Synthesis and Ambiphilic Reactivity of Metalated Diorgano-Phosphonite Boranes

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Experimental Procedures

If not stated otherwise, all manipulations were performed in flame-dried glassware under inert conditions using purified argon. Chlorophosphites and diethoxyphosphine borane were prepared as described elsewhere.[1]-[4] LiBH₄, metal hexamethyldisilazides (MHMDS, M = Li, K), Ph₃SnCl and 1,4-diazabicyclo(2.2.2)octane (DABCO) were purchased from Sigma Aldrich and stored under inert atmosphere. DABCO was sublimed prior to use. NMR spectra were recorded on Bruker Avance 250 (¹H: 250.0 MHz, ¹³C: 62.9 MHz, ³¹P: 101.2 MHz, ¹¹⁹Sn: 93.2 MHz) or Bruker Avance 400 (¹H: 400.1 MHz, ¹³C: 155.4 MHz, ¹¹B: 128.4 MHz, ¹⁰²P: 100.5 MHz, ¹¹⁹Sn: 161.9 MHz) NMR spectrometers at 293 K if not stated otherwise.¹H Chemical shifts were referenced to TMS using the signals of the residual protons of the deuterated solvent (δ¹H = 7.27 (CDCl₃), 7.15 (CD₂Cl₂), 2.09 (toluene-d₈), 1.73 (THF-d₈)) as secondary reference. Spectra of heteronuclei were referenced using the ⁴⁺⁻scale[5] employing 85 % H₃PO₄ (Ξ = 40.480747 MHz, ³¹P), SnMe₄ (Ξ = 37.290655 MHz, ¹¹⁹Sn), BF₃·OEt₂ (Ξ = 32.083974 MHz, ¹¹B) and LiCl (Ξ = 38.863797, ¹³C) as secondary reference, respectively.¹¹⁹Sn NMR spectra were recorded using the DEPT pulse sequence. Coupling constants involving boron and tin nuclei refer to the isotopes ¹¹B and ¹¹⁹Sn if not stated otherwise and prefixes i-, o-, m-, p- denote the atomic positions in aromatic rings. FTIR spectra were recorded with a Thermo Scientific/Nicolet iS5 instrument equipped with an iD5 ATR accessory. Mass spectra were obtained with a Bruker Daltonics MicroToF-Q mass spectrometer. Given masses refer to the peak representing the most abundant isotope combination. Elemental analyses were performed with an Elementar Micro Cube elemental analyser.

D(iisopropoxy)phosphine borane (2c)

A solution of chlorodiisopropylphosphite (8.24 g, 4.46 mmol) in THF (80 mL) was cooled to -78 °C. Solid LiBH₄ (2.90 g, 4.46 mmol) representing the most abundant isotope combination. Elemental analyses were performed with an Elementar Micro Cube elemental analyzer.

Bis(2,6-diisopropoxy)phosphine borane (2b)

A solution of chloro-bis(2,6-diisopropoxy)phosphine (4.18 g, 10.7 mmol) in THF (30 mL) was cooled to -78 °C. LiBH₄ (4 M solution, 2.920 g, 21.48 mmol) was added dropwise, resulting in precipitation of the phosphide. The suspension was warmed to room temperature and filtered. The filtrate was evaporated to approx. 5 mL and stored at -25 °C to afford colourless crystals (1.533 g, 3.830 mmol, 36 %). – ¹H NMR (C₆D₆): δ = 7.27 (CDCl₃), 7.15 (C₆D₆), 1.27 (OCH, 1.19 (d, 3Jₖ = 6.7 Hz, 12 H, CH₃), 0.57 (broad dq, 1J₂ = 96 Hz, 3J₁ = 13 Hz, 3 H, BH₂). – ³¹P NMR (CDCl₃): δ = 119.3 (broad dq, 1J₂ = 444 Hz, 1J₁ = 76 Hz). – ¹⁵C(¹H) NMR (CDCl₃): δ = 148.4 (d, 1J₁ = 11 Hz, o-C), 142.0 (d, 1J₂ = 3 Hz, o-C), 126.4 (d, 1J₂ = 2 Hz, p-C), 124.5 (d, 1J₁ = 2 Hz, m-C), 27.5 (s, CH), 23.5 (s, CH₂), 23.1 (s, CH₃). – IR (cm⁻¹): ν = 2939, 2346 (νP, νBH). – (+)ESI-MS: m/z = 187.1028 (MNa⁺, calcld. 187.1031). – ¹1B NMR (CD₂Cl₂): δ = 302.3 (q, 1J₂ = 88 Hz, 3 H, BH). – (+)ESI-MS: m/z = 423.2581 (MNa⁺, calcld. 423.2599). – C₂₄H₃₈BO₂P (163.99 g mol⁻¹): calcd. C 43.94 H 11.06, found C 43.66 H 10.85.

Potassium diethoxyphosphate borane (K[3b])

KHMDS (4.285 g, 21.48 mmol) was dissolved in hexane/Et₂O (80 mL/10 mL). Diethoxyphosphine borane 2b (2.920 g, 21.48 mmol) was added dropwise, resulting in precipitation of the phosphide. The suspension was warmed to room temperature and filtered. The precipitate was washed with hexane (50 mL) and dried in vacuum to afford K[3b] as colourless solid (2.417 g, 13.89 mmol, 65 %). – ¹H NMR (THF-d₈): δ = 3.95-3.70 (m, 4 H, OCH), 1.19 (t, 1J₁ = 7.0 Hz, 6 H, CH₃), 0.29 (q, 1J₂ = 88 Hz, 3 H, BH₂). – ³¹P[¹H] NMR (THF-d₈): δ = 302.3 (q, 1J₁ = 37 Hz). – ¹₁B[¹H] NMR (THF-d₈): δ = -27.4 (d, 1J₁ = 37 Hz). – IR (cm⁻¹): ν = 2394, 2340(sh) (νBH). – (+)ESI-MS: m/z = 432.2 (MNa⁺, calcld. 432.2599). – C₂₄H₃₉BO₂P (400.35 g mol⁻¹): calcd. C 72.00 H 9.57, found C 71.70 H 9.50.

