Diphosphino-Functionalized 1,8-Naphthyridines: a Multifaceted Ligand Platform for Boranes and Diboranes

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Methods and materials

All manipulations were performed either under an atmosphere of dry argon or in vacuo using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired either on a Bruker Avance 500 or a Bruker Avance 400 NMR spectrometer. Chemical shifts (δ) are yield in ppm and internally referenced to the carbon nuclei (13C{1H}) or residual protons (1H) of the solvent. Heteronuclei NMR spectra are referenced to external standards (11B: BF3·OEt2; 31P NMR: 85% H3PO4). High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer.

Solvents and reagents were purchased from Sigma-Aldrich, Alfa Aesar or Fluorochem. Ligand 1,[1] B2Br4(SMe2)2,[2] and PhCH2K[3] were synthesized using literature procedures.
Synthetic procedures

(LB₂Br₃)Br, 2:
Free ligand 1 (44.7 mg, 0.1 mmol) and B₂Br₄(SMe₂)₂ (46.6 g, 0.1 mmol) were mixed before adding 2 mL of CHCl₃. The reaction was stirred for 30 min and then all volatiles were removed under vacuum. The yellow powder was washed with benzene (three times with 2 mL) and thoroughly dried to give compound 2 as a bright yellow powder (75.1 mg).

Yield: 95%.

¹H NMR (400 MHz, CDCl₃) δ: 9.08 (dd, ¹Jp-H = 474.4 Hz, ³JH-H = 13.3 Hz, 1H, P-H), 7.83 (d, ³JH-H = 9.6 Hz, 1H, Ar-H), 7.72 (d, ³JH-H = 7.6 Hz, 1H, Ar-H), 7.32 (d, ³JH-H = 7.6 Hz, 1H, Ar-H), 7.04 (d, ³JH-H = 9.6 Hz, 1H, Ar-H), 6.18 (dd, ³JH-H = 13.3 Hz, ²Jp-H = 6.9 Hz, 1H, C=CH), 4.19 (dd, ²Jp-H = 17.6 Hz, ³JH-H = 7.1 Hz, 1H, PCH₂), 3.92 (dd, ³JH-H = 17.6 Hz, ²Jp-H = 9.9 Hz, 1H, PCH₂), 1.78 (d, ³Jp-H = 15.4 Hz, 9H, CMe₃), 1.56 (d, ³Jp-H = 4.9 Hz, 9H, CMe₃), 1.52 (d, ³Jp-H = 4.9 Hz, 9H, CMe₃), 1.21 - 1.60 (br, 9H, CMe₃).

¹³C NMR (101 MHz, CDCl₃) δ: 152.7 (d, J = 6.4 Hz, Ar-C), 151.0 (dd, J = 9.3, 2.3 Hz, Ar-C), 149.6 (d, J = 1.3 Hz, Ar-C), 139.6 (s, Ar-CH), 128.3 (s, Ar-CH), 127.8 (d, J = 8.7 Hz, Ar-CH), 118.7 (s, Ar-C), 115.4 (d, J = 5.3 Hz, Ar-CH), 76.1 (s, C=CH), 35.7 (d, ¹Jp-C = 12.6 Hz, CMe₃), 35.5 (d, ¹Jp-C = 7.0 Hz, CMe₃), 34.9 (d, ¹Jp-C = 5.5 Hz, CMe₃), 34.5 (d, ¹Jp-C = 5.2 Hz, CMe₃), 31.0 (s, CMe₃), 28.1 - 28.9 (br, CMe₃), 27.6 (s, CMe₃).

³¹P NMR (162 MHz, CDCl₃) δ: 56.0 (s), 19.8 (d, ¹Jp-H = 474.4 Hz).

¹¹B NMR (128 MHz, CDCl₃) δ: 0.3 (br).

HRMS: Calcd for [C₂₆H₄₃B₂Br₄N₂P₂]⁺ 786.9775, found 786.9757, method FTMS + p ESI. We are unsure how the elimination of hydride happened but in the same measurement, we also find three other peaks with reasonable fragmentation patterns, so we believe this HRMS is reliable.
L((BBR₃)₂), 3:
This was prepared via an NMR-scale reaction as 3 is only used as the intermediate for the synthesis of 4a. Free ligand 1 (13.5 mg, 0.03 mmol) and BBR₃(SMe₂) (18.6 mg, 0.06 mmol) were mixed before adding CDCl₃, and the NMR spectrum was recorded shortly afterwards.
Yield: not calculated.

¹H NMR (400 MHz, CDCl₃) δ: 8.19 (d, ¹J_H-H = 8.3 Hz, 2H), 7.80 (d, ¹J_H-H = 8.3 Hz, 2H), 4.28 (d, ²J_P-H = 12.0 Hz, 4H), 1.76 (d, ³J_P-H = 14.0 Hz, 36H).

¹³C{¹H} NMR (101 MHz, CDCl₃) δ: 158.9 (d, J = 8.1 Hz, Ar-C), 154.3 (s, Ar-C), 137.7 (s, Ar-CH), 125.7 (d, J = 5.3 Hz, Ar-CH), 120.3 (s, Ar-C), 39.0 (d, ¹J_P-C = 22.0 Hz, CMe₃), 31.0 (s, CMe₃), 30.5 (d, ¹J_P-C = 27.0 Hz, P-CH₂). Note: compound 3 slowly isomerizes to 4a at room temperature during the recording of the ¹³C{¹H} NMR spectrum, as indicated by the emergence of peaks at 29.0 and 28.0 ppm (Figure S7).

³¹P{¹H} NMR (162 MHz, CDCl₃) δ: 9.9 (dd, J = 261.4 Hz, ¹J_B-P = 130.6 Hz).

