe)₂B₂H₆ (4a) as a colorless solid (1.25 g, 4.7 mmol, 98.2%). M.p. 65.8–66.9 °C. ¹H NMR (250.1 MHz, CDCI₃): δ = 0.34 (d, 3J(Hp) = 5.7 Hz, 18H; Si(CH₃)₃), 7.32–7.41 (m, 3H, mp-PPh₃), 7.56–7.67 (m, 2H, o-PPh₃), signals for BH₂ were unresolved; ¹H(B) NMR (400.1 MHz, CDCI₃): δ = 0.34 (d, 3J(Hp) = 5.7 Hz, 18H; Si(CH₃)₃), 0.88 (d, 3J(Hp) = 10.4 Hz; 3H, BH₃), 7.32–7.41 (m, 3H, mp-PPh₃), 7.56–7.67 (m, 2H, o-PPh₃); ¹B NMR (128.4 MHz, CDCI₃): δ = –40.1 (dq, 3J(BH) = 98.3 Hz; 3J(BP) = 24.7 Hz); ¹³C NMR (62.9 MHz, CDCI₃); δ = –1.3 (J(CP) = 8.6 Hz; Si(CH₃)₃), 126.5 (δ, 3J(CP) = 31.3 Hz; ipso-PPh₃), 128.6 (δ, 3J(CP) = 0.9 Hz; m-PPh₃), 129.3 (δ, 3J(CP) = 2.5 Hz; p-PPh₃). ¹³C NMR (79.5 MHz, CDCI₃): δ = 6.0 (δ, 1J(SiP) = 48.5 Hz); ³¹P NMR (162.0 MHz, CDCI₃): δ = –95.6 ppm (br. d, 3J(PB) = 32.4 Hz).

Pr₂NP(SMe)₂B₂H₆ (4e): 2 equiv of nBuLi (10.46 mL, 1.6 M in hexanes, 19.74 mmol) was added slowly to a solution of Pr₂NP(B₂H₆) (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 Me₅SiCl (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 Pr₂NP(SMe)₂B₂H₆ (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. ¹H NMR (250.1 MHz, CDCI₃): δ = 0.39 (d, 3J(Hp) = 5.3 Hz, 18H; Si(CH₃)₃), 1.29 (d, 3J(HH) = 6.8 Hz, 12H; CH(CH₃)₂), 3.29 (d, sept, 3J(Hp) = 14.7 Hz; 3J(HH) = 6.8 Hz, 2H; CH₂CH₂Si), signals for BH₂ were unresolved; ¹H(B) NMR (400.1 MHz, CDCI₃): δ = 0.39 (d, 3J(Hp) = 5.3 Hz, 18H; Si(CH₃)₃), 1.03 (d, 3J(HH) = 7.9 Hz, 3H; BH₂), 1.29 (d, 3J(HH) = 6.8 Hz, 12H; CH(CH₃)₂), 3.29 (d, sept, 3J(Hp) = 14.7 Hz; 3J(HH) = 6.8 Hz, 2H; CH₂CH₂Si): ¹³B NMR (128.4 MHz, CDCI₃): δ = –35.4 (dq, 3J(BH) = 98.8 Hz; 3J(BP) = 34.7 Hz); ¹³C NMR (125.8 MHz, CDCI₃): δ = –0.3 (d, 2J(CP) = 8.6 Hz; Si(CH₃)₃), 24.1 (d, 3J(CP) = 1.3 Hz; CH₂CH₂Si), 51.6 (d, 3J(CP) = 0.9 Hz; CH₂CH₂Si); ³¹P NMR (79.5 MHz, CDCI₃): δ = 0.2 (dq, 3J(SiP) = 72.2 Hz); ³¹P(H) NMR (162.0 MHz, CDCI₃): δ = 1.11 ppm (br. d, 3J(PB) = 26.6 Hz).

X-ray crystal structure determinations

2 d: C₅H₅B₆P₅, Fw = 169.73, colorless needle, 0.60 x 0.18 x 0.18 mm³, orthorhombic, Pbcn (no. 61), a = 9.2604(4), b = 8.0989(2), c = 26.4819(7) Å, V = 1986.12(11) Å³, Z = 8, D₁ = 1.135 g·cm⁻³, μ = 0.37 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 θ/λ)max = 0.65 Å⁻¹. The intensity integration was performed with the EvalCCD software.¹⁹ A multi-scan absorption correction and scaling was performed with SADABS²⁰ (correction range 0.73–0.94). A total of 22295 reflections was measured, 2274 reflections were unique (Rint = 0.028), 1921 reflections were ob-

served (l>2σ(I)). The structure was solved with direct methods using SHELXS-97.²¹ Structure refinement was performed with SHELXL-2018 on F² 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 [l > 2σ(I)]: 0.0293/ 0.0714. R1/wR2 [all refl.]: 0.0395/ 0.0771. S = 1.051. Residual electron densi-
ty between –0.22 and 0.32 e Å⁻³. Geometry calculations and check-
ing for higher symmetry was performed with the PLATON pro-
gram.²²

2e: C₅H₅B₆NP₅, Fw = 291.37, colorless block, 0.60 x 0.60 x 0.42 mm³, monoclinic, P2₁/c (no. 14), a = 17.1577(4), b = 12.5113(3), c = 18.4370(6) Å, β = 99.7061(1)°, V = 3965.94(18) Å³, Z = 8, D₁ = 1.143 g·cm⁻³, μ = 0.87 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 θ/λ)max = 0.65 Å⁻¹. The intensity integration was performed with the HKL2000 software.²³ A multi-scan absorption correction and scaling was performed with SADABS₂⁰ (correction range 0.65–0.90). A total of 8401 reflections was measured, 1203 reflections were unique (Rint = 0.033), 1030 re-
flections were observed [l>2σ(I)]. The structure was solved with direct methods using SHELXS-97.²¹ Structure refinement was performed with SHELXL-2018 on F² 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 kept refined freely with isotropic displacement parameters. 86 Parameters were refined with no restraints. R1/wR2 [l > 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 pro-
gram.²⁰
0.976 g cm⁻³, χ = 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 θ/λ)max = 0.65 Å⁻¹. The intensity integration was performed with the Eval15 software.¹⁰ A multi-scanning absorption correction and scaling was performed with SADABS¹¹ (correction range 0.74–0.90). A total of 103227 reflections was measured, 9124 reflections were unique (Rint = 0.032), 7809 reflections were observed (I > 2σ(I)). The structure was solved with direct methods using SHELXS-97.¹² Structure refinement was performed with SHELXL-2018 on F² for 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/ 0.0882. 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.¹³

Deposition Numbers 2001504, 2001505, 2001507, and 2001506 (2d, 2e, 3a, 4e, respectively) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Services service www.ccdc.cam.ac.uk/structures.

Acknowledgements

This work was partially supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (NWO/CW). We thank B. Bruyneel for high-resolution mass spectrometry, Frans J. J. de Kanter for NMR spectroscopy, and Erik P. A. Couzijn for preliminary findings. N.O. thanks the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO/CW). We thank B. Bruyneel for high-resolution crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Services service www.ccdc.cam.ac.uk/structures.

Conflict of interest

The authors declare no conflict of interest.

Keywords: crystal structures • phosphanedilide • phosphine borane • primary phosphine • synthesis


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Manuscript received: May 13, 2020
Revised manuscript received: June 29, 2020
Accepted manuscript online: June 30, 2020
Version of record online: October 23, 2020