Potassium diisopropoxyphosphate borane (K[3c])

The synthesis was performed as described for K[3b] using KHMDS (4.087 g, 20.49 mmol) and 2c (3.360, 20.49 mmol) in hexane/Et₂O (80 mL/10 mL). Colourless solid (2.303 g, 11.96 mmol, 55 %). – ¹H NMR (THF-d₈): δ = 3.95 (sept, 3J₁ = 6.7 Hz, 12 H, CH₃), 1.14 (d, 1J₂ = 6.7 Hz, 12 H, CH₃). – ³¹P[¹H] NMR (THF-d₈): δ = -290.9 (b). – ¹₁B[¹H] NMR (THF-d₈): δ = -30.3 (d, 1J₁ = 36 Hz). – ¹³C¹H NMR (THF-d₈): δ = 72.9 (b, OCH), 25.5 (s, CH₂), 25.4 (s, CH₃). – IR (cm⁻¹): ν = 2325, 2279 (νBH).

In situ preparation of potassium bis(2,6-diisopropoxyphenox)phosphate borane (K[3d])

A NMR tube was charged with bis(2,6-diisopropoxyphenox)phosphate (2d) (40 mg, 50 µmol) and KHMDS (22 mg, 60 µmol) and cooled to -78°C. Toluene-d₈ (0.6 mL) was slowly added maintaining the temperature. After homogenization, the mixture was investigated by NMR-spectroscopy. – ¹H NMR (Toluene-d₈): δ = 7.12-6.86 (m, aryl-H, 6 H), 3.73 (sept, 1J₁ = 6.7 Hz, CH, 4 H), 1.26 (d, 1J₂ = 7.0 Hz, CH₃, 12 H), 1.23 (d, 1J₂ = 6.8 Hz, CH₂, 12 H). – ³¹P[¹H] NMR (Toluene-d₈): δ = 325.8 (br). – ¹₁B[¹H] NMR (Toluene-d₈):
In situ preparation of lithium diethoxyphosphide borane (Li[3b])

LiHMDS (25 mg, 0.15 mmol) was dissolved in THF-d8 (0.6 mL) in an NMR tube. The solution was cooled to -78 °C and 2b (20 mg, 0.15 mmol) was added carefully. The sample was transferred into a precooled NMR spectrometer and characterised by multinuclear NMR spectra recorded at 203 K. 1H NMR (THF-d8): δ = 3.54 (broad, 4 H, OCH2), 1.69 (broad, 6 H, CH3). 11B{1H} NMR (THF-d8): δ = -10.7 (q, J_{BH} = 87 Hz). Li[3b]·1H NMR (THF-d8): δ = 4.08-3.87 (m, 8 H, OCH2), 0.20 (t, J_{BH} = 7.0 Hz, 6 H, CH3). 31P{1H} NMR (THF-d8): δ = -18.5 (d, J_{PP} = 449 Hz, P-BH3), 127.4 (t, J_{PP} = 449 Hz, P-BH3). – 11B{1H} NMR (THF-d8): δ = -31.4 (d, J_{BH} = 70 Hz). – 119Sn{1H} NMR (C6D6): δ = 68.7 (s, OCH2), 22.1 (d, J_{PC} = 4 Hz, CH3), 22.0 (d, J_{PC} = 4 Hz, CH3).

ReACTION of lithium diethoxyphosphide borane Li[3b] with BuLi

A solution of Li[3b] was prepared by dropwise addition of 2b (75 mg, 0.55 mmol) to a solution of LiHMDS (92 mg, 0.55 mmol) in THF (4 mL) at -78 °C. After the solution had been stirred for an additional 15 minutes, BuLi (1 mL of a 2.5 M solution in hexanes, 2.48 mmol) was added dropwise. 31P reaction monitoring disclosed the formation of a new product in an instantaneous reaction at -50 °C. The mixture was then allowed to warm to room temperature. Volatiles were removed under reduced pressure and the residue dissolved in CD2Cl2 (0.6 mL). NMR studies revealed the presence of a mixture of Li[6c] and Et3NBH3.

Data for Li[6c]: 1H NMR (CD2Cl2): δ = 5.05-4.83 (m, 4 H, OCH2), 1.32 (d, J_{BH} = 6 Hz, 6 H, CH3), 1.31 (d, J_{BH} = 6 Hz, 6 H, CH3). 31P{1H} NMR (CD2Cl2): δ = 180.2 (broad d, J_{PP} = 449 Hz, P-P). – 11B{1H} NMR (CD2Cl2): δ = -33.2 (d, J_{BH} = 70 Hz). – 119Sn{1H} NMR (CD2Cl2): δ = 65.7 (s, OCH2), 22.1 (d, J_{PC} = 4 Hz, CH3), 22.0 (d, J_{PC} = 4 Hz, CH3).