¹¹B{¹H} NMR (128 MHz, CDCl₃) δ: −15.0 (d, ¹J_P,B = 130.6 Hz).

(LBBR₂)(BBR₄), 4a:
In-situ-generated 3 in CDCl₃ was heated at 80 °C overnight and then all volatiles were removed to give 25.4 mg of 4a as a deep yellow solid. This solid is a mixture of 4a and the protonated ligand [LH]⁺ in a ratio of ca. 5:1 as shown in the ¹H and ³¹P{¹H} NMR spectra.
Yield: 89%.
$^1$H NMR of 4a: (400 MHz, CDCl$_3$) $\delta$: 7.73 (dt, $^1J_{P-H} = 490.6$ Hz, $^3J_{H-H} = 4.9$ Hz, 1H, PH), 7.49 (d, $^3J_{H-H} = 7.6$ Hz, 1H, Ar-H), 7.45 (d, $^3J_{H-H} = 7.6$ Hz, 1H, Ar-H) 6.90 (dd, $^3J_{H-H} = 9.3$ Hz, $^4J_{P-H} = 1.8$ Hz, 1H, Ar-H), 6.49 (d, $^3J_{H-H} = 9.3$ Hz, 1H, Ar-H), 4.43 (dd, $^2J_{P-H} = 7.3$ Hz, 1H, C=C-H), 4.23 (dd, $^2J_{P-H} = 12.2$ Hz, $^3J_{H-H} = 4.9$ Hz, 2H, PCH$_2$), 1.56 (d, $^3J_{P-H} = 16.4$ Hz, 18H, CMe$_3$), 1.36 (d, $^3J_{P-H} = 14.2$ Hz, 18H, CMe$_3$).

$^{13}$C($^1$H) NMR of 4a: (101 MHz, CDCl$_3$) $\delta$: 161.59 (d, $J_{P-C} = 10.2$ Hz, Ar-C), 151.5 (d, $J_{P-C} = 9.6$ Hz, Ar-C), 150.5 (d, $J_{P-C} = 9.3$ Hz, Ar-C), 136.6 (s, Ar-CH), 132.9 (s, Ar-CH), 122.4 (d, $J_{P-C} = 14.2$ Hz, Ar-CH), 118.8 (d, $J_{P-C} = 7.3$ Hz, Ar-CH), 117.4 (d, $J_{P-C} = 1.3$ Hz, Ar-C), 70.0 (d, $J_{P-C} = 61.7$ Hz, C=CH), 37.2 (d, $J_{P-C} = 30.8$ Hz, CMe$_3$), 28.0 (s, CMe$_3$), 24.9 (d, $J_{P-C} = 45.4$ Hz, PCH$_2$).

$^{31}$P NMR of 4a: (162 MHz, CDCl$_3$) $\delta$: 36.3 (dm, $J_{H-P} = 490.6$ Hz), 18.5 (br).

$^{11}$B($^1$H) NMR of 4a: (128 MHz, CDCl$_3$) $\delta$: $-5.5$ (d, $J_{B-P} = 137.3$ Hz), $-24.1$ (s).

(LBBr$_2$)Br, 4b:
Free ligand 1 (26.8 mg, 0.06 mmol) and BBr$_3$(SMe$_2$) (18.8 mg, 0.06 mmol) were mixed before adding 5 mL CHCl$_3$, and the mixture was heated at 80 $^\circ$C overnight. All volatiles were removed and the yellow solid received was washed with 5 mL benzene to give 29.5 mg of 4b.

Yield: 71%.

$^1$H NMR: (400 MHz, CDCl$_3$) $\delta$: 7.68 (d, $^3J_{H-H} = 7.6$ Hz, 1H, Ar-H), 7.58 (d, $^1J_{P-H} = 485.8$, $^3J_{H-H} = 5.0$ Hz, 1H, P-H), 7.39 (d, $^3J_{H-H} = 7.6$ Hz, 1H, Ar-H), 6.86 (dd, $^3J_{H-H} = 9.4$ Hz, $^4J_{P-H} = 1.8$ Hz, 1H, Ar-H), 6.45 (d, $^3J_{H-H} = 9.4$ Hz, 1H, Ar-H), 4.63 (dd, $^2J_{P-H} = 12.5$ Hz, $^3J_{H-H} = 5.0$ Hz, 2H, PCH$_2$), 4.39 (d, $^2J_{P-H} = 7.3$ Hz, 1H, C=C-H), 1.56 (d, $^3J_{P-H} = 14.6$ Hz, 18H), 1.54 (d, $^3J_{P-H} = 16.4$ Hz, 18H).

$^{13}$C($^1$H) NMR: (101 MHz, CDCl$_3$) $\delta$: 161.6 (d, $J_{P-C} = 10.2$ Hz, Ar-C), 151.5 (d, $J_{P-C} = 9.6$ Hz, Ar-C), 150.5 (d, $J_{P-C} = 9.3$ Hz, Ar-C), 136.6 (s, Ar-CH), 132.9 (s, Ar-CH), 122.4 (d, $J_{P-C} = 14.2$ Hz, Ar-CH), 118.8 (d, $J_{P-C} = 7.3$ Hz, Ar-CH), 117.4 (d, $J_{P-C} = 1.3$ Hz, Ar-C), 70.0 (d, $J_{P-C} = 61.7$ Hz, C=CH), 37.2 (d, $J_{P-C} = 30.8$ Hz, CMe$_3$), 28.0 (s, CMe$_3$), 24.9 (d, $J_{P-C} = 45.4$ Hz, PCH$_2$).

