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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 (RPH₂BH₃) from the corresponding dichlorophosphines, simply by using Li[BH₄] as reductant and provider of the BH₃ protecting group. The method offers facile access not only to alkyl- and arylphosphine-boranes, but also to aminophosphine-boranes (R₂NPH₂BH₃) that are convenient building blocks but without the protecting BH₃ 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[RP-BH₃] of which the phenyl-derivative Li[PhP(BH₃)] was structurally characterized in the solid state.

Introduction

Primary phosphines (RPH₂) are the archetypical building blocks that are used for the creation of a plethora of functionalized phosphorus compounds via addition (hydrophosphinacation) or substitution reactions. The latter proceeds typically by in situ mono or double deprotonation affording the reactive phosphane diide M[RP] and phosphanediide M₂[RP] intermediates. Notable examples include the pyrophoric phenylphosphine (PhPH₂) that provides the useful, but poorly characterized, phosphanediide M₂[PhP] and the pyrophoric and hazardous 1,2-bis-phosphinobenzene 1,2-(PH₂)₂C₆H₄ that is required to produce the privileged DuPhos ligand class. A clear drawback of these primary phosphines is their pyrophoric nature, high sensitivity to oxidation and noxious character, which requires experienced chemists with dedicated lab facilities to handle these compounds safely. Furthermore, the appealing primary (dialkylamino)phosphines (R₂NPH₂) that are suitable for further functionalization (treatment with HCl provides the corresponding chlorophosphines) are, in addition, thermally labile. For example, iPr₂NPH₂ decomposes upon attempted isolation.

Protecting the phosphorus lone pair with a borane (BH₃) moiety offers advantages, as the corresponding primary phosphine-boranes (RPH₂BH₃) are easier to handle, but also provide access to interesting polyphosphinoborane material [RP-BH₃]ₙ by catalytic dehydrogenation/dehydrocoupling. Typically, primary phosphine-boranes are prepared in a two-step procedure by Li[AlH₄] reduction of the corresponding dichlorophosphines and subsequent treatment of the resulting primary phosphine with BH₃, THF or BH₃·SMe₂. Yet, Nöth and later Manners et al. described that the direct synthesis of some selected primary phosphine-boranes is also feasible by using Li[BH₄], which does not require the handling of primary phosphate 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 (R₂NPH₂BH₃). We were further curious if the stabilizing BH₃ moiety would also offer the possibility for characterizing phosphanediides M₂[RP] in the solid state. Herein, we report on a robust protocol for the synthesis of a range of substituted phosphate-borane building blocks (RPH₂BH₃), including the bis-borane protected 1,2-bis-phosphinobenzene 1,2-(PH₂)₂C₆H₄ and present the first single-crystal structure of the phenylphosphanediide Li[PhP(BH₃)].

Results and Discussion

Treatment of dichlorophosphines 1a–c (R = Ph (a), Mes (b), tBu (c)) with 2 equiv of Li[BH₄] 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]₄ (cf. PPhCl₂ reduction to PhPPh₂ max. 55% yield (lit. value)⁴¹). Interestingly, treatment of 1,2-bis(dichlorophosphino)benzene (1d; 1,2-(P(Cl)₂C₆H₄)₂) with Li[BH₄] in diethyl ether afforded the novel bis-phosphine-borane 1,2-(P(H₂)₂B)₂C₆H₄ 2d, δ¹³P(H) = −52.4 (J(P,B) = 34.4 Hz), δ¹¹B 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) Å, 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),²⁵ where the B₄H₄ moiety functions as the acceptor.

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[BH₄]. Indeed, treatment of 1e–h (R₈iPr N (e), C₆H₆ N (f), TMP (g), (Me₅Si)₂N (h)) with 2 equiv of Li[BH₄] in diethyl ether at 0 °C afforded after work-up the colorless primary aminophosphine-boranes 2e–h (81–98%; δ¹³P(H) = −18.6 (2e), −13.2 (2f), −15.9 (2g), 2.1 (2h); Scheme 1). We obtained suitable crystals for iPr₈NPH₂B₄H₄ 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. Twenty-three 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 synths 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-butylthiium in THF at −78 °C (3a; δ¹³P(H) = −166.4, δ¹¹Li = 0.6). Subsequent treatment with Me₅SiCl and work-up afforded Ph₂P(SiMe₃)₂B₄H₄ 4a; 98%; δ¹³P(H) = −95.6 (J(P,B) = 32.4 Hz), δ²³Si = 6.0 (J(Si,P) = 48.5 Hz), δ¹¹B = −40.1 (J(B,H) = 98.3 Hz, J(B,P) = 24.7 Hz) and iPr₈N(SiMe₃)₂B₄H₄ 4e; 89%; δ¹³P(H) = 1.1 (J(P,B) = 26.6 Hz), δ²³Si = 2.2 (J(Si,P) = 72.2 Hz), δ¹¹B = −35.4 ppm (J(B,H) = 98.8 Hz, J(B,P) = 34.7 Hz) as colorless solids. Single crystals of 4a were obtained from a
The crystal structure of 3a contains two independent molecules. The minor disorder component is 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).