Diisoproxytriphenylstannylphosphine borane (9c)

The synthesis was performed as described for 9b with K[3c] (210 mg, 1.04 mmol) and Ph2SnCl (400 mg, 1.04 mmol). Colourless solid (200 mg, 391 µmol, 38%; m.p.(dec.) 99 °C). Single crystals suitable for X-Ray crystallography were grown from a concentrated hexane solution. 1H NMR (CD2Cl2): δ = 7.92-7.70 (m, 6 H, Ph), 7.30-7.04 (m, 9 H, Ph), 4.72 (dsept, J_{Jpc} = 6 Hz, J_{Jpp} = 10 Hz, 2 H, 2 H).
Phosphine borane 2d (250 mg, 0.62 mmol) and KHMDS (125 mg, 0.62 mmol) were dissolved in toluene (12 mL) at -78°C. The mixture was stirred for 1h at -78°C and then allowed to warmed to room temperature until it became homogeneous. After re-cooling to -78°C, a solution of Ph₃SnCl (241 mg, 0.62 mmol) in toluene (2 mL) was slowly added. The mixture was stirred for 1 h at -78°C and then for 1 h at room temperature. Volatiles were removed in vacuum and the residue treated with hexane (5 mL). The resulting suspension was filtered. Evaporation of the filtrate to dryness afforded a colourless solid (285 mg, 85% yield, 60%). Single crystal suitable for X-Ray crystallography were grown from a saturated hexane solution.

Dielophenoxytrihexylstannylphosphine boreane 9b (25 mg, 52 μmol) and DABCO (27 mg, 258 μmol) were dissolved in C₆D₆ (0.6 mL). The solution was heated to 50 °C in an oil bath and NMR spectra were measured after 0, 30, 60 and 90 minutes. Reaction products were identified in situ by their NMR data. – ²³P{¹²¹H} NMR: δ = 236.0 (s, J₉Sn = 860 Hz), 2.0 (s, EIO₃pPO(OEt₃)). – ¹³⁵Sn{¹²¹H} NMR: δ = 189.8 (s, J₉Sn = 860 Hz), 10b. – ¹³¹P{¹²¹H} NMR: δ = 231.3 (s, J₉Sn = 830 Hz), 10c. – ¹³¹P{¹²¹H} NMR: δ = 179.5, δJ₉Sn = 830 Hz, 10c. – ¹³¹P{¹²¹H} NMR: δ = -141.3 (s, J₉Sn = 860 Hz), 10b. – ¹³¹P{¹²¹H} NMR: δ = -10.2 (s, DABCO-BH₃).

**Bis(2,6-diisopropoxyphenoxy)trihexylstannylphosphine boreane 10d**

A solution of 9d (50 mg, 67 μmol) in toluene (3 mL) and NET₃ (1.5 mL) was stirred for 16 h. Volatiles were removed under reduced pressure and the residue treated with pentane (3 mL). Insoluble components were removed by filtration and the volume of the filtrate was reduced to 0.5 mL. The product separated as colourless crystals (40 mg, 54 μmol, 82%). – ¹¹HNMR (C₆D₆): δ = 7.91-7.68 (m, 6 H, SnPh), 7.25-6.99 (m, 15 H, SnPh and Oaryl), 3.45 (sept, J₉Sn = 6.8 Hz, 4 H, CH), 1.01 (d, J₉Sn = 6.8 Hz, 12 H, CH₃), 0.97 (d, J₉Sn = 6.8 Hz, 12 H, CH₃). – ³¹P{¹²¹H} NMR (C₆D₆): δ = 273.0 (s, J₉Sn = 770 Hz). – ¹³⁵Sn{¹²¹H} NMR (C₆D₆): δ = -185.2 (d, J₉Sn = 770 Hz). – ¹³¹C{¹²¹H} NMR (C₆D₆): δ = -152.3 (d, J₉Sn = 1 Hz, Oaryl), 140.7 (d, J₉Sn = 2 Hz, m-Oaryl), 139.8 (d, J₉Sn = 3 Hz, o-SnPh), 138.0 (s, J₉Sn = 38 Hz i-SnPh), 129.3 (s, m-SnPh), 129.1 (s, o-SnPh), 125.2 (d, J₉Sn = 1 Hz, p-Oaryl), 124.5 (d, J₉Sn = 1 Hz, m-Oaryl), 28.2 (d, J₉Sn = 6 Hz, CH), 24.0 (d, J₉Sn = 1 Hz, CH₃), 23.9 (broad, CH₃). – (+)ESI-MS: m/z 775.2123 (MK⁺, calcd. 775.2131). – C₁₂H₁₈O₃P₃Sn (735.54 g mol⁻¹): calcd. C 68.58 H 6.72, found C 68.60 H 6.72.

**Crystallographic studies**

X-ray diffraction data were collected on a Bruker Kappa Apex II Duo diffractometer equipped with an APEX II CCD-detector and a KRYO-FLEX cooling device with Mo-Kα radiation (λ = 0.71073 Å) at 130(2) K (K(3d)[K[Ni(SiMe₃)₃]_3(THF)]²⁺), 135(2) K (2d, Li[5c], 9b-d or 140(2) K (Li[6b], 10d), respectively. The structures were solved with direct methods (SHELXS-2014 [17]) and refined with a full-matrix least squares scheme on F² (SHELXL-2014 [17]). Semi-empirical or numerical absorption corrections (see Table S1) were applied. Non-hydrogen atoms were refined anisotropically and hydrogen atoms except those bound to phosphorus and boron using a riding model. One SiMe₃ moiety and the THF moieties in K(3b)-KNTM₃b, the ethoxy groups in 9b, and two iPr-groups in 9d as well as all iPr-groups in 10d are disordered. Further details on the refinement of the disorder is given in the cif-files and the incorporated res-files. CCDC-2046650 to CCDC-2046657 contain the crystallographic data for this paper, which can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Table S1 Crystallographic data for 2d, [K(THF)][3d][K(THF)][N(SiMe3)]2, Li[5c], Li[6b], 9b-d, 10d.