$^{31}$P NMR: (162 MHz, CDCl$_3$) $\delta$: 37.5 (d, $^1J_{P-H} = 485.9$ Hz, P-H), 18.4 (m).

$^{11}$B($^1$H) NMR: (128 MHz, CDCl$_3$) $\delta$: $-5.6$ (d, $^1J_{B-P} = 137.3$ Hz).

HRMS: Calcd for [C$_{26}$H$_{44}$N$_2$P$_2$BBr$_2$]$^+$ 617.1414, found 617.1405, method FTMS + p ESI.

LK-18C6, 5-18-C-6:
Free ligand 1 (0.223 g, 0.5 mmol) and KHMDS (0.100 g, 0.5 mmol) were mixed in THF at room temperature before adding 18-crown-6 (0.132 g, 0.5 mmol). Reaction was stirred for 30
min and then all volatiles were removed. The dark red solid received was washed with 15 mL cold pentane to give 0.326 g of **5-18-C-6** as a fine powder. The sample received contains a small amount of **1** and the amount of **1** varies between batches. The NMR data following are recorded for the in-situ-generated **5-18-C-6**.

**Yield:** 87%.

**1H NMR:** (400 MHz, C₆D₆) δ: 8.07 (dd, Jₕ-H = 9.3 Hz, Jₚ-H = 5.0 Hz, 1H, Ar-H), 6.98 – 6.83 (m, 2H, Ar-H), 6.60 (d, Jₕ-H = 9.3 Hz, 1H, Ar-H), 4.68 (d, Jₚ-H = 8.1 Hz, 1H, PCH=C), 2.92 (d, Jₕ-H = 2.9 Hz, 2H, PCH₂), 1.47 (d, Jₚ-H = 10.5 Hz, 18H), 1.22 (d, Jₕ-H = 10.4 Hz, 18H).

**13C{1H} NMR:** (101 MHz, C₆D₆) δ: 166.6 (d, Jₚ-C = 33.2 Hz, Ar-C), 163.9 (dd, Jₚ-C = 3.5, 1.4 Hz, Ar-C), 159.4 (d, Jₚ-C = 15.1 Hz, Ar-C), 132.4 (s, Ar-CH), 128.6 (s, Ar-CH), 123.9 (d, Jₚ-C = 30.7 Hz, Ar-C), 116.6 – 116.5 (m, Ar-C), 108.4 (d, Jₚ-C = 16.4 Hz, Ar-CH), 80.7 (d, Jₚ-C = 3.8 Hz, PCH=C), 32.6 (d, Jₚ-C = 18.4 Hz, CMe₃), 31.7 (d, Jₚ-C = 24.5 Hz, CMe₃), 30.9 (d, Jₚ-C = 14.6 Hz, CMe₃), 30.3 (d, Jₚ-C = 13.7 Hz, CMe₃).

**31P{1H} NMR:** (162 MHz, C₆D₆) δ: 28.0 (s), 13.4 (s).

**HRMS:** Calcd for [C₂₆H₄₃N₂P₂K+H]⁺ 485.2611, found 485.2602, method FTMS + p ESI.

**LK₂, 6:**

Free ligand **1** (8.9 mg, 0.02 mmol) and PhCH₂K (5.2 mg, 0.02 mmol) were mixed in THF-d₈ at room temperature to give a pale orange solution. NMR data were recorded using this in-situ-generated sample. All attempts to purify **LK₂** provided only the monodeprotonated product.

**Yield:** not calculated.

**1H NMR:** (500 MHz, THF-d₈) δ: 6.02 (d, Jₕ-H = 8.4 Hz, 2H, Ar-H), 5.42 (d, Jₕ-H = 8.4 Hz, 2H, Ar-H), 3.16 (d, Jₚ-H = 8.1 Hz, 2H, C=CH₂P), 1.10 (d, Jₕ-H = 10.3 Hz, 36H, tBu).

**13C{1H} NMR:** (126 MHz, THF-d₈) δ: 168.2 (d, Jₚ-C = 21.1 Hz, Ar-C), 163.0 (s, Ar-C), 129.9 (s, Ar-CH), 110.2 (d, Jₚ-C = 7.5 Hz, Ar-CH), 102.5 (s, Ar-CH), 65.0 (d, Jₚ-C = 5.4 Hz, C=CH-P), 33.1 (d, Jₚ-C = 16.8 Hz, CMe₃), 30.7 (d, Jₚ-C = 13.7 Hz, CMe₃).

**31P{1H} NMR:** (202 MHz, THF) δ: 11.8 (s).

**Note:** Compound **6** is too sensitive for both elemental analysis and HRMS.

**LN₃B₂Cl, 7:**

Free ligand **1** (44.7 mg, 0.1 mmol) and KHMDS (20.0 mg, 0.1 mmol) were mixed in 1 mL benzene at room temperature and the full consumption of **1** was confirmed by **31P** NMR spectroscopy. At room temperature, the solution of **LK** was added to a solution of B₂(NMe₂)₂Cl₂ (18.0 mg, 0.1 mmol, 0.5 mL benzene). The mixture was heated at 80 °C and
monitored by $^{31}$P NMR spectroscopy until all $\text{LK}$ was consumed (normally 2 h). The yellow solution received was filtered and recrystallized to give 13.4 mg of compound 7. The sample received always contains small amount of 1 even when recrystallized in a glovebox.

Yield: 23%.