During our investigations,[19] Oulyadi, Gaumont, Harrison-Marchanda et al. reported on the characterization of the gem-dilithium phosphido-borane Li₂[PhP·BH₃] 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 BH₃ moiety might assist the crystallization of this unique dianion and indeed found it to be possible to obtain the highly reactive phosphaneide 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·BH₃] 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⁺ 2.540(4), P1–Li2⁺ 2.561(4) Å; Figure 4). The polymeric chain is supported by the BH₃ 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 2.138 Å, O2–Li1 2.015(4), O2–Li2 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·BH₃] dianion, and one DME molecule. The presence of H₈–H–Li interactions has been reported for related lithium borane phosphinides Li[R,P·BH₃][22,23] but the crystal structure of 3a represents, in fact, the first structural characterization of an arylphosphaneide M₂[ArP] in the solid state.
Conclusion

We herein provide a facile protocol that gives easy access to a range of substituted primary phosphine-boranes (RPPh·BH₃). 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,NPh·BH₃) 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 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. All commercial chemicals were used without further purification. Chemical shifts are reported in ppm. High resolution mass 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 and ¹³C(¹H) NMR spectra were recorded on a Bruker Avance 250, Bruker Avance 400 or Bruker Avance 500 and internally referenced. The residual solvent resonances (CDCl₃). ¹H and ¹³C(¹H) NMR spectra were recorded on a Bruker Avance 250, Bruker Avance 400 or Bruker Avance 500 and externally referenced (85 % H₂O, BF₃·OEt₂ or 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.

Synthesis and characterization

PhPPh·BH₃ (2a): A solution of PhPCl₂ (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 mol 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 × 100 mL) and then filtered over Celite. Removal of pentane in vacuo afforded a colorless solid. Recrystallization from pentane at −30 °C yielded PhPPh·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) = 100.2 Hz, 3H; BH₄). 5.52 (dq, J(H,Ph) = 371.5 Hz, J(H,H) = 7.8 Hz, 2H; PhC). 7.43−7.59 (m, 3H, m-p-PhH); 7.65−7.77 (m, 2H, o-PhH); ¹³B NMR (400.1 MHz, CDCl₃): δ = 0.90 (dt, J(B,Ph) = 16.1, J(H,H) = 8.0 Hz, 3H; BH₄). 5.52 (dq, J(H,Ph) = 371.5 Hz, J(H,H) = 7.8 Hz, 2H; PhC). 7.43−7.59 (m, 3H, m-p-PhH); 7.65−7.77 (m, 2H, o-PhH); ¹³B NMR (128.4 MHz, CDCl₃): δ = −42.2 (dd, J(B,Ph) = 101.2 Hz, J(B,P) = 36.2 Hz); ¹¹C NMR (100.6 MHz, CDCl₃): δ = 119.9 (d, J(C,P) = 57.7 Hz; ipso-PhC), 129.2 (d, J(C,P) = 10.6 Hz; m-PhC), 132.0 (d, J(C,P) =

Figure 4. Part of the polymeric chain in the crystal structure of Li[PhP·BH₃](DME) (3a). Displacement ellipsoids are 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–L11 2.500(3), P1–Li2 2.524(4), P1–Li3 2.540(4), P1–Li2′ 2.561(4), B1–H1B 1.13(3), B1–H2B 1.17(3), B1–H3B 1.16(3), O1–Li1 2.307(4), O1–Li2 1.995(4), O2–Li1 2.014(4), O2–Li2′ 2.520(4), Li1–H2B 1.83(3), Li2–H3B 1.96(3); B1–P1–Li1 113.61(11), B1–P1–Li2 60.62(11), B1–P1–Li3 64.42(10), B1–P1–Li2′ 117.10(11), P1–Li1–P1 111.56(13), O1–Li1–P1 94.92(13), O1–Li1–P1 98.87(15), O1–Li1–P1 102.97(15), O1′–Li2–P1 144.57(18), O2′–Li2–P1 107.13(15), O1′–Li2–P1 102.97(15), O2′–Li2–P1 86.60(12).