|                | 2d | K[3d][K(N(SiMe3))2][THF] | Li[5c] | Li[6b] |
|----------------|----|--------------------------|--------|--------|
| CCDC           | 2046654 | 2046650               | 2046652 | 2046657 |
| Empirical formula | C24H38BO2P | C18H47BK2NO4PSi2 | C20H53B3LiO6P3 | C8H26B2LiO4P3 |
| Formula weight/g mol⁻¹ | 400.32 | 517.72               | 521.90 | 307.76 |
| Wavelength/Å   | 0.71073 | 0.71073               | 0.71073 | 0.71073 |
| Crystal system | triclinic | monoclinic           | monoclinic | triclinic |
| Space group    | P1   | P2₁/n                  | P2₁/c  | P1     |
| a/Å            | 9.4978(4) | 12.4127(4)           | 16.6630(5) | 8.7094(5) |
| b/Å            | 10.8815(5) | 10.6275(3)          | 9.6999(3) | 10.1661(6) |
| c/Å            | 12.4747(6) | 23.2684(8)          | 19.8825(6) | 10.7159(6) |
| α/°            | 74.228(3) | 90                  | 90     | 108.372(2) |
| β/°            | 88.499(2) | 101.947(2)          | 103.554(2) | 99.768(3) |
| γ/°            | 77.850(2) | 90                  | 90     | 103.710(3) |
| V/Å³           | 1212.27(10) | 3002.99(17)       | 3161.59(17) | 843.49(9) |
| Z              | 2   | 4                      | 4      | 2      |
| ρcalcd/Mg m⁻³  | 1.097 | 1.145                 | 1.145 | 1.212 |
| F(000)         | 436  | 1120                 | 1136  | 328    |
| Crystal size/mm³ | 0.571 x 0.443 x 0.428 | 0.602 x 0.552 x 0.294 | 0.340 x 0.270 x 0.220 | 0.366 x 0.226 x 0.206 |
| Θ-range for data | 1.697 to 25.242 | 1.729 to 28.375 | 2.107 to 28.338 | 2.077 to 30.681 |
| Refl. collected | 35409 | 51893               | 31949  | 26856 |
| Independent refl. | 9113 | 7488              | 7851   | 5198 |
| Completeness to θ = 25.242° | 97.7% | 99.6%           | 99.6% | 99.2% |
| Abs. correction | semi-empirical | semi-empirical  | semi-empirical | semi-empirical |
| Max. and min. transmission | 0.7465 and 0.7163 | 0.7457 and 0.6633 | 0.7457 and 0.7002 | 0.7461 and 0.7107 |
| Refinement method | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| Data / restraints / parameters | 9113 / 3 / 265 | 7488 / 841 / 379 | 7851 / 9 / 325 | 5198 / 6 / 187 |
| G.o.f. on F² | 1.035 | 1.066                | 1.021  | 1.044 |
| Final R indices | R₁ = 0.0453 | R₁ = 0.0367        | R₁ = 0.0328 | R₁ = 0.0305 |
| [I > 2σ(I)] | wR₂ = 0.1175 | wR₂ = 0.0849      | wR₂ = 0.0769 | wR₂ = 0.0711 |
| R indices | R₁ = 0.0609 | R₁ = 0.0545        | R₁ = 0.0507 | R₁ = 0.0461 |
| (all data) | wR₂ = 0.1296 | wR₂ = 0.0946      | wR₂ = 0.0834 | wR₂ = 0.0774 |
| Largest diff. peak and hole/e Å⁻³ | 0.697 and -0.422 | 0.573 and -0.278 | 0.314 and -0.243 | 0.390 and -0.280 |
|        | 9b         | 9c         | 9d         | 10d         |
|--------|------------|------------|------------|------------|
| CCDC   | 2046651    | 2046655    | 2046653    | 2046656    |
| Empirical formula | C_{22}H_{28}BO_2PSn | C_{24}H_{32}BO_2PSn | C_{42}H_{52}BO_2PSn | C_{42}H_{49}O_2PSn |
| Formula weight/g mol^{-1} | 484.91 | 512.96 | 749.30 | 735.47 |
| T/K    | 135(2)     | 135(2)     | 135(2)     | 140(2)     |
| Wavelength/nm | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | monoclinic | triclinic | triclinic | Monoclinic |
| Space group | P_2_1/n | P_bar_1 | P_bar_1 | P_2_1/n |
| a/A    | 10.4232(5) | 9.6946(4) | 12.8287(6) | 17.5903(9) |
| b/A    | 16.3193(6) | 10.8325(5) | 73.894(2)  | 74.358(3)  |
| c/A    | 13.5035(6) | 12.8287(6) | 79.830(2)  | 73.428(2)  |
| α/°    | 90         | 73.894(2)  | 72.892(3)  | 70.064(2)  |
| β/°    | 90         | 74.358(3)  | 73.428(2)  | 92.342(2)  |
| γ/°    | 90         | 90         | 90         | 90         |
| V/Å^3  | 2246.81(18) | 1230.44(10)| 1967.96(18)| 3753.9(4)  |
| Z      | 4          | 2          | 2          | 4          |
| ρ calc/Mg m^{-3} | 1.434 | 1.385 | 1.265 | 1.301 |
| Absorption coeff./mm^{-1} | 1.222 | 1.120 | 0.722 | 0.756 |
| F(000) | 984       | 524        | 780        | 1528       |
| Crystal size/mm^3 | 0.812 x 0.276 x 0.174 | 0.476 x 0.257 x 0.130 | 0.938 x 0.583 x 0.468 | 0.200 x 0.175 x 0.166 |
| θ-range for data collection/° | 1.984 to 25.026 | 1.661 to 30.583 | 1.957 to 33.274 | 1.602 to 25.027 |
| Refl. collected | 26536 | 34158 | 63478 | 30664 |
| Independent refl. | 3962 | 7552 | 14987 | 6591 |
| Completeness to θ = 25.242°/66.548° | 99.9% | 99.8% | 98.9% | 99.4% |
| Absorption correction | numerical | semi-empirical | numerical | semi-empirical |
| Max. and min. transmission | 0.8512 and 0.5041 | 0.6421 and 0.7461 | 0.8082 to 0.6540 | 0.9605 to 0.8431 |
| Refinement method | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 | Full-matrix least-squares on F^2 |
| Data / restraints / parameters | 3962 / 117 / 291 | 7552 / 3 / 271 | 14987 / 153 / 470 | 6591 / 142 / 451 |
| G.o.f. on F2 | 1.124 | 1.043 | 1.125 | 1.090 |
| Final R indices | R1 = 0.0178 | R1 = 0.0188 | R1 = 0.0267 | R1 = 0.0363 |
| [I > 2σ(I)] | wR2 = 0.0378 | wR2 = 0.0417 | wR2 = 0.0619 | wR2 = 0.0810 |
| R indices | R1 = 0.0224 | R1 = 0.0232 | R1 = 0.0339 | R1 = 0.0599 |
| (all data) | wR2 = 0.0405 | wR2 = 0.0436 | wR2 = 0.0666 | wR2 = 0.0937 |
| Largest diff. peak and hole/e Å^{-3} | 0.301 and -0.422 | 0.464 and -0.298 | 0.949 and -0.522 | 1.445 and -0.516 |
Figure S1: Representation of a section of the coordination polymeric structure in crystalline \([\text{K(THF)}][3b][\text{K(THF)}][\text{N(SiMe}_3)]\). Thermal ellipsoids are drawn at the 50% probability level. For clarity, carbon atoms are drawn using a wire model, hydrogen atoms except those in BH$_3$-units are omitted, and only one orientation of disordered fragments (one SiMe$_3$ group and one THF) is shown.