$^1$H NMR: (500 MHz, C$_6$D$_6$) $\delta$: 7.88 (dd, $^3$J$_{H-H}$ = 9.7 Hz, $^4$J$_{P-H}$ = 5.5 Hz, 1H, Ar-H), 6.78 (dd, $^3$J$_{H-H}$ = 7.6 Hz, $^4$J$_{P-H}$ = 1.3 Hz, 1H, Ar-H), 6.68 (d, $^3$J$_{H-H}$ = 7.6 Hz, 1H, Ar-H), 6.18 (dd, $^3$J$_{H-H}$ = 9.7 Hz, $^5$J$_{H-H}$ = 1.4 Hz, 1H, Ar-H), 4.85 (dd, $^2$J$_{P-H}$ = 6.9 Hz, $^5$J$_{H-H}$ = 1.4 Hz, 1H, PC=CH), 2.88 (br, 7H, 6H from NMe2 and one H of PCMe2), 2.80–2.78 (m, 4H, NMe2 and the other H of PCMe2), 2.59 (s, 3H, NMe), 1.37 (d, $^3$J$_{P-H}$ = 11.3 Hz, 9H, CMe3), 1.31 (d, $^3$J$_{P-H}$ = 11.1 Hz, 9H, CMe3), 1.20 (dd, $^3$J$_{P-H}$ = 10.6 Hz, 18H, CMe3).

$^{13}$C{$^1$H} NMR: (126 MHz, C$_6$D$_6$) $\delta$: 160.3 (d, $^3$J$_{P-C}$ = 14.1 Hz, Ar-C), 154.4 (d, $^3$J$_{P-C}$ = 1.5 Hz, Ar-C), 151.8 (d, $^3$J$_{P-C}$ = 30.5 Hz, Ar-C), 133.5 (s, Ar-CH), 126.6 (d, $^3$J$_{P-C}$ = 2.1 Hz, Ar-CH), 124.7 (d, $^3$J$_{P-C}$ = 32.1 Hz, Ar-CH), 115.6 (d, $^3$J$_{P-C}$ = 10.2 Hz, Ar-CH), 114.5 (t, $^3$J$_{P-C}$ = 1.8 Hz), 90.9 (d, $^3$J$_{P-C}$ = 12.8 Hz, PC=CH), 41.2 (s, NMe2), 40.8 (br, NMe2), 38.7 (s, NMe2), 32.6 (d, $^3$J$_{P-C}$ = 17.3 Hz, CMe3), 32.1 (d, $^3$J$_{P-C}$ = 4.1 Hz, CMe3), 31.9 (d, $^3$J$_{P-C}$ = 3.9 Hz, CMe3), 31.8 (d, $^3$J$_{P-C}$ = 24.6 Hz, CMe3), 31.6 (d, $^3$J$_{P-C}$ = 26.1 Hz), 30.2 (d, $^3$J$_{P-C}$ = 12.1 Hz, CMe3), 30.1 (d, $^3$J$_{P-C}$ = 3.9 Hz, CMe3), 29.9 (d, $^3$J$_{P-C}$ = 13.8 Hz, CMe3).

$^{31}$P{$^1$H} NMR: (202 MHz, C$_6$D$_6$) $\delta$: 34.0 (s, PCH2), 7.6 (s, PC=CH).

$^{11}$B{$^1$H} NMR: (160 MHz, C$_6$D$_6$) $\delta$: 38.5 (br).

HRMS: Calcd for [C$_{30}$H$_{55}$B$_2$Cl$_4$N$_4$P$_2$]$^+$, 590.3771, found 590.3758, method FTMS + p ESI.

L$_2$N$_2$B$_2$, 8:

Free ligand 1 (8.9 mg, 0.02 mmol) and KHMDS (4.0 mg, 0.02 mmol) were mixed in 0.3 mL C$_6$D$_6$ at room temperature and the full consumption of 1 was confirmed by $^{31}$P NMR spectroscopy. At room temperature, the solution of $\text{LK}$ was added to the solution of B$_2$(NMe$_2$)$_2$Cl$_2$ (1.8 mg, 0.01 mmol, 0.2 mL of C$_6$D$_6$). The mixture was heated at 80 $^\circ$C overnight and monitored by $^{31}$P NMR spectroscopy until all $\text{LK}$ was consumed. The yellow solution received was a mixture of 8 and 1 and directly used for NMR spectroscopy. All purification operations provided only 1 as the major product.

Yield: not calculated.

$^1$H NMR: (400 MHz, C$_6$D$_6$) $\delta$: 7.25 (dd, $^3$J$_{H-H}$ = 9.6 Hz, $^4$J$_{P-H}$ = 4.2 Hz, 2H, Ar-H), 6.24 (dd, $^3$J$_{H-H}$ = 8.9 Hz, $^3$J$_H$ = 1.7 Hz, 2H, Ar-H), 6.12 (dd, $^3$J$_{H-H}$ = 9.6 Hz, $^3$J$_H$ = 1.3 Hz, 2H, Ar-H), 5.75 (dd, $^3$J$_{H-H}$ = 8.9 Hz, $^4$J$_H$ = 0.7 Hz, 2H, Ar-H), 4.82 (d, $^2$J$_{P-H}$ = 6.9 Hz, 2H, PC=CH), 3.60 (d, $^2$J$_{P-H}$ = 3.6 Hz, 2H, one type of H of PCH2), 2.78 (s, 6H, NMe2), 2.58 (s, 6H, NMe2), 1.32 (d, $^3$J$_H$ = 11.1 Hz, 6H, 1H, NMe2).
Hz, 18H, CMe$_3$), 1.28 (d, $J = 5.5$ Hz, 18H, CMe$_3$), 1.25 (d, $J = 3.9$ Hz, 18H, CMe$_3$), 1.02 (d, $J = 12.1$ Hz, 18H, CMe$_3$). Note: the signal for the second H nucleus of PCH$_2$ is suspected to be overlapped with the broad peak at ca. 2.99–2.80 ppm.