Figure 5. One-dimensional coordination chains in β-direction in the crystal structure of Li[PhP·BH₃](DME) (3a). View approximately along the α1-diagonal. Shown are two of the one-dimensional coordination chains which are related by the inversion center of the space group.
2.7 Hz; p-PhCl, 133.7 (d, J(C,P) = 9.1 Hz; o-PhCl); 31P[H] NMR (101.3 MHz, CDCl3); δ = −47.4 ppm (q, J(31P, 31P) = 34.8 Hz). 

MesPh-BH₂ (2b): A solution of MesPCl (1.10 g, 4.98 mmol) in Et₂O (10 mL) was added dropwise in about 30 minutes to a solution of Li[B(Mes)] (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 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(31P, H) = 98.2 Hz, 3H; BH3); 2.30 (s, 3H; p-PhCl); 2.45 (s, 6H; o-PhCl); 5.46 (dq, J(31P, H) = 370.4 Hz, J(31P, H) = 7.6 Hz, 2H; PhH); 6.94 (d, J(31P, H) = 3 Hz, 2H; m-PhH); 1H NMR (400.1 MHz, CDCl3); δ = 0.84 (dt, J(31P, H) = 15.6, J(31P, H) = 7.8 Hz, 3H; BH3); 2.30 (s, 3H; p-PhCl); 2.45 (s, 6H; o-PhCl); 5.46 (dq, J(31P, H) = 370.4 Hz, J(31P, H) = 7.6 Hz, 2H; PhH); 6.94 (d, J(31P, H) = 3 Hz, 2H; m-PhH); 18NMR (128.4 MHz, CDCl3); δ = −40.7 (d, J(31P, H) = 101.3 Hz, J(31P, 31P) = 34.8 Hz); 13C NMR (100.6 MHz, CDCl3); δ = 21.1 (d, J(C,P) = 1.0 Hz; p-PhCl); 21.6 (d, J(C,P) = 8.5 Hz; o-PhCl); 116.8 (d, J(C,P) = 57.9 ppm; ipso-PhCl); 129.4 (d, J(C,P) = 8.3 Hz; m-PhCl); 141.0 (d, J(C,P) = 6.0 ppm; o-PhCl); 141.7 (d, J(C,P) = 2.3 Hz; p-PhCl); 131P[H] NMR (101.3 MHz, CDCl3); δ = −68.3 ppm (br. d, J(31P, 31P) = 40.5 Hz). 