Figure S2: Representation of the molecular structure of 2d in the crystal. Thermal ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms except those in PH- and BH$_3$-units are omitted. Selected distances [Å]: P1–O2 1.5903(7), P1–O1 1.5987(7), P1–B1 1.8697(11), P1–H1 1.347(13).
Figure S3: Representation of the molecular structure of 9b in the crystal. Thermal ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms except those in BH3-units are omitted. Selected distances [Å] and angles [°]: P1–O2 1.5927(14), P1–O1 1.6007(15), P1–B1 1.890(2), P1–Sn1 2.5324(5), O1–P1–Sn1 99.95(5), O2–P1–Sn1 109.44(5), O1–P1–O2 106.64(8).

Figure S4: Representation of the molecular structure of 9c in the crystal. Thermal ellipsoids are drawn at the 50% probability level. For clarity, hydrogen atoms except those in BH3-units are omitted. Selected distances [Å] and angles [°]: P2–O2 1.5946(10), P2–O1 1.6015(9), P2–B1 1.8946(15), P2–Sn1 2.5193(3), O1–P2–Sn1 96.49(4), O2–P2–Sn1 112.88(4), O1–P2–O2 107.76(5).
NMR-Spectra

Figure S5: $^1$H NMR spectrum of 2c in CDCl$_3$.

Figure S6: $^{31}$P{$^1$H} NMR spectrum of 2c in CDCl$_3$. 
Figure S7: $^{31}$P NMR spectrum of 2c in CDCl₃.

Figure S8: $^{11}$B($^1$H) NMR spectrum of 2c in CDCl₃.
Figure S9: $^{13}$C($^1$H) NMR spectrum of 2c in CDCl$_3$.

Figure S10: $^1$H NMR spectrum of 2d in C$_6$D$_6$. 
Figure S11: $^{31}$P($^1$H) NMR spectrum of 2d in C6D6.

Figure S12: $^{31}$P NMR spectrum of 2d in C6D6.
Figure S13: $^{11}$B($^1$H) NMR spectrum of 2d in C$_6$D$_6$.

Figure S14: $^{13}$C ($^1$H) NMR spectrum of 2d in C$_6$D$_6$. 
Figure S15: $^1$H NMR spectrum of in-situ generated Li[3b] at 203 K in THF-d$_8$ (● LiHMDS/HMDS; ♯ (EtO)$_3$P(BH$_3$) (impurity)).

Figure S16: $^{31}$P{1H} NMR spectrum of in-situ generated Li[3b] at 203 K in THF-d$_8$. (♯ (EtO)$_3$P(BH$_3$), impurity)
Figure S17. $^{11}$B($^1$H) NMR spectrum of in-situ generated Li[3b] at 203 K in THF-d$_8$ ($\neq$ (EtO)$_3$P(BH$_3$))

Figure S18. $^{13}$C($^1$H) NMR spectrum of in-situ generated Li[3b] at 203 K in THF-d$_8$. 
Figure S19. $^1$H,$^7$Li gs-HOESY NMR spectrum of in-situ generated Li[3b] at 203 K in THF-$d_8$ with the $^1$H and $^7$Li NMR spectra as horizontal and vertical projections, respectively.