$^{31}$P{$^1$H} NMR: (202 MHz, C$_6$D$_6$) $\delta$: 32.6 (br, PCH$_2$), 6.0 (s, PC=CH)

$^{11}$B NMR: too broad to be detected.

HRMS: Theory data for [C$_{56}$H$_{98}$B$_2$N$_6$P$_4$]$^+$1000.6984, found 1000.6978, method FTMS + p ESI.
NMR spectra of compounds

**Figure S1.** $^1$H NMR spectrum of 2 in CDCl$_3$. 
Figure S2. $^{13}$C{$^{1}$H} NMR spectrum of 2 in CDCl$_3$. 


Figure S3. $^{31}$P NMR spectrum of 2 in CDCl$_3$. 
Figure S4. $^{31}\text{P}^1\text{H}$ NMR spectrum of 2 in CDCl$_3$. 
Figure S5. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of 2 in CDCl$_3$. 
Figure S6. $^1$H NMR spectrum of 3 in CDCl$_3$. 
Figure S7. $^{13}$C{$^1$H} NMR spectrum of 3 in CDCl$_3$. 

28.042 28.987 30.332 30.599 30.962 38.852 39.071 76.843 77.160 77.477 120.318 125.640 125.692 137.682 154.272 158.867 158.947
Figure S8. $^{31}$P{$^1$H} NMR spectrum of 3 in CDCl$_3$. 
Figure S9. $^{11}$B{¹H} NMR spectrum of 3 in CDCl$_3$. 

[Image of the NMR spectrum showing peaks at around -24.113 ppm and -15.511 ppm, labeled as $[BBr_4]$]
**Figure S10.** $^1$H NMR spectrum of 4a in CDCl$_3$ (The blue and pink stars represent 4a and [LH]$^+$, respectively).
Figure S11. $^{13}$C{^1}H NMR spectrum of 4a in CDCl$_3$. 
Figure S12. $^{31}$P NMR spectrum of 4a in CDCl$_3$. 
Figure S13. $^{11}$B/$^1$H NMR spectrum of 4a in CDCl$_3$. 
Figure S14. $^1$H NMR spectrum of 4b in CDCl$_3$.  

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Figure S15. $^{13}$C\{\textsuperscript{1}H\} NMR spectrum of 4b in CDCl$_3$. 
Figure S16. $^{31}$P{$^1$H} NMR spectrum of 4b in CDCl$_3$. 
Figure S17. $^{11}$B{$^1$H} NMR spectrum of 4b in CDCl$_3$. 
Figure S18. $^1$H NMR spectrum of 5-18C6 in C$_6$D$_6$. 
Figure S19. $^{13}$C–$^1$H NMR spectrum of 5-18C6 in C$_6$D$_6$. 
Figure S20. $^{31}$P$\{^1$H$\}$ NMR spectrum of 5-18C6 in C$_6$D$_6$. 
Figure S21. $^1$H NMR spectrum of 6 in THF-d8.
Figure S22. $^{13}$C{$^1$H} NMR spectrum of 6 in THF-d$_8$. 
Figure S23. DEPT135 NMR spectrum of 6 in THF-d8.
Figure S24. $^{31}P\{^1H\}$ NMR spectrum of 6 in THF-d$_8$. 
Figure S25. $^1$H NMR spectrum of 7 in C$_6$D$_6$. 
Figure S26. $^{13}$C-{$^1$H} NMR spectrum of 7 in C$_6$D$_6$. 
Figure S27. $^{31}$P{$^{1}$H} NMR spectrum of 7 in C$_6$D$_6$. 
Figure S28. $^{11}$B-$^1$H NMR spectrum of 7 in C₆D₆.
Figure S29. $^1$H NMR spectrum of 8 in C$_6$D$_6$ (Note: the blue stars correspond to free ligand 1, the pink stars to L$_2$B$_2$N$_2$ 8).
Figure S30. $^{31}P$ NMR spectrum of 8 in C₆D₆. (Note: the blue stars correspond to free ligand 1 while the pink ones to L₂B₂N₂ 8.)
X-ray crystallographic data

The crystal data of 4b were collected on a Bruker X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated MoKα radiation. The crystal data of 2, 5-18C6 were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated MoKα radiation. The crystal data of 6, 8 were collected on a κ-Helios diffractometer with an APEX II CCD detector and Helios multilayeroptics (mirrors) MoKα radiation. The structures were solved using the intrinsic phasing method,[4] refined with the ShelXL program[5] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations.

Deposition Numbers 2099390 (for 2), 2099391 (for 4b), 2099392 (for 5-18-C-6), 2099393 (for 6b), 2099394 (for 8) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe.
Crystal data for 2: C_{29}H_{47}BzBrCN_{2}P_{2}, \textit{M}_r = 1145.93, yellow block, 0.352×0.157×0.11 \text{mm}^3, monoclinic space group \textit{C}2/c, \textit{a} = 38.284(19) \text{Å}, \textit{b} = 8.394(3) \text{Å}, \textit{c} = 31.084(10) \text{Å}, \beta = 112.915(13)^{\circ}, \textit{V} = 9200(6) \text{Å}^3, \textit{Z} = 8, \rho_{\text{calcd}} = 1.655 \text{g cm}^{-3}, \mu = 4.116 \text{mm}^{-1}, \textit{F}(000) = 4544, \textit{T} = 100(2) \text{K}, \textit{R}_I = 0.0528, \textit{wR}^2 = 0.0752, 9084 independent reflections \[20 \leq \theta \leq 52.044^{\circ}\] and 522 parameters.