fBuPH₂-BH₂ (2c): A solution of fBuPCl (3.15 g, 19.8 mmol) in Et₂O (40 mL) was added dropwise in about 30 minutes to a solution of Li[B(Ph)] (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 min during which the temperature was allowed to warm to room temperature. The solvent was removed in vacuo, the product was extracted into pentane (3×20 mL) and then filtered over Celite. After removal of all volatiles, subsequent distillation (89–91 °C, 10 mbar) yielded fBuPH₂-BH₂ (2c) as a colorless oil (1.82 g, 17.5 mmol, 88.4%). H NMR (250.1 MHz, CDCl3); δ = 0.51 (br. q, J(31P, H) = 100.1 Hz, 3H; BH3); 1.25 (d, J(C,P) = 15.5 Hz, 9H; C(CH3)3); 4.38 (dq, J(31P, H) = 353.1 Hz, J(31P, H) = 7.6 Hz, 2H; PhH); 1H NMR (400.1 MHz, CDCl3); δ = 0.51 (dt, J(31P, H) = 15.7, J(31P, H) = 7.8 Hz, 3H; BH3); 1.25 (d, J(31P, H) = 15.5 Hz, 9H; C(CH3)3); 4.38 (dq, J(31P, H) = 353.1 Hz, J(31P, H) = 7.6 Hz, 2H; PhH); 18NMR (128.4 MHz, CDCl3); δ = −43.1 (d, J(31P, H) = 100.4 Hz, J(31P, 31P) = 55.5 Hz); 13C NMR (100.6 MHz, CDCl3); δ = 24.9 (d, J(C,P) = 36.2 ppm; C(CH3)3); 27.7 (d, J(C,P) = 2.8 Hz; C(CH3)3); 131P[H] NMR (101.3 MHz, CDCl3); δ = −10.7 ppm (q, J(31P, 31P) = 37.0 Hz).
afforded iPr₂NPH₂BH, (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; 1H NMR (250.1 MHz, CDCl₃): δ = 1.12 (d, 3J(HH) = 6.8 Hz, 12H; CH₂(CH₃)₂), 1.37 (sept, 3J(HH) = 6.8 Hz, 2H; CH₃H), 5.93 (dq, 1J(HP) = 379.4 Hz, 1J(HH) = 6.3 Hz, 2H; PH₃, signals for BH₃ were unresolved; 11B(NMR (400.1 MHz, CDCl₃): δ = 0.67 (dt, 3J(PH) = 15.2, 2J(HH) = 6.3 Hz, 3H; BH₃), 1.12 (d, 3J(HH) = 6.8 Hz, 12H; CH₂(CH₃)₂), 1.37 (sept, 3J(HH) = 6.8 Hz, 2H; CH₃H), 5.93 (dq, 1J(HP) = 379.4 Hz, 1J(HH) = 6.3 Hz, 2H; CH₂(CH₃)₂), 41B NMR (128.4 MHz, CDCl₃): δ = −41.4 (dq, 1J(BP) = 99.9 Hz, 1J(BH) = 50.9 Hz); 13C NMR (100.6 MHz, CDCl₃): δ = 21.5 (d, 3J(CP) = 3.2 Hz; CH₂(CH₃)₂), 47.2 (d, 3J(CP) = 3.7 Hz; CH₂(CH₃)₂), 11B(N) NMR (101.3 MHz, CDCl₃): δ = −18.6 ppm (q, 1J(NP) = 50.8 Hz); HR ESI-MS: m/z (‰): ν = 146.13 (0.2) [M⁺−H], 144.11 (0.3) [M⁺−H₂]; Elemental analysis calcd (%) for C₅H₆B₃N: M (+H) = 186.1590, found 186.1587.

(MeSe₂NPH₂BH₂, (2h): Step 1. Synthesis of (MeSe₂N)_2NPCI₂: (MeSe₂N)N(S) (25.0 mL, 0.10 mmol) in THF (25.0 mmol) was added slowly to a solution of Li[BH₄] (25.0 mL, 2.0 mmol, 50.0 mmol) in Et₂O at 0 °C and subsequently stirred for 60 minutes at the same temperature. The following purification steps were all carried out at 0 °C. The solvent was removed in vacuo, the product extracted into diethyl ether (3 x 30 mL) and then filtered. Removal of diethyl ether yielded (MeSe₂N)(NPCI₂) as a colorless oil. Step 2. Synthesis of (MeSe₂NPH₂BH₂: The resulting (MeSe₂N)(NPCI₂) was dissolved in Et₂O (50 mL) and added slowly to a solution of Li[BH₄] (25.0 mL, 2.0 mmol) in THF (50.0 mmol) in Et₂O at 0 °C and subsequently stirred for 60 minutes. 1H NMR (400.1 MHz, CDCl₃): δ = 0.60 (br. s, 18H; (CH₃)₂Si), 0.67 (br. q, 1J(BH) = 94.3 Hz, 3H; BH₃), 6.06 (dq, 1J(HP) = 47.1 Hz, 1J(HH) = 6.7 Hz, 2H; PH₃); 11B(N) NMR (101.3 MHz, CDCl₃): δ = −36.7 (dq, 1J(BP) = 98.2, 1J(BH) = 54.4 Hz); 13C NMR (62.9 MHz, CDCl₃): δ = 2.1 (d, 1J(CP) = 3.4 Hz; CH₃N), 2.1 (s; CH₃), 29.1 (s; CH₃), 129.1 (s; CH₃); δ = 12.9 (br. s); 13B(N) NMR (162.0 MHz, CDCl₃): δ = −2.1 ppm (q, 1J(BP) = 51.6 Hz); HR ESI-MS: m/z (‰): ν = 206.11 (1.0) [M⁺−H], 160.10 (100.0) [M⁺−PH₃]; Elemental analysis calcd (%) for C₄H₈B₃N₄Si: M (+H) = 206.1129, found 206.1124.