Figure S20: $^1$H DOSY spectrum of in-situ generated Li[3b] recorded at 203 K in THF-$d_8$ (top) and extracted signal integral decays for the resonances at 1.33 ppm (bottom left) and 1.35 ppm (bottom right) attributable to the CH$_3$-signals of Li[3b] and 4, respectively. Evaluation of the decay curves gave $D$(Li[3b]) = 1.3 m$^2$s$^{-1}$ and $D$(4) = 1.8 m$^2$s$^{-1}$, respectively.
Figure S21: $^1$H NMR spectrum of K[3b] in THF-d$_8$. The signal at 0.05 ppm is due to HMDS.

Figure S22: $^{31}$P NMR spectrum of K[3b] in THF-d$_8$. 
Figure S23: $^{11}$B{H} NMR spectrum of K[3b] in THF-d$_8$.

Figure S24: $^1$H NMR spectrum of K[3c] in THF-d$_8$. 
Figure S25: $^{31}\text{P}$ NMR spectrum of K[3c] in THF-d$_8$. The signal at 99 ppm is assigned to K[(iPrO)$_2$PO(BH$_3$)].

Figure S26: $^{11}\text{B}'{\text{H}}$ NMR spectrum of K[3c] in THF-d$_8$. The signal at -37 ppm is assigned to K[(iPrO)$_2$PO(BH$_3$)].
Figure S27: $^1$H-$^{13}$C-HSQC spectrum of $\text{K[3c]}$ in THF-d$_8$.

Figure S28: $^1$H NMR spectrum of in situ generated $\text{K[3d]}$ in Toluene-d$_8$. The signal at 0.1 ppm is due to HMDS.

Figure S29: $^{31}$P NMR spectrum of in situ generated $\text{K[3d]}$ in toluene-d$_8$. 
Figure S30: $^{11}$B($^1$H) NMR spectrum of in situ generated K[3d] in toluene-$d_8$.

Figure S31: $^{13}$C($^1$H) NMR spectrum of in situ generated K[3d] in toluene-$d_8$. The signal at 2.6 ppm is due to HMDS.
Figure S32: $^1$H NMR spectrum of 9b in C$_6$D$_6$.

Figure S33: $^{31}$P($^1$H) NMR spectrum of 9b in C$_6$D$_6$. 
Figure S34: $^{11}$B\{$^1$H\} NMR-spectrum of 9b in C$_6$D$_6$.

Figure S35: $^{13}$C NMR-spectrum of 9b in C$_6$D$_6$. 
Figure S36: $^{135}$Sn-DEPT spectrum of 9b in C$_6$D$_6$.

Figure S37: $^1$H NMR spectrum of 9c in CDCl$_3$. 
Figure S38: $^{31}$P{1H} NMR spectrum of 9c in CDCl$_3$.

Figure S39: $^{11}$B{1H} NMR-spectrum of 9c in CDCl$_3$. 
Figure S40: $^{13}$C (^1H) NMR spectrum of 9c in CDCl₃.

Figure S41: $^{119}$Sn-DEPT spectrum of 9c in CDCl₃.
Figure S42: $^1$H NMR spectrum of 9d in C$_6$D$_6$.

Figure S43: $^{31}$P{$^1$H} NMR spectrum of 9d in C$_6$D$_6$. 
Figure S44: $^{11}$B($^1$H) NMR spectrum of 9d in C$_6$D$_6$.

Figure S45: $^{13}$C($^1$H) NMR spectrum of 9d in C$_6$D$_6$. 
Figure S46: $^{119}\text{Sn}$-DEPT spectrum of 9d in C₆D₆.

Figure S47: $^1\text{H}$ NMR spectrum of Li[6b] in THF-d₈.
Figure S48: $^{31}$P{$^1$H} NMR spectrum of Li[6b] in THF-$d_8$.

Figure S49: $^{11}$B{$^1$H} NMR spectrum of Li[6b] in THF-$d_8$. 
Figure S50: $^1$H, $^{11}$B HSQC spectrum of Li[6b] in THF-d$_8$.

Figure S51: $^1$H, $^7$Li HOESY spectrum of Li[6b] in THF-d$_8$ with the $^7$Li NMR spectrum as vertical projection.
Figure S52: $^1$H NMR spectrum of Li[6c] in C$_6$D$_6$.

Figure S53: $^{31}$P{^1}H NMR spectrum of Li[6c] in C$_6$D$_6$. 
Figure S54: $^{11}B(1H)$ NMR spectrum of Li[6c] in C$_6$D$_6$.

Figure S55: $^1H$ NMR spectrum of Li[5c] in C$_6$D$_6$.
Figure S56: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of Li[5c] in C$_6$D$_6$.

Figure S57: $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of Li[5c] in C$_6$D$_6$. 
Figure S58: $^1$H NMR spectrum of the reaction of 9b with DABCO in C$_6$D$_6$ after 90 minutes at 50 °C.

Figure S59: $^{119}$Sn-DEPT spectrum of the reaction of 9b with DABCO in C$_6$D$_6$ after 90 minutes at 50 °C.
Figure S60: $^{31}$P{$^1$H} NMR spectra of the reaction of 9b with DABCO in C$_6$D$_6$ after 0, 30, 60, 90 minutes at 50 °C.

Figure S61: $^{11}$B{$^1$H} NMR spectra of the reaction of 9b with DABCO in C$_6$D$_6$ at 50°C after 0, 30, 60, 90 minutes at 50 °C.
Figure S62: $^1$H NMR spectrum of the reaction of \(9c\) with DABCO in C\(_6\)D\(_6\) after 90 minutes at 50°C.

Figure S63: $^{31}$P{\(^1\)H} NMR spectrum of the reaction of \(9c\) with DABCO in C\(_6\)D\(_6\) after 90 minutes at 50°C.
Figure S64: $^{11}B\{^1H\}$ NMR spectrum of the reaction of 9c with DABCO in $C_6D_6$ after 90 minutes at 50°C.