**Figure S31.** Crystallographically-derived solid-state structure of the cation of 2. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and hydrogen atoms (except H bound to C9, C10) are omitted for clarity.

Note: The coordinates of H15_1 were refined freely. The chloroform molecules showed disorder. The atomic displacement parameters (ADPs) of overlapping atoms from different PARTs (C1, Cl2, Cl3, Cl4 of RESIs 8/18 and 9/19) were restrained using similarity restraint (SIMU) and rigid body restraint (RIGU). The C1-Cl2, C1-Cl3, C1-Cl4 distances as well as the Cl2-Cl3, Cl3-Cl4, Cl4-Cl1 distances of RESIs 8/18 and 9/19 were restrained using same distance restraint (SADI).
Crystal data for 4b: C$_{32}$H$_{48}$BB$_3$F$_2$N$_2$P$_2$, $M_r = 811.20$, yellow plate, 0.474×0.157×0.086 mm$^3$, triclinic space group $P$-$I$, $a = 8.2639(11)$ Å, $b = 14.807(7)$ Å, $c = 15.3084(16)$ Å, $\alpha = 101.303(17)$ °, $\beta = 95.287(7)$°, $\gamma = 101.638(19)$ °, $V = 1782.1(9)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.512$ g cm$^{-3}$, $\mu = 3.520$ mm$^{-1}$, $F(000) = 824$, $T = 99(2)$ K, $R_I = 0.0616$, $wR^2 = 0.1143$, 7331 independent reflections [$2 \theta \leq 52.880$°] and 695 parameters.

Figure S32. Crystallographically-derived solid-state structure of the cation of 4b. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and hydrogen atoms are omitted for clarity.

Note: The whole molecule showed severe rotational disorder. The atomic displacement parameters (ADPs) of overlapping atoms from different PARTs were restrained using similarity restraint (SIMU) and rigid body restraint (RIGU). All corresponding bonds of the two PARTs were restrained using same distance restraint (SADI). All hydrogen atoms except H1_1 and H1_11 were assigned to idealized positions. The coordinates of H1_1 and H1_11 were refined freely, but restrained to a P-H bond length of 1.30 Å using the DFIX command.
Crystal data for **5-18C6**: C₄₈H₈₇KN₂O₁₀P₂, \( M_r = 953.23 \), red plate, \( 0.470\times0.344\times0.214 \) mm³, monoclinic space group \( P2_1/c \), \( a = 17.786(11) \) Å, \( b = 26.688(14) \) Å, \( c = 11.340(7) \) Å, \( \beta = 95.825(16)^\circ \), \( V = 5355(5) \) Å³, \( Z = 4 \), \( \rho_{\text{calc}} = 1.182 \) g·cm⁻³, \( \mu = 0.212 \) mm⁻¹, \( F(000) = 2072 \), \( T = 100(2) \) K, \( R_1 = 0.0980 \), \( wR^2 = 0.1742 \), 10533 independent reflections \([\theta \leq 52.044^\circ]\) and 690 parameters.

**Figure S33.** Crystallographically-derived solid-state structure of the cation of **5-18C6**. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and hydrogen atoms (except H bound to C9/C10) are omitted for clarity.

Note: The THF and the crown ether showed disorder. The atomic displacement parameters (ADPs) of overlapping atoms from different PARTs (O1, C2, C3, C4, C5 of RESIs 8/18; C1, O2, C3, C4, O5, C6, C7, C8, C9 of RESIs 7/17) were restrained using similarity restraint (SIMU) and rigid body restraint (RIGU). The C9-C1, C3-C4, C6-C7 distances as well as the C1-O2, O2-C3, C4-O5, O5-C6, C7-O8, O8-C9 distances of the (symmetry-generated) crown ether moieties (RESIs 7/17) were restrained using same distance restraint (SADI).
Crystal data for 6: C_{55}H_{87}K_{4}N_{4}P_{4}, \( M_r = 1084.56 \), red plate, 0.026×0.084×0.145 mm³, monoclinic, space group C2/c, \( a = 25.930(12) \) Å, \( b = 18.949(4) \) Å, \( c = 24.858(14) \) Å, \( \alpha = 90^\circ \), \( \beta = 101.17(3) ^\circ \), \( \gamma = 90^\circ \), \( V = 11982(9) \) Å³, \( Z = 8 \), \( \rho_{calc} = 1.202 \) g·cm⁻³, \( \mu = 0.441 \) mm⁻¹, \( F(000) = 4648 \), \( T = 101(2) \) K, \( R_I = 0.0815 \), \( wR^2 = 0.0969 \), 10982 independent reflections [\( 20 \leq \theta \leq 50.750^\circ \)] and 645 parameters.

Figure S34. Crystallographically-derived solid-state structure of the cation of 6. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and hydrogen atoms (except H bound to C9, C10, C29, C30, C12, C32) are omitted for clarity.

Note: Three reflections are omitted because they are affected by the beamstop. The hkl are (0 0 2) (1 1 1) and (-2 0 2).
Crystal data for 8: C_{56}H_{98}B_{2}N_{6}P_{4}, \( M_r = 1000.90 \), yellow block, 0.719×0.299×0.227 mm\(^3\), monoclinic space group \( C2/c \), \( a = 27.958(11) \) Å, \( b = 21.987(11) \) Å, \( c = 10.318(5) \) Å, \( \alpha = 90^\circ \), \( \beta = 99.77(2)^\circ \), \( \gamma = 90^\circ \), \( V = 6250(5) \) Å\(^3\), \( Z = 8 \), \( \rho_{calc} = 1.064 \) g cm\(^{-3}\), \( \mu = 0.158 \) mm\(^{-1}\), \( F(000) = 2184 \), \( T = 100(2) \) K, \( R_1 = 0.0819 \), \( wR^2 = 0.1858 \), 6828 independent reflections [\( 2\theta \leq 53.484^\circ \)] and 322 parameters.

