Supporting Information for:

Hydrophosphination of Boron-Boron Multiple Bonds

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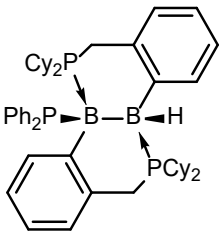
Synthetic Procedures

General Considerations

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 and stored under argon over activated 4 Å molecular sieves. NMR spectra were acquired on a Bruker Avance 500 NMR spectrometer (^{1}H: 500.1 MHz, ^{11}B: 160.5 MHz, ^{13}C{^{1}H}: 125.8 MHz, ^{31}P: 202 MHz) or on a Bruker Avance 400 NMR spectrometer (^{1}H: 400.1 MHz, ^{11}B: 128.4 MHz, ^{13}C{^{1}H}: 125.8 MHz, ^{31}P: 162 MHz) at 298 K unless otherwise stated. Chemical shifts (δ) are given in ppm and internally referenced to the carbon nuclei (^{13}C{^{1}H}) or residual protons (^{1}H) of the solvent. ^{11}B and ^{31}P NMR spectra were referenced to external standards ($BF_3{\cdot}OEt_2$; 85% aq. H_3PO_4). High-resolution mass spectrometry data was obtained from a Thermo Scientific Exactive Plus spectrometer in ASAP or LIFDI mode. $HPPh_2$ was purchased from Sigma-Aldrich and used without further purification. Diborenes **1**,[1] **2**,[2] **3**[2] and **4**[2] and B_2(SIDep)$_2$ (**9**)[3] were synthesized following literature procedures.

Synthesis of New Compounds

Compound 5



Diborene **1** (30 mg, 50 µmol) was dissolved in THF (1.3 ml), and $HPPh_2$ (0.28 ml of a 0.18 M solution in THF, 51 µmol) was added. The mixture was heated to 60 °C for 1 h, resulting in a colour change from red to yellow. Volatiles were removed under reduced pressure and the residue washed with pentane (2 x 0.5 ml) with use of an ultrasound bath to reduce the particle size. The resulting colourless solid was washed with pentane and dried under vacuum. Yield 31 mg, 79%. Single crystals were obtained by slow evaporation of a diethyl ether solution of the compound.

^{1}H{^{11}B} NMR (500 MHz, C_6D_6): δ/ppm 8.13 (d, 1H, $^{3}J_{HH}$ = 7.5 Hz, Ar*H,*), 7.82 (d, 1H, $^{3}J_{HH}$ = 6.1 Hz, Ar*H*), 7.66 (br, 4H, Ar*H*, o-PPh_2*H*), 7.36-7.31 (m, 1H, Ar*H*), 7.30-7.26 (m, 1H, Ar*H*), 7.20-7.15 (m, 1H, Ar*H*), 7.13-7.09 (m, 2H, Ar*H*), 7.06-7.01 (m, 4H, Ar*H*, m-PPh_2*H*), 7.00-6.96 (m, 2H, Ar*H*, p-PPh_2*H*), 6.89 (d, 1H, $^{3}J_{HH}$ = 7.5 Hz, Ar*H*), 3.23-3.14 (m, 1H, PCH_2), 3.12-3.00 (br, m, 1H, B*H*), 2.93-2.82 (m, 2H, PCH_2), 2.66-2.56 (m, 1H, $C^{Cy}H$), 2.41-2.34 (m, 1H, $C^{Cy}H$), 2.34-2.26 (m, 1H, PCH_2), 2.22 (d, 1H, $^{2}J_{HH}$ = 12.6 Hz, $C^{Cy}H_2$), 1.98-1.87 (m, 2H, $C^{Cy}H_2$), 1.87-0.74 (m, 40H, 38 $C^{Cy}H_2$ und 2 $C^{Cy}H$), 0.62-0.41 (m, 2H, $C^{Cy}H_2$).

Note: The remaining cyclohexyl signals between 1.87 and 0.75 ppm could not be unambiguously assigned due to insufficient resolution.

^{11}B NMR (126 MHz, C_6D_6): δ/ppm –15.9 (br, *B*PPh_2), –27.2 (br, *B*H).

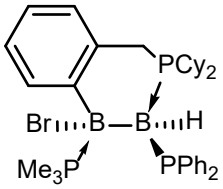
^{31}P NMR (203 MHz, C_6D_6): δ/ppm 10.4 (br), 6.1 (d, $^{3}J_{PP}$ = 77.8 Hz), –13.3 (br, *P*Ph_2).

$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6): δ/ppm 154.4 (br, $C^{Ar}B$), 151.1 (br, $C^{Ar}B$), 145.6-145.2 (m, 2C, *i*-PPh_2), 139.3-139.0 (m, $C^{Ar}CH_2$), 138.5 (br, s, $C^{Ar}H$, *p*-PPh_2), 137.7-137.4 (m, $C^{Ar}H$), 136.6 (d, $^{2}J_{CP}$ = 13.5 Hz, $C^{Ar}H$, *o*-PPh_2), 130.2 (d, J_{CP} = 6.3 Hz, $C^{Ar}H$), 129.6 (d, J_{CP} = 5.5 Hz), $C^{Ar}H$), 127.1 (d, J_{CP} = 4.5 Hz, $C^{Ar}H$, *m*-PPh_2), 126.1 (s, $C^{Ar}H$), 125.9 (s, $C^{Ar}H$), 124.9 (s, 2C, $C^{Ar}H$), 124.4 (d, J_{CP} = 2.6 Hz, $C^{Ar}H$), 34.9-34.7 (m, PCH), 33.8 (d, $^{1}J_{CP}$ = 25.4 Hz, PCH), 33.7-33.4 (m, PCH), 33.2 (d, $^{1}J_{CP}$ = 20.5 Hz, PCH), 29.5-26.2 (m, 20C*) 26.5 (dd, $^{1}J_{CP}$ = 35.8, 5.2 Hz PCH_2), 25.5 (dd, $^{1}J_{CP}$ = 36.2, 4.2 Hz, PCH_2).