Li₂[Ph-PHB₃H₉] (3a): A stock solution of Ph₂P-BH₃ (2a; 14.6 mL, 0.25 mmol in THF, 5.0 mmol) was cooled to −78 °C, subsequently 2 equiv of nBuLi (6.25 mL, 1.6 mmol 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 (2 x 20 mL). Evaporation of the residue to dryness at 0 °C yielded Li₂[Ph-PHB₃H₉] (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. 1H NMR (400.1 MHz, THF-D₉): δ = −0.68 (br. q, 1J(BH) = 84.9 Hz, 3H; BH₃), 0.87 (m, 12H; Hex), 1.30 (m, 16H; Hex), 1.72 (br. s, 2H; THF-D₂), 1.78 (m, 3H; THF), 3.56 (br. s, 2H; THF-D₂), 3.61 (m, 3H; THF), 6.24–6.28 (m, 1H; p-PhH), 6.53–6.57 (m, 2H; m-PhH), 7.28–7.31 (m, 2H; o-PhH); 13B(N) NMR (100.6 MHz, THF-D₂): δ = −0.62 (s); 11B(N) NMR (128.4 MHz, THF-D₂): δ = −34.0 (br. q, 1J(BH) = 84.5 Hz); 13C NMR (100.6 MHz, THF-D₂): δ = 153.5 (s; C₆H₅Hex), 24.41 (s; C₆H₅Hex), 68.3 (m, C₆H₅THF), 33.4 (s; C₆H₅Hex), 68.3 (m, C₆H₅THF), 69.1 (s; C₆H₅THF-complex), 117.1 (s; p-PhH), 126.7 (d, 1J(CP) = 4.6 Hz; m-PhH); 133.6 (d, 3J(CP) = 12.1 Hz; o-PhC), 165.9 (d, 1J(CP) = 14.0 Hz; m-PhC).
X-ray crystal structure determinations

2 d: \( \text{C}_6\text{H}_{10}\text{BP} \), Fw = 169.73, colorless needle, 0.60 x 0.18 x 0.18 mm, orthorhombic, \( \text{Pbcn} (no. 61) \), \( a = 9.2604(9) \), \( b = 8.0899(2) \), \( c = 26.4819(7) \, \text{Å} \), \( V = 1986.12(11) \, \text{Å}^3 \), \( Z = 8 \), \( D_c = 1.135 \, \text{g cm}^{-3} \), \( \mu = 0.37 \, \text{mm}^{-1} \). The diffraction experiment was performed on a Nonius KappaCCD diffractometer with rotating anode and graphite mono-chromator (\( \lambda = 0.71073 \, \text{Å} \) at a temperature of 150(2) K up to a resolution of \( \sin \theta/\lambda_{\max} = 0.65 \, \text{Å}^{-1} \). The intensity integration was performed with the EvAlCCD software.[1] A multi-scan absorption correction and scaling was performed with SADABS[2] (correction range 0.73-0.94). A total of 22295 reflections were measured, 2274 reflections were unique (\( R_{int} = 0.028 \)), 1921 reflections were ob-

erved (\( I > 2\sigma(I) \)). The structure was solved with direct methods using SHELXS-97.[3] Structure refinement was performed with SHELXL-2018[4] on \( F^2 \) of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydro-
gen 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 dens-
ity between –0.22 and 0.32 e Å\(^{-3} \). Geometry calculations and check-
ing for higher symmetry was performed with the PLATON pro-
gram.[8]

2e: \( \text{C}_6\text{H}_{10}\text{BNP} \), Fw = 147.00, colorless block, 0.60 x 0.50 x 0.50 mm\(^2\), monoclinic, \( \text{C2} \, m \) (no. 12), \( a = 11.7953(3) \), \( b = 8.9864(2) \), \( c = 8.6272(2) \, \text{Å} \), \( \beta = 90.1828(10) \, ^\circ \). \( V = 1006.09(4) \, \text{Å}^3 \), \( Z = 4 \), \( D_c = 0.970 \, \text{g cm}^{-3} \), \( \mu = 0.21 \, \text{mm}^{-1} \). The diffraction experiment was performed on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (\( \lambda = 0.71073 \, \text{Å} \) at a temperature of 150(2) K up to a resolution of \( \sin \theta/\lambda_{\max} = 0.65 \, \text{Å}^{-1} \). The intensity integration was performed with the HKL2000 software.[39] A multi-
scan absorption correction and scaling was performed with SADABS[2] (correction range 0.65-0.90). A total of 8401 reflections was measured, 1203 reflections were unique (\( R_{int} = 0.033 \)), 1030 re-
flexions were observed (\( I > 2\sigma(I) \)). The structure was solved with direct methods using SHELXS-97[3] Structure refinement was per-
formed with SHELXL-2018[4] on \( F^2 \) of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement param-
ters. 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. \( R1/wR2 (I > 2\sigma(I)) \): 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 check-
ing for higher symmetry was performed with the PLATON pro-
gram.[8]