Figure S65: $^{119}Sn$-DEPT NMR spectrum of the reaction of 9c with DABCO in $C_6D_6$ after 90 minutes at 50°C.
Figure S66: $^{13}$C($^1$H) NMR spectrum of the reaction of 9c with DABCO in C$_6$D$_6$ after 90 minutes at 50°C.

Figure S67: $^1$H NMR spectrum of 10d in C$_6$D$_6$. 
Figure S68: $^{31}$P NMR spectrum of 10d in C$_6$D$_6$.

Figure S69: $^{119}$Sn-DEPT spectrum of 10d in C$_6$D$_6$. 
Figure S70: $^{13}$C{'H} NMR spectrum of 10d in C$_6$D$_6$.

IR-Spectra

Figure S71: ATR-FTIR spectrum of 2c (liquid, bulk).
Figure S72 ATR-FTIR spectrum of 2d (solid).

Figure S73 ATR-FTIR spectrum of K[3b] (solid).
Figure S74 ATR-FTIR spectrum of K[3c] (solid).

Figure S75: ATR-FTIR spectrum of Li[5c] (solid).
Figure S76: ATR-FTIR spectrum of 9b (solid).

Figure S77: ATR-FTIR spectrum of 9c (solid).
Figure S78: ATR-FTIR spectrum of 9d (solid).

Figure S79: ATR-FTIR spectrum of 10d (solid).
Figure S80: Observed and calculated isotopic patterns of the (pseudo)molecular ions in (+)-ESI mass spectra of 2c,d (top row) and 9c, 10d (bottom row).

Computational Studies

General remarks. DFT calculations were performed with the Gaussian 16 program package\(^8\) using the B3LYP functional,\(^9\) which is an established standard in main group element chemistry, with basis sets from Weigend’s and Ahlrichs’ def2-family,\(^10\) and application of the D3 version of Grimme’s dispersion correction with Becke-Johnson damping\(^11\) and the PCM formalism (keyword scrf, solvent=THF) to model solvation. The molecular structures were established by full energy optimization at the PCM-B3LYP-D3BJ/def2-svp level and identified as local minima on the potential energy hypersurface by subsequent harmonic vibrational frequency calculations. Magnetic shieldings were obtained from single point calculations at the PCM-B3LYP-D3BJ/def2-tzvpp level at the optimised geometries. NBO population analyses of electron densities were carried out using the NBO module implemented in the Gaussian package. The analysis of magnetic shieldings was carried out with NBO6.\(^12\)
Chemical shifts were computed as $\delta_s = (\sigma_{\text{ref}} - \sigma_s - 266.1)$ relative to 85% H$_3$PO$_4$ \cite{13} using the magnetic shielding constants of PH$_3$ ($\sigma_{\text{ref}} = 590.5$ ppm) calculated at the same computational level for referencing.

Table S2 Computed $^{31}$P magnetic shielding parameters and HOMO-LUMO gaps for 2b, 3b\textsuperscript{−}, HP(OEt)$_2$, and Me$_3$SnP(OEt)$_2$ (10b\textsuperscript{b}).

| Compound | $\Delta$E$_{\text{HOMO-LUMO}}$/eV | $\delta^{31}$P/ppm | $\sigma_{\text{iso}}$(31P) | $\sigma_{\text{dia}}$(31P) | $\sigma_{\text{para}}$(31P) |
|----------|-------------------------------|-------------------|---------------------|------------------|---------------------|
| 2b       | 8.43                          | 206.4             | 121.4               | 961.2            | -891.0              |
| 3b\textsuperscript{−} | 6.08                          | 316.1             | -86.7               | 965.2            | -1004.7             |
| HP(OEt)$_2$ | 7.16                          | 155.2             | 70.2                | 960.3            | -838.9              |
| 10b\textsuperscript{b} | 6.09                          | 363.3             | -39.5               | 960.6            | -1047.3             |

\textsuperscript{a)} calculated at the PCM-B3LYP-D3BJ/def2-tzvpp//PCM-B3LYP-D3BJ/def2-svp level of theory; \textsuperscript{b)} $\sigma_{\text{iso}}$(31P) and $\delta^{31}$P for 10b were calculated as -39.3 and 315.9 ppm but the limitations of the available NBO module precluded further analysis. $\Delta$E$_{\text{HOMO-LUMO+6}}$ of 10b (the LUMO+6 is in this case the lowest unoccupied MO with a significant local contribution at phosphorus) was computed as 5.98 eV.

Table S3 Natural orbital contributions (in ppm) to the $^{31}$P paramagnetic shielding term in 2b, 3b\textsuperscript{−}, HP(OEt)$_2$, and Me$_3$SnP(OEt)$_2$ (10b\textsuperscript{b}).

| Compound | $\sigma$(P–O) | $\sigma$(P–B) | $\sigma$(P–H) | l.p.(P) |
|----------|---------------|---------------|---------------|--------|
| 2b       | -125          | -123          | -315          | -210   |
| 3b\textsuperscript{−} | -103          | -89           | -398          | -368   |
| HP(OEt)$_2$ | -111          | -123          | --            | -231   |
| 10b\textsuperscript{b} | -123          | -125          | --            | -272$^b$ |

\textsuperscript{a)} $\sigma$(P–Sn) for 10b\textsuperscript{b}.