Note: Despite the use of several 2D NMR techniques and ^{31}P decoupling, the remaining cyclohexyl signals between 29.5 and 26.2 ppm could not be unambiguously identified due to insufficient resolution.

HRMS (LIFDI): m/z 781.4546 (calc'd for $C_{50}H_{66}B_2P_3$ ($M - H^-$) 781.4563).

Compound 6



Diborene **2** (30 mg, 65 µmol) was dissolved in C_6D_6 (0.6 ml) and $HPPh_2$ (0.1 ml of a 0.65 M solution in benzene, 65 µmol) was added. After 3 h at room temperature, NMR showed full conversion to the product. After 16 h at room temperature, colourless crystals precipitated, which were washed with benzene and pentane and dried under vacuum (35 mg, 83%). Single crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a dichloromethane solution of the product.

$^{1}H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2): δ/ppm 8.09-8.01 (m, 2H, C_6H_5), 8.00-7.95 (m, 1H, Ar*H*), 7.93-7.86 (m, 2H, C_6H_5), 7.73-7.59 (m, 4H, C_6H_5), 7.57-7.50 (m, 2H, C_6H_5), 7.37-7.31 (m, 1H, Ar*H*), 7.26-7.19 (m, 1H, Ar*H*), 7.18-7.13 (m, 1H, Ar*H*), 3.19-3.06 (m, 1H, PCH_2), 2.83-2.71 (m, 1H, PCH_2), 2.27-2.07 (m, 1H, B*H*), 2.13-1.99 (m, 1H, $C^{Cy}H_2$), 1.79-0.75 (m, 19H, $C^{Cy}H$ and $C^{Cy}H_2$), 1.39 (d, $^{2}J_{CP}$ = 10.8 Hz, $P(CH_3)_3$), 0.64-0.44 (m, 2H, $C^{Cy}H_2$).

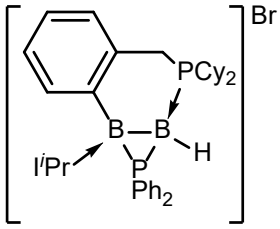
^{11}B NMR (126 MHz, CD_2Cl_2): δ/ppm –7.7 (br, *B*Br), –34.2 (br, *B*H).

$^{31}P\{^{1}H\}$ NMR (203 MHz, CD_2Cl_2): δ/ppm 23.1 (br, PCy_2), 13.8 (br, PMe_3), –6.9 (br, PPh_2).

$^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2): δ/ppm 144.0 (br, $C^{Ar}B$), 136.3 (d, J_{CP} = 9.9 Hz, *o*- or *m*-$C^{Ph}H$), 134.5 (br d, J_{CP} = 5.4 Hz, $C^{Ar}H$), 134.2 (d, J_{CP} = 9.0 Hz, *o*- or *m*-$C^{Ph}H$), 134.0 (d, $^{4}J_{CP}$ = 2.7 Hz, p-$C^{Ph}H$), 133.4 (pseudo t, J_{CP} = 5.5 Hz, $C^{Ar}CH_2$), 132.9 (d, J_{CP} = 2.6 Hz, p-$C^{Ph}H$), 131.2 (dd, J_{CP} = 6.8, 4.2 Hz, $C^{Ar}H$), 129.9 (d, J_{CP} = 10.6 Hz, *o*- or *m*-$C^{Ph}H$), 129.0 (d, J_{CP} = 11.0 Hz, *o*- or *m*-$C^{Ph}H$), 127.6 (dd, J_{CP} = 3.9, 1.8 Hz, $C^{Ar}H$), 127.5 (d, J_{CP} = 4.8 Hz, $C^{Ar}H$), 124.7 (d, J_{CP} = 65.1 Hz, *i*-C^{Ph}), 121.0 (d, J_{CP} = 61.7 Hz, *i*-C^{Ph}), 32.7 (d, $^{1}J_{CP}$ = 31.0 Hz, PCH), 32.3 (d, $^{1}J_{CP}$ = 28.7 Hz, PCH), 28.6 (d, J_{CP} = 5.8 Hz, $C^{Cy}H_2$), 27.7 (d, J_{CP} = 2.3 Hz, $C^{Cy}H_2$), 27.6 (d, J_{CP} = 5.6 Hz, $C^{Cy}H_2$), 27.3 (d, J_{CP} = 10.0 Hz, $C^{Cy}H_2$), 27.2 (s, $C^{Cy}H_2$), 27.1 (d, J_{CP} = 10.0 Hz, $C^{Cy}H_2$), 26.9 (d, J_{CP} = 11.8 Hz, $C^{Cy}H_2$), 26.4 (d, J_{CP} = 12.0 Hz, $C^{Cy}H_2$), 25.8 (s, $C^{Cy}H_2$), 25.6 (dd, J_{CP} = 38.0, 10.5 Hz, PCH_2), 25.5 (s, $C^{Cy}H_2$), 8.6 (d, $^{1}J_{CP}$ = 38.5 Hz, $P(CH_3)_3$).

HRMS (LIFDI): m/z 575.1957 (calc'd for $C_{34}H_{49}B_2BrP_3$ (M^+) 650.2338; calc'd for $C_{31}H_{40}B_2BrP_2$ (MH^+ – PMe_3) 575.1975).