3a: \( \text{C}_3\text{H}_6\text{BLiOP} \), Fw = 225.90, yellow needle, 0.60 x 0.24 x 0.09 mm\(^2\), monoclinic, \( \text{P2}_1/\text{c} \, m \) (no. 14), \( a = 12.4001(9) \), \( b = 7.2198(7) \), \( c = 14.7720(8) \, \text{Å} \), \( \beta = 94.983(3) \, ^\circ \). \( V = 1317.47(17) \, \text{Å}^3 \), \( Z = 4 \), \( D_c = 1.139 \, \text{g cm}^{-3} \), \( \mu = 0.19 \, \text{mm}^{-1} \). The diffraction experiment was performed on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (\( \lambda = 0.71073 \, \text{Å} \) at a temperature of 125(2) K up to a resolution of \( \sin \theta/\lambda_{\max} = 0.65 \, \text{Å}^{-1} \). The crystal ap-
ppeared 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.[40] A multi-scan absorption correction and scaling was performed with TWINABS[2] (correction range 0.64-1.00). A total of 16125 reflections was mea-
sured, 3014 reflections were unique (\( R_{int} = 0.068 \), 2693 reflections were observed (\( I > 2\sigma(I) \)). The structure was solved with direct methods using SIR97.[41] Structure refinement was performed with SHELXL-2018[4] on \( F^2 \) of all reflections based on an HKLF-5 files.[58] Non-hydrogen atoms were refined freely with anisotropic displacement param-
ters. 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 re-
finied with a riding model. 160 Parameters were refined with no re-
straints. \( R1/wR2 (I > 2\sigma(I)) \): 0.0447/ 0.1255. \( R1/wR2 \) [all refl.]: 0.0524/ 0.1313. \( S = 1.264 \). Twin fraction \( \text{BASF} = 0.507(3) \). Residual electron dens-
ity between –0.29 and 0.45 e Å\(^{-3} \). Geometry calculations and check-
ing for higher symmetry was performed with the PLATON pro-
gram.[8]

4c: \( \text{C}_6\text{H}_{10}\text{BNPSi} \), Fw = 291.37, colorless block, 0.60 x 0.60 x 0.42 mm\(^2\), monoclinic, \( \text{P2}_1/c \, m \) (no. 14), \( a = 17.1577(4) \), \( b = 12.5115(3) \), \( c = 18.430(6) \, \text{Å} \), \( \beta = 99.706(1) \, ^\circ \). \( V = 3963.94(18) \, \text{Å}^3 \), \( Z = 8 \), \( D_c = 1.135 \, \text{g cm}^{-3} \), \( \mu = 0.37 \, \text{mm}^{-1} \). The diffraction experiment was performed on a Nonius KappaCCD diffractometer with rotating anode and graphite monochromator (\( \lambda = 0.71073 \, \text{Å} \) at a temperature of 150(2) K up to a resolution of \( \sin \theta/\lambda_{\max} = 0.65 \, \text{Å}^{-1} \). The intensity integration was performed with the EvalCCD software.[1] A multi-scan absorption correction and scaling was performed with SADABS[2] (correction range 0.73-0.94). A total of 22295 reflections were measured, 2274 reflections were unique (\( R_{int} = 0.028 \)), 1921 reflections were ob-

erved (\( I > 2\sigma(I) \)). The structure was solved with direct methods using SHELXS-97.[3] Structure refinement was performed with SHELXL-2018[4] on \( F^2 \) of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydro-
gen 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 dens-
ity between –0.22 and 0.32 e Å\(^{-3} \). Geometry calculations and check-
ing for higher symmetry was performed with the PLATON pro-
gram.[8]

The authors declare no conflict of interest.

**Keywords:** crystal structures • phosphaneidide • phosphine borane • primary phosphine • synthesis


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Conflict of interest

The authors declare no conflict of interest.


[19] The SARS-CoV-2 coronavirus that is responsible 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 apologize for not sharing these results any sooner.


[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.


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