**Figure S35.** Crystallographically-derived solid-state structure of the cation of 8. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and hydrogen atoms (except H bound to C9, C10, C29, C30, C12, C32) are omitted for clarity.

Note: The crystal was twinned by rotation around the [-0.5 1 1] real axis by 180.0° and was refined as a two-component twin with a final BASF of 0.28552. Two reflections are omitted because they are affected by the beam stop. The hkl are (2 0 0) (1 1 0).
Figure S36. Fragmentation of 2 by eliminating a hydride.
Figure S37. Fragmentation of 2 by eliminating HBr and a single electron.
Figure S38. Further fragmentation from figure S37 by eliminating a neutral tBu group.
Figure S39. Further fragmentation from figure S37 by eliminating a bromine radical.
Figure S40. HRMS of compound 4b.
Figure S41. The [M+H]^+ peak for compound 5-18-C-6.
Figure S42. The molecular ion peak of compound 7.
Figure S43. The molecular ion peak of compound 8.
**Computational details**

Geometry optimizations and Hessian calculations were performed for $2$ and $2a$ at the density functional theory level. The PBE0$^6$ functional was employed in conjunction with the 6-31+G**$^7$ basis set for light elements, while Br was described with the LanL2DZ$^8$ basis set and effective core potential. Dispersion corrections were considered using Grimme’s D3$^9$ model with the Becke-Johnson (BJ)$^{10}$ damping function. All optimized structures were characterized as minimum energy structures by the analysis of the computed vibrational frequencies, as in all cases only positive eigenvalues were found. The canonical Kohn-Sham molecular orbitals of the systems, their corresponding HOMO-LUMO gaps, and their electronic energies corrected by the zero-point energy (ZPE) were obtained at their corresponding optimized structures at the PBE0-D3(BJ)/6-31+G**/LanL2DZ(Br) level. Additionally, free energy calculations were conducted for investigating the relative stability of $2$ and $2a$ in chloroform (CHCl$_3$) medium. Solvation effects were considered using the solvation model based on density (SMD)$^{11}$ implicit solvation model with CHCl$_3$ ($\epsilon = 4.7113$) as the solvent. The free energies were obtained from single-point calculations at the SMD(CHCl$_3$)/PBE0-D3(BJ)/6-311++G**/LanL2DZ(Br) level. All calculations were performed using Gaussian 16, revision C.01.$^{12}$
## Cartesian coordinates

**Compound 2**

| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| N    | 0.526085000 | 0.545749000 | -0.821997000 |
| C    | 1.876063000 | 0.830519000 | -0.998237000 |
| C    | 2.212696000 | 1.844590000 | -1.981721000 |
| H    | 3.263064000 | 2.045580000 | -2.156818000 |
| C    | 1.283398000 | 2.563619000 | -2.651117000 |
| H    | 1.577442000 | 3.329020000 | -3.362776000 |
| C    | -0.109524000 | 2.312771000 | -2.410783000 |
| C    | -1.196773000 | 2.986200000 | -2.967627000 |
| H    | -1.013422000 | 3.795198000 | -3.669471000 |
| C    | -2.513023000 | 2.653066000 | -2.625716000 |
| H    | -3.352648000 | 3.196212000 | -3.043233000 |
| C    | -2.724676000 | 1.606478000 | -1.744083000 |
| N    | -1.664527000 | 0.948900000 | -1.236455000 |
| C    | -0.388315000 | 1.274683000 | -1.501058000 |
| C    | 2.801721000 | 0.173653000 | -0.235694000 |
| H    | 2.445212000 | -0.550343000 | 0.490111000 |
| P    | 4.544084000 | 0.257473000 | -0.268198000 |
| C    | -4.030808000 | 1.067610000 | -1.231332000 |
| H    | -4.418011000 | 0.324384000 | -1.938349000 |
| H    | -4.780107000 | 1.853118000 | -1.112688000 |
| P    | -3.608610000 | 0.170903000 | 0.348321000 |
| H    | 4.985028000 | 0.942233000 | -1.417008000 |
| B    | -1.801346000 | -0.316696000 | -0.355878000 |
| B    | -0.164534000 | -0.422471000 | 0.234348000 |
| Br   | 0.291546000 | 0.417754000 | 2.100399000 |
| Br   | 0.633935000 | -2.313736000 | 0.224830000 |
| Br   | -2.128464000 | -1.794969000 | -1.811939000 |
| C    | 5.140768000 | 1.288745000 | 1.156298000 |
| C    | 6.659985000 | 1.223117000 | 1.312002000 |
| H    | 6.962715000 | 1.956762000 | 2.066876000 |
| H    | 7.189562000 | 1.469527000 | 0.385596000 |


H  -4.852986000  3.042027000  2.492449000
C  -4.796641000 -1.252594000  0.690661000
C  -5.963899000 -0.874606000  1.608632000
H  -6.572188000 -1.775605000  1.742897000
H  -6.611242000 -0.113009000  1.165890000
H  -5.652572000 -0.549973000  2.602089000
C  -3.946079000 -2.343085000  1.361626000
H  -3.500561000 -1.996620000  2.299232000
H  -3.145387000 -2.700832000  0.709977000
H  -4.595075000 -3.193361000  1.597805000
C  -5.415085000 -1.765934000  0.616948000
H  -6.007451000 -2.655060000  1.374787000
H  -4.673710000 -2.055258000  1.360669000
H  -6.100524000 -1.030895000 -1.051877000