Table S4 Computed energies and Gibbs enthalpy corrections (in Hartree) and atomic coordinates (in Å) for 2b, 3b\textsuperscript{−}, HP(OEt)$_2$, and Me$_3$SnP(OEt)$_2$ (10b\textsuperscript{b}).

| 3b\textsuperscript{−} | 2b |
|------------------------|----|
| E1                     | -677.224537073 |
| $\Delta$G-corr.         | -677.725397323 |
| E2                     | -677.754113127 |
| X Y Z                  | X Y Z         |
| C -2.372450            | -1.521249     |
| C -2.478104            | -0.039925     |
| O -1.362260            | 0.704103      |
| P 0.016333             | 0.926960      |
| B 1.113519             | 2.206022      |
| O 0.662237             | -0.533951     |
| C 1.442157             | -1.223113     |
| C 2.922404             | -1.100121     |
| H -0.413374            | 1.209651      |
| H 2.079339             | 2.326840      |
| H 0.416370             | 3.207994      |
| H -0.413374            | 1.739807      |
| H -2.55539             | 1.682085      |
| H -1.514517            | 1.972577      |
| H -3.288643            | 2.035633      |
| H -3.369766            | 0.406890      |
| H -1.514517            | 1.972577      |
| H -3.288643            | 2.035633      |
| H -3.369766            | 0.406890      |
| H -1.514517            | 1.972577      |
| H -3.288643            | 2.035633      |
| H -3.369766            | 0.406890      |
| H -1.514517            | 1.972577      |
| H -3.288643            | 2.035633      |
| H -3.369766            | 0.406890      |
| H -1.514517            | 1.972577      |
| H -3.288643            | 2.035633      |
| H -3.369766            | 0.406890      |
| H -1.514517            | 1.972577      |
| H -3.288643            | 2.035633      |
| H -3.369766            | 0.406890      |
| H -1.514517            | 1.972577      |
| H -3.288643            | 2.035633      |
| H -3.369766            | 0.406890      |
| H -1.514517            | 1.972577      |
| H -3.288643            | 2.035633      |
| H -3.369766            | 0.406890      |

\textsuperscript{a)} E1, $\Delta$G-correction and atomic coordinates calculated at the PCM-B3LYP-D3BJ/def2-svp level of theory and E2 at the PCM-B3LYP-D3BJ/def2-tzvpp//PCM-B3LYP-D3BJ/def2-svp level of theory.
### Table S4 (continued)

| 10b' | HP(OEt)_2 |
|------|-----------|
| E1   | -984.02098197 | -650.569328329 |
| ΔG-corr. | 0.196403 | 0.115022 |
| E2   | -984.664687646 | -651.064124698 |

| X   | Y   | Z   | X   | Y   | Z   |
|-----|-----|-----|-----|-----|-----|
| C   | -2.493130 | 1.828993 | -0.685015 | C   | -1.722146 | 1.768600 | 0.051215 |
| Sn  | -1.532947 | 0.027908 | 0.062831 | C   | -2.285109 | 0.361981 | 0.173559 |
| C   | -2.716395 | -1.740659 | -0.381305 | O   | -1.521920 | -0.595370 | -0.568411 |
| P   | 0.780508  | -0.197215 | -0.993198 | P   | -0.197152 | -1.374770 | 0.041584 |
| O   | 1.316053  | 1.191800  | -0.198419 | O   | 0.880470  | -0.168360 | 0.463360 |
| C   | 2.526277  | 1.834061  | -0.605599 | C   | 1.810684  | 0.282177  | -0.524863 |
| C   | 3.324956  | 2.238582  | 0.619103  | C   | 3.107230  | 0.677567  | 0.152950  |
| C   | -1.160793 | 0.187093  | 2.196146  | H   | -0.655455 | -1.517554 | 1.397598  |
| O   | 1.194488  | -1.457682 | 0.050763  | H   | -1.636026 | 2.056774  | -1.008266 |
| C   | 2.344095  | -2.257195 | -0.234885 | H   | -0.726101 | 1.828255  | 0.512148  |
| C   | 3.594920  | -1.722527 | -0.440960 | H   | -2.388164 | 2.489171  | 0.552211  |
| H   | 2.113813  | -3.271614 | 0.123966  | H   | -3.308787 | 0.314747  | -0.231829 |
| H   | 2.494197  | -2.322266 | -1.329008 | H   | -2.331853 | 0.513966  | 1.234446  |
| H   | 4.437419  | -2.417271 | 0.294184  | H   | 3.953669  | -0.186515 | 0.696226  |
| H   | 3.885600  | -0.745497 | 0.025539  | H   | 2.930083  | 1.470283  | 0.896496  |
| H   | 4.27786  | -1.600711 | 1.522410  | H   | 3.828777  | 1.053957  | -0.589135 |
| H   | 3.115371  | 1.159862  | -1.254952 | H   | 1.372901  | 1.142192  | -1.062445 |
| H   | 2.269571  | 2.722786  | -1.209316 | H   | 1.985892  | -0.515988 | -1.270988 |
| H   | 4.242807  | 2.770934  | 0.322456  | H   | 2.731059  | 2.905574  | 1.263185  |
| H   | 3.607592  | 1.354133  | 1.210142  | H   | -2.106392 | 0.308358  | 2.744978  |
| H   | -0.648486 | -0.722170 | 2.540797  | H   | -0.512306 | 1.054935  | 2.381690  |
| H   | -1.803323 | 2.679117  | -0.580572 | H   | -2.756952 | 1.707019  | -1.745734 |
| H   | -3.407254 | 2.033649  | -0.107882 | H   | -2.141306 | -2.640694 | -0.119257 |
| H   | -3.647191 | 1.053957  | -0.589135 | H   | -2.966180 | -1.771616 | -1.451942 |

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