Compound 7



Diborene **3** (20 mg, 37 µmol) was dissolved in C_6D_6 (0.6 mL) and $HPPh_2$ (57 µl of a 0.65 M solution in benzene) was added. After 1 h a crystalline solid precipitated from the reaction mixture, which was filtered off and dried under vacuum (22 mg, 82%). Single crystals suitable for X-ray diffraction were obtained by diffusion of pentane into a THF solution of the product.

$^1H\{^{11}B\}$ NMR (400 MHz, CD_2Cl_2): δ/ppm 7.46 (br, 1H, $C^{Ar}H$), 7.44-7.23 (br, m, 5H, PPh_2), 7.18-7.16 (br, m, 1H, $C^{Ar}H$), 7.12-6.97 (br, m, 3H, PPh_2), 6.92-6.86 (m, 2H, $C^{Ar}H$), 6.77-6.69 (br, m, 2H, *p*-PPh_2), 6.77-6.73 (m, 1H, imidazole C*H*), 6.42-6.38 (m, 1H, imidazole C*H*), 5.35-5.26 (br, m, 1H, C*H*$(CH_3)_2$), 4.94-4.84 (br, m, 1H, C*H*$(CH_3)_2$), 2.75-2.64 (m, 1H, PCH_2), 1.85-1.27 (m, 15H, 1 PCH_2 und $C^{Cy}H$), 1.49-1.42 (br m, 1H, B*H*), 1.43 (d, 3H, $^3J_{HH}$ = 6.9 Hz, CH(CH_3)$_2$), 1.31 (d, 3H, $^3J_{HH}$ = 6.5 Hz, CH(CH_3)$_2$), 1.20-0.66 (m, 8H, $C^{Cy}H$), 1.06 (d, 3H, $^3J_{HH}$ = 7.1 Hz, CH(CH_3)$_2$), 0.21 (d, 3H, $^3J_{HH}$ = 6.6 Hz, CH(CH_3)$_2$).

Note: The remaining cyclohexyl signals between 1.85 and 1.27 ppm and between 1.20 and 0.66 ppm could not be unambiguously assigned due to insufficient resolution.

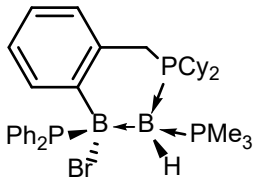
^{11}B NMR (101 MHz, CD_2Cl_2): δ/ppm –21.6 (*B*(I*i*Pr)), –37.6 (*B*H).

$^{31}P\{^1H\}$ NMR (121 MHz, CD_2Cl_2): δ/ppm 8.9 (br, m, PCy_2), –70.9 (d, J_{PP} = 14.9 Hz, PPh_2).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ/ppm 157.3 (br, $C^{carbene}$), 143.1 (br, $C^{Ar}B$), 135.9 (br, $C^{Ph}H$), 135.0 (d, J_{CP} = 5.1 Hz, $C^{Ar}H$), 133.6-133.5 (m, $C^{Ar}CH_2P$), 132.6 (br, $C^{Ph}H$), 131.1 (dd, J_{CP} = 3.7, 7.8 Hz, $C^{Ar}H$), 130.5 (br, $C^{Ph}H$), 130.1 (br, $C^{Ph}H$), 129.3 (br, $C^{Ph}H$), 129.1 (br, $C^{Ph}H$), 126.7 (s, $C^{Ar}H$), 126.5 (d, J_{CP} = 4.0 Hz, $C^{Ar}H$), 125.3 (br d, J_{CP} = 34 Hz, $C^{Ph}P$), 119.6 (s, H*C*=CH), 119.5 (s, HC=*C*H), 50.9 (d, J_{CP} = 4.1 Hz, *C*H$(CH_3)_2$), 50.3 (d, J_{CP} = 7.8 Hz, *C*H$(CH_3)_2$), 33.6 (dd, J_{CP} = 13.5, 38.9 Hz, $C^{Cy}H$), 32.8 (dd, J_{CP} = 1.8, 35.9 Hz), 29.5 (d, J_{CP} = 1.9 Hz, $C^{Cy}H_2$), 28.3 (d, J_{CP} = 1.7 Hz, $C^{Cy}H_2$), 27.2 (d, J_{CP} = 11.7 Hz, $C^{Cy}H_2$), 27.1 (s, $C^{Cy}H_2$), 27.0-26.8 (m, 4C, $C^{Cy}H_2$), 26.6 (d, J_{CP} = 10.9 Hz, $C^{Cy}H_2$), 25.8 (s, 2C, $C^{Cy}H_2$), 25.1 (s, CH(*C*H_3)$_2$), 25.0 (d, J_{CP} = 40.6 Hz, P*C*H_2), 24.1 (s, CH(*C*H_3)$_2$), 22.5 (s, CH(*C*H_3)$_2$), 22.4 (s, CH(*C*H_3)$_2$).

HRMS (LIFDI): m/z 647.4016 (calc'd for $C_{40}H_{55}B_2N_2P_2$ ($M - H^-$) 647.4027).

Compound 8



Borylborylene **4** (15 mg, 32 µmol) was suspended in C_6D_6 (0.6 ml), and $HPPh_2$ (50 µl of a 0.65 M solution in benzene, 32 µmol) was added. The mixture was placed in an ultrasound bath for 30 min and left to stand overnight. The resulting pale yellow solid was separated by filtration, washed with benzene (2 x 0.3 ml) and dried under vacuum (18 mg, 87%).

$^{1}H\{^{11}B\}$ NMR (400 MHz, THF-d_8): δ/ppm 8.20-7.44 (br m, 2H, *p*-C_6H_5), 7.94-7.83 (m, 1H, Ar*H*), 7.25-6.53 (br m, 8H, *o*-C_6H_5 and *m*-C_6H_5), 6.93-6.78 (m, 3H, Ar*H*), 3.71-3.57 (m, 1H, PCH_2), 3.01-2.88 (m, 1H, PCH_2), 2.09-1.96 (m, 1H, $C^{Cy}H$), 1.95-1.65 (m, 7H, 1 x $C^{Cy}H$ and 6 x $C^{Cy}H_2$), 1.62-0.89 (m, 14H, $C^{Cy}H_2$), 1.55 (d, $^{2}J_{PH}$ = 11.3 Hz, P(CH_3)$_3$), 0.83-0.68 (m, 1H, $C^{Cy}H_2$). Note: The signal corresponding to the B-H moiety could not be unambiguously identified.

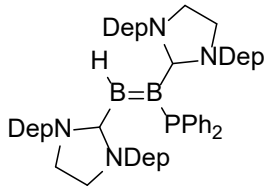
^{11}B NMR (126 MHz, THF-d_8): δ/ppm –0.7 (*B*(PPh_2)), –34.5 (*B*H).

$^{31}P\{^{1}H\}$ NMR (151 MHz, THF-d_8): δ/ppm 16.4 (br m, *P*Cy_2), –4.7 (br m, *P*Me_3), –20.5 (m, *P*Ph_2).

$^{13}C\{^{1}H\}$ NMR (161 MHz, THF-d_8): δ/ppm 152.7 (br, $C^{Ar}B$), 144.8 (d, $^{2}J_{CP}$ = 19.8 Hz, $C^{Ar}CH_2$), 137.4 (dd, J_{CP} = 2.2, 4.6 Hz, $C^{Ar}H$), 135.9 (br, C^{Ph}), 134.8-134.6 (m, C^{Ph}), 128.6 (dd, J_{CP} = 7.6, 1.6 Hz, $C^{Ar}H$), 126.7 (d, J_{CP} = 6.0 Hz, C^{Ph}), 125.8 (s, $C^{Ar}H$), 125.5 (br, C^{Ph}), 124.6 (d, J_{CP} = 2.1 Hz, $C^{Ar}H$), 34.2 (d, J_{CP} = 31.2 Hz, P*C*H), 33.1 (d, J_{CP} = 28.1 Hz, P*C*H), 28.9 (d, J_{CP} = 1.4 Hz, $C^{Cy}H_2$), 28.1 (pseudo t, J_{CP} = 2.4 Hz, $C^{Cy}H_2$) 28.0 (d, J_{CP} = 1.3 Hz, $C^{Cy}H_2$), 26.7 (d, J_{CP} = 1.2 Hz, $C^{Cy}H_2$), 26.6 (d, J_{CP} = 1.1 Hz, $C^{Cy}H_2$), 26.4 (dd, J_{CP} = 14.2, 9.1 Hz, PCH_2), 26.1 (dd, J_{CP} = 14.0, 9.0 Hz, PCH_2), 15.3 (ddd, J_{CP} = 42.3, 4.3, 3.4 Hz, P(CH_3)$_3$).

Note: The remaining cyclohexyl signals between 27.9 and 27.4 ppm could not be unambiguously assigned due to insufficient resolution. The compound was found to decompose upon application of dynamic vacuum for longer periods. We were therefore unable to remove residual benzene from the product. LIFDI mass spectrometry did not show any signals in the expected range of the product.

Compound 10



B_2(SIDep)$_2$ (20 mg, 29 µmol) was dissolved in toluene (0.5 ml) and cooled to –78 °C. To the precooled red solution was added an excess of $HPPh_2$ by syringe, causing an immediate colour change to purple. After 2 h at room temperature and screening by ^{11}B and ^{31}P NMR spectroscopy, all volatiles were removed under reduced pressure. The purple, oily residue was washed three times with 0.5 mL pentane and the product was extracted with 15 mL pentane. Removal of the solvent under reduced pressure gave the product as a red solid (16 mg, 63%). Crystals suitable for X-ray diffraction were obtained by slow evaporation of a saturated pentane solution.

$^{1}H\{^{11}B\}$ NMR (500 MHz, C_6D_6): δ/ppm 7.12-7.09 (m, 4H, CH_{Ar}), 7.03-6.95 (m, 12H, CH_{Ar}), 6.79-6.77 (m, 4H, CH_{Ar}), 4.19 (br. d, 1H, $^{3}J_{P,H}$ = 46 Hz, B*H*), 3.17 (s, 4H, NCH_2), 3.11 (s, 4H, NCH_2), 2.67-2.45 (m, 16H, CH_{2Et}), 1.14 (t, 24H, $^{3}J_{H,H}$ = 7.5 Hz, CH_{3Et}).

Note: The signals for the *para* protons of the NHC aryl groups are obscured by the solvent. The signals 1.23 (m) and 0.87 (t) can be assigned to residual pentane.

^{11}B NMR (160.5 MHz, C_6D_6): δ/ppm 38.3 (*B*P), 18.0 (*B*H).

^{31}P NMR (500 MHz, C_6D_6): δ/ppm –25.9 (d, $^{3}J_{P,H}$ = 46 Hz).

$^{13}C\{^{1}H\}$ NMR (125.8 MHz, C_6D_6): δ/ppm 191.5 ($C^{Carbene}$, detected by HMBC), 187.9 ($C^{Carbene}$, detected by HMBC), 147.4 (C^{q}), 147.2 (C^{q}), 141.7 (C^{q}), 141.1 (C^{q}), 140.8 (C^{q}), 138.6 (C^{q}), 133.2 (C^{q}), 133.1 (C^{q}), 128.6

(*C*H^{Ar}), 127.6 (*C*H^{Ar}), 127.3 (*C*H^{Ar}), 126.7 (*C*H^{Ar}), 126.7 (*C*H^{Ar}), 126.1 (*C*H^{Ar}), 125.7 (*C*H^{Ar}), 122.9 (*C*H^{Ar}), 52.1 (N*C*H$_2$), 51.0 (N*C*H$_2$), 24.7 (*C*H$_2^{Et}$), 24.6 (*C*H$_2^{Et}$), 24.6 (*C*H$_2^{Et}$), 14.0 (*C*H$_3^{Et}$), 13.9 (*C*H$_3^{Et}$) ppm.

Note: The signals 34.5, 22.7 and 14.3 can be assigned to residual pentane.

HRMS (LIFDI): m/z 876.5578 (calc'd for $C_{58}H_{71}B_2N_4P$ (M) 876.5597).

NMR spectra of new compounds

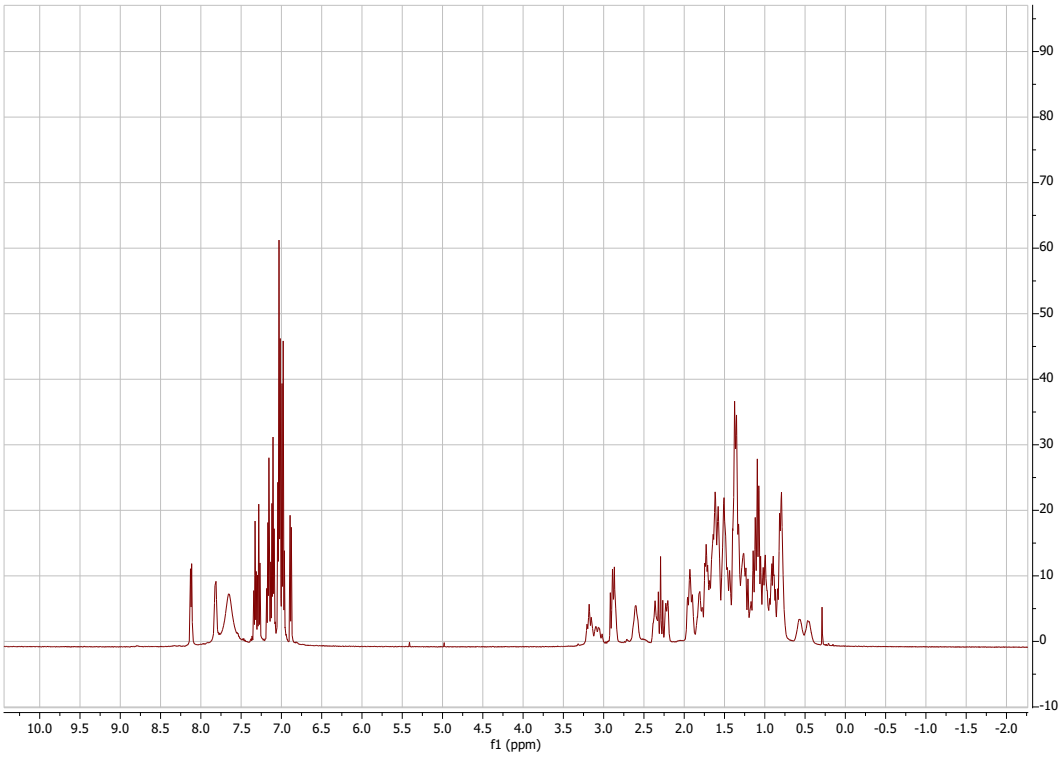


Figure S1. $^{1}H\{^{11}B\}$ NMR spectrum of **5**

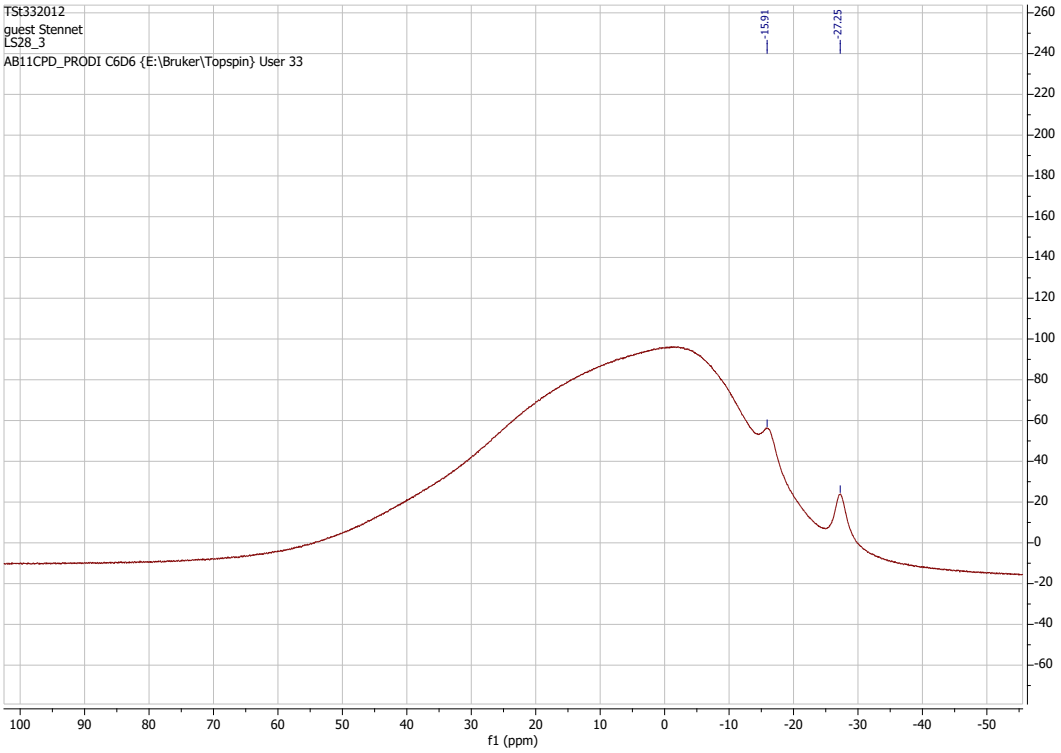


Figure S2. ^{11}B NMR spectrum of **5**

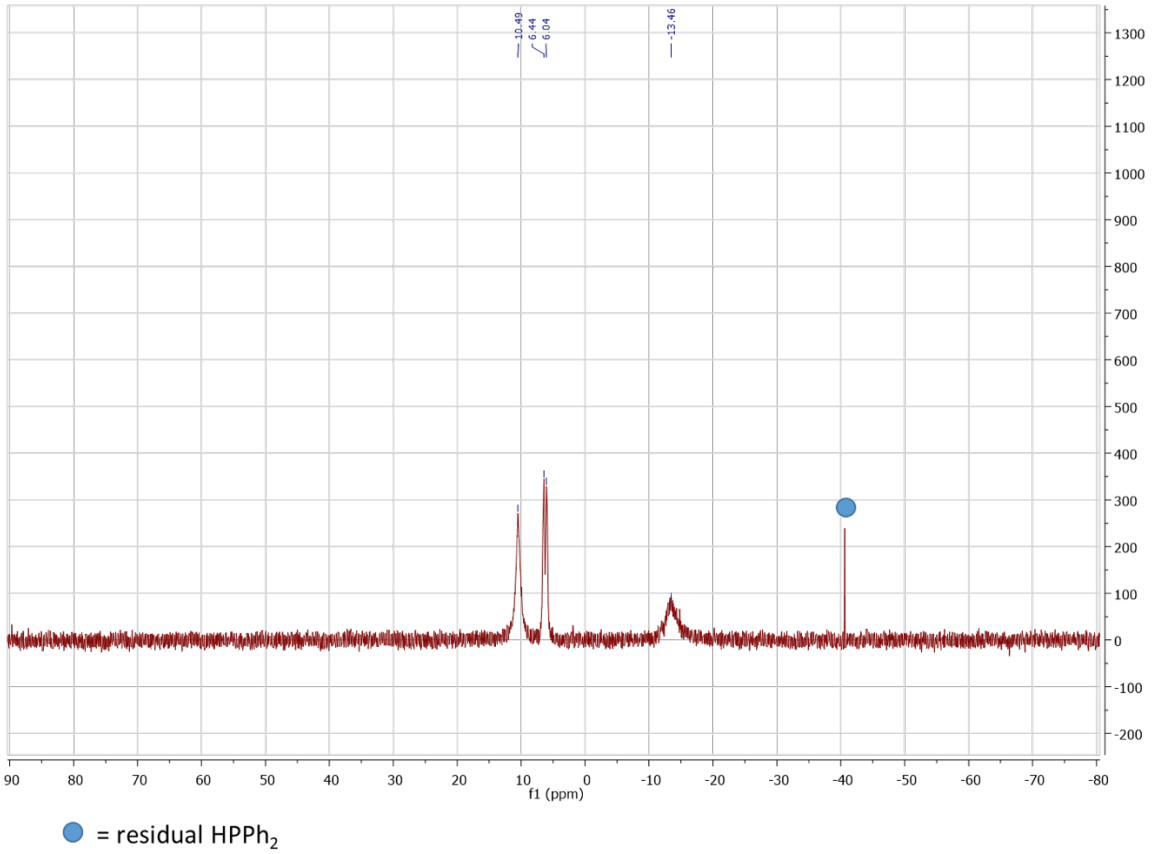


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **5**

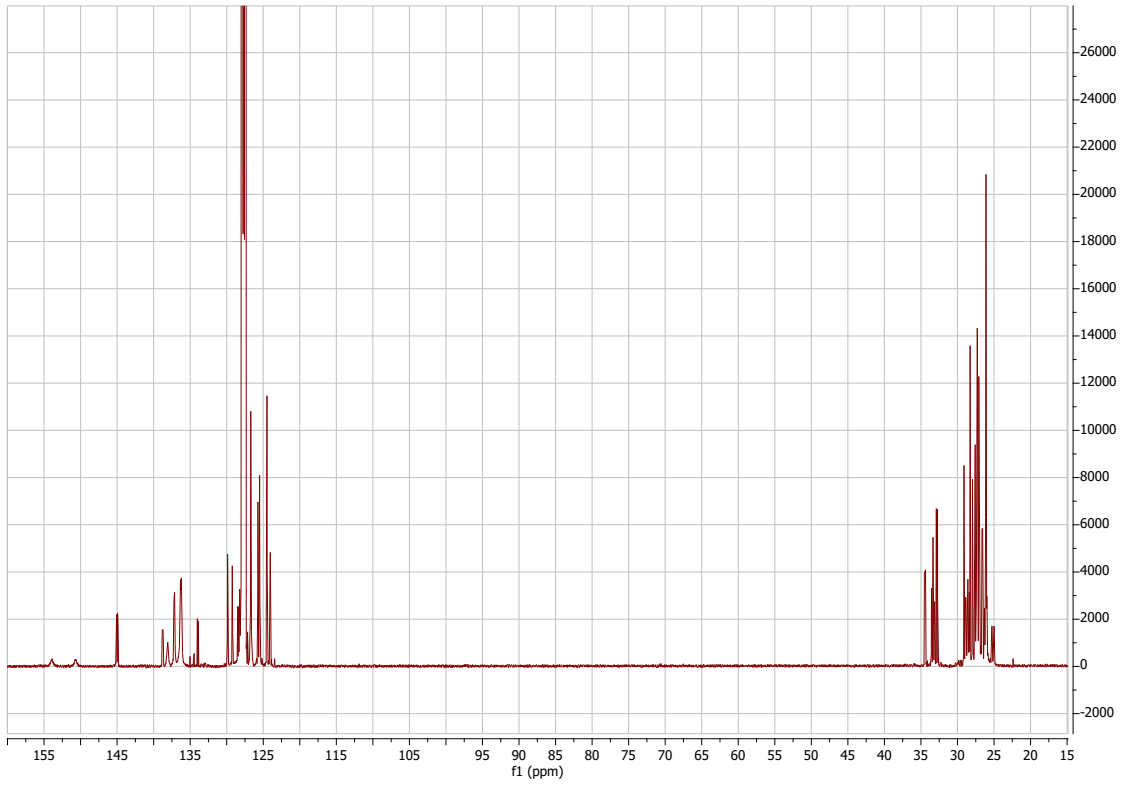


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **5**

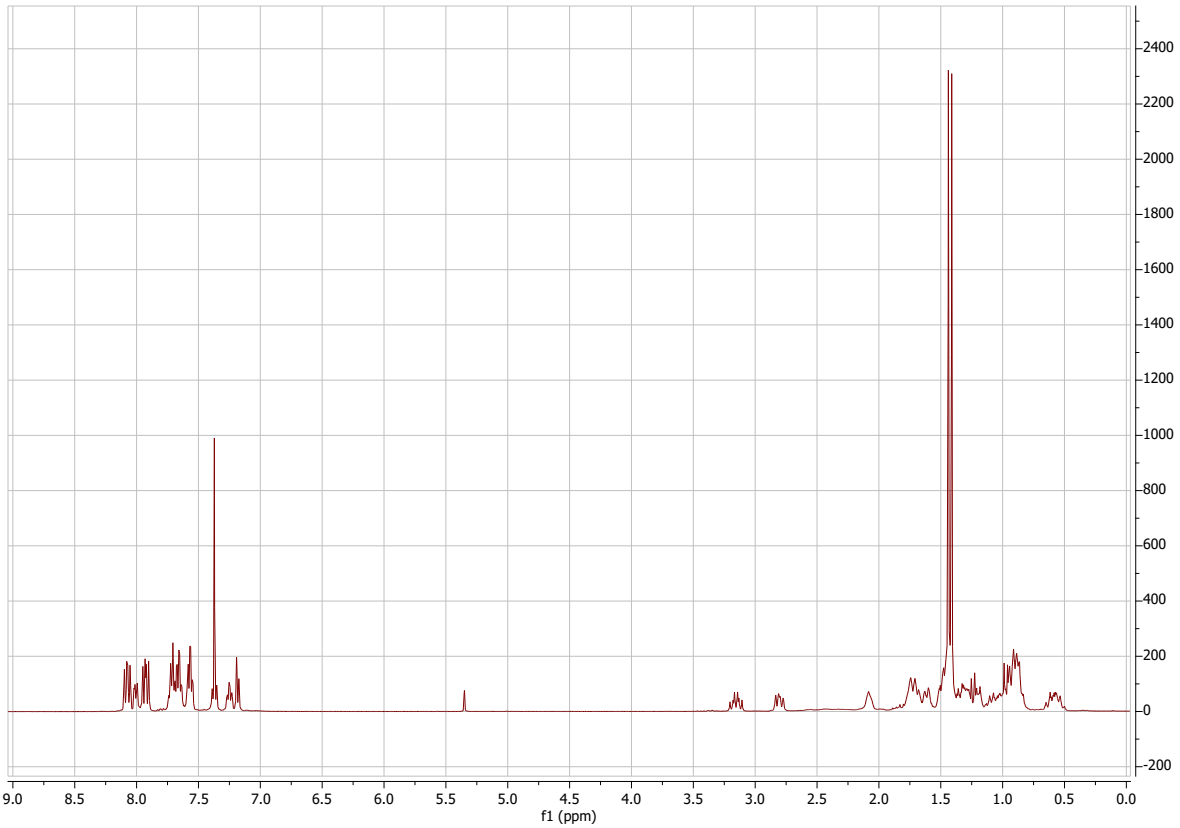


Figure S5. ^{1}H NMR spectrum of **6**

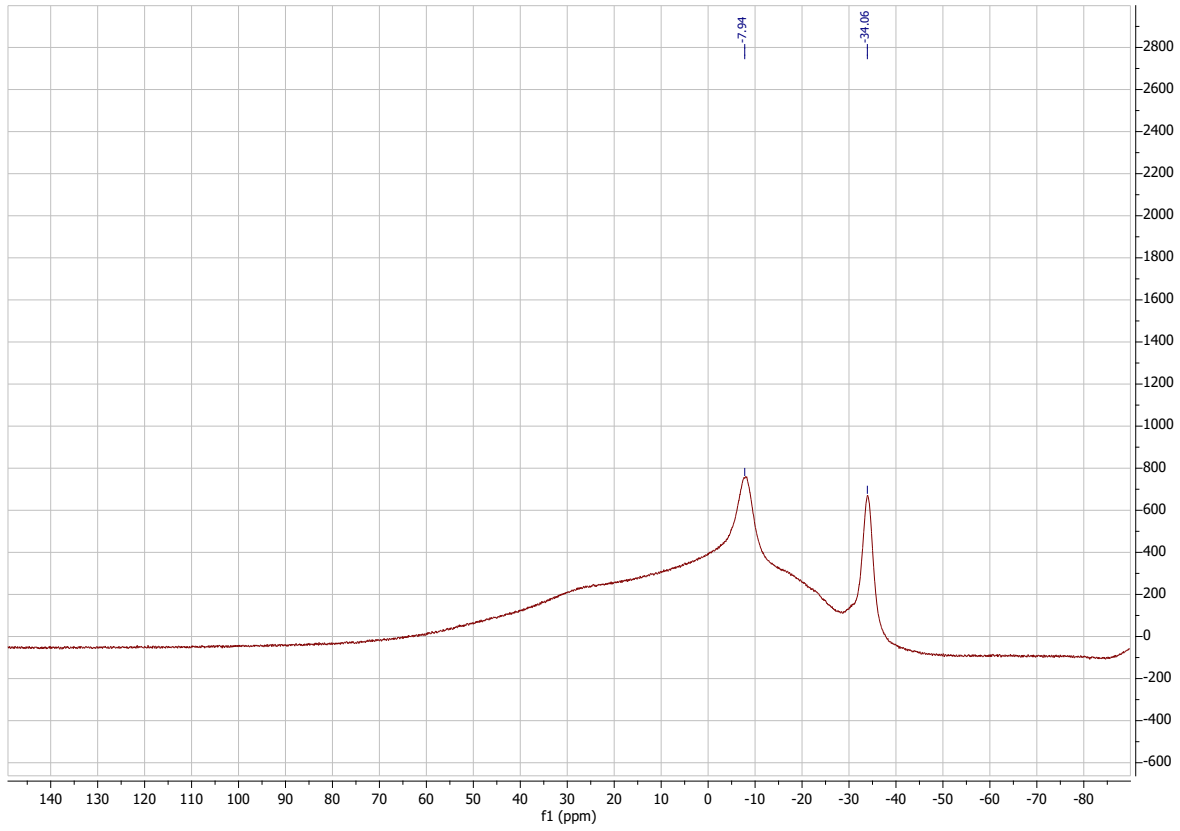


Figure S6. ^{11}B NMR spectrum of **6**

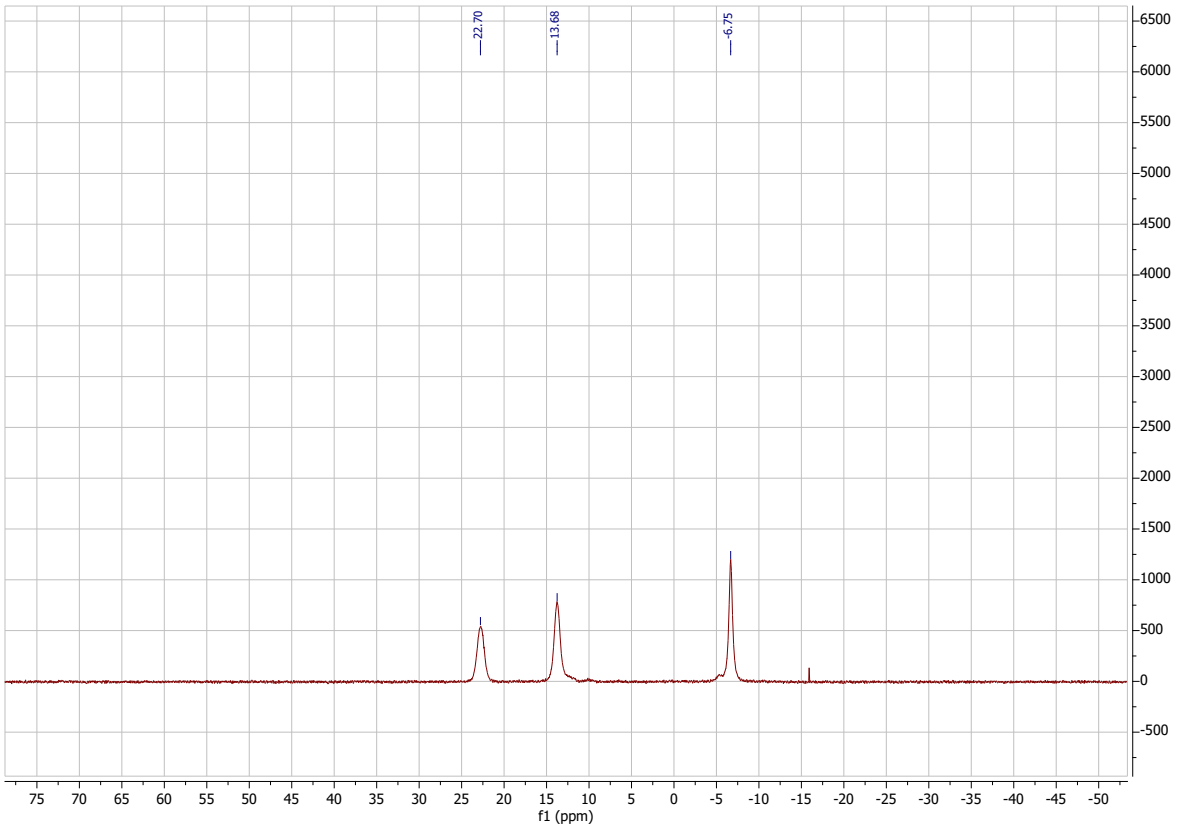


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **6**