Compound 2a

N  -1.662788000  1.252535000 -0.886705000
C  -2.771813000  1.857099000 -1.463970000
C  -2.487700000  2.971809000 -2.340969000
H  -3.321414000  3.503322000 -2.787001000
C  -1.209193000  3.338198000 -2.608944000
H  -1.008067000  4.171823000 -3.275344000
C  -0.084640000  2.636660000 -2.028991000
C  1.259518000  2.889770000 -2.220380000
H  1.577175000  3.697354000 -2.875307000
C  2.219161000  2.097595000 -1.568801000
H  3.269069000  2.303016000 -1.732571000
C  1.838233000  1.067532000 -0.729560000
N  0.518725000  0.815403000 -0.501363000
C  -0.406804000  1.575796000 -1.149614000
C  -3.961270000  1.277926000 -1.132057000
H  -4.913957000  1.639487000 -1.496921000

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|  | X          | Y          | Z          |
|---|------------|------------|------------|
| P | -3.704440000 | -0.236649000 | -0.182586000 |
| C | 2.768851000  | 0.125040000  | -0.034264000 |
| H | 2.392203000  | -0.889204000  | -0.223191000 |
| H | 2.672288000  | 0.240198000  | 1.054143000 |
| P | 4.536954000  | 0.080886000  | -0.407821000 |
| H | 4.775276000  | 0.693210000  | -1.652066000 |
| B | -0.219125000  | -0.380940000  | 0.318594000 |
| B | -1.828294000  | 0.287002000  | 0.285617000 |
| Br | 0.242288000 | -2.090087000  | -0.830002000 |
| Br | -1.946361000  | 1.646382000  | 1.912004000 |
| Br | 0.576254000  | -0.721325000  | 2.176946000 |
| C | -4.914253000  | -0.428579000  | 1.248275000 |
| C | -4.171882000  | -1.162489000  | 2.374562000 |
| H | -4.862378000  | -1.296234000  | 3.214881000 |
| H | -3.307514000  | -0.601950000  | 2.735272000 |
| H | -3.836704000  | -2.156232000  | 2.061634000 |
| C | -6.167124000  | -1.226652000  | 0.876376000 |
| H | -6.816646000  | -1.240576000  | 1.758624000 |
| H | -5.952376000  | -2.265635000  | 0.619328000 |
| H | -6.733515000  | -0.763727000  | 0.064049000 |
| C | -5.379166000  | 0.962678000  | 1.698873000 |
| H | -5.992021000  | 1.443271000  | 0.930127000 |
| H | -4.554386000  | 1.626989000  | 1.952744000 |
| H | -6.003069000  | 0.835954000  | 2.591047000 |
| C | -3.815962000  | -1.623887000  | -1.455090000 |
| C | -2.811085000  | -1.291490000  | -2.566930000 |
| H | -3.119246000  | -0.403357000  | -3.125741000 |
| H | -2.787636000  | -2.135454000  | -3.265442000 |
| H | -1.795303000  | -1.151330000  | -2.199948000 |
| C | -5.196057000  | -1.700457000  | -2.120181000 |
| H | -5.967138000  | -2.122179000  | -1.478423000 |
| Atoms | X-Coordinates | Y-Coordinates | Z-Coordinates |
|-------|---------------|---------------|---------------|
| H     | -5.109575000  | -2.352374000  | -2.996936000  |
| H     | -5.530828000  | -0.721587000  | -2.479654000  |
| C     | -3.449023000  | -2.949713000  | -0.783747000  |
| H     | -4.178942000  | -3.246813000  | -0.026104000  |
| H     | -2.458296000  | -2.913246000  | -0.322871000  |
| H     | -3.428925000  | -3.738166000  | -1.544743000  |
| C     | 5.474957000   | 1.091939000   | 0.828683000   |
| C     | 4.722967000   | 2.422990000   | 0.975762000   |
| H     | 5.269230000   | 3.039866000   | 1.697029000   |
| H     | 3.705564000   | 2.300181000   | 1.357063000   |
| H     | 4.682060000   | 2.938988000   | 0.037087000   |
| C     | 6.888961000   | 1.364993000   | 0.302742000   |
| H     | 7.397573000   | 2.024162000   | 1.013783000   |
| H     | 6.875997000   | 1.877000000   | -0.664713000  |
| H     | 7.490293000   | 0.459175000   | 0.209831000   |
| C     | 5.518114000   | 0.360109000   | 2.174234000   |
| H     | 6.127030000   | -0.546480000  | 2.130500000   |
| H     | 4.522254000   | 0.098170000   | 2.546747000   |
| H     | 5.975256000   | 1.026101000   | 2.913210000   |
| C     | 4.972455000   | -1.702857000  | -0.664662000  |
| C     | 4.448000000   | -2.560878000  | 0.494203000   |
| H     | 4.701711000   | -3.603458000  | 0.276175000   |
| H     | 3.360981000   | -2.514654000  | 0.607724000   |
| H     | 4.910204000   | -2.304964000  | 1.450043000   |
| C     | 6.487837000   | -1.862286000  | -0.811798000  |
| H     | 7.015364000   | -1.682609000  | 0.128479000   |
| H     | 6.907240000   | -1.211812000  | -1.586412000  |
| H     | 6.694652000   | -2.895955000  | -1.107404000  |
| C     | 4.272380000   | -2.099613000  | -1.975140000  |
| H     | 4.478585000   | -3.159180000  | -2.159397000  |
| H     | 4.652826000   | -1.536191000  | -2.833391000  |
| H   | 3.183836000 | -1.991424000 | -1.929309000 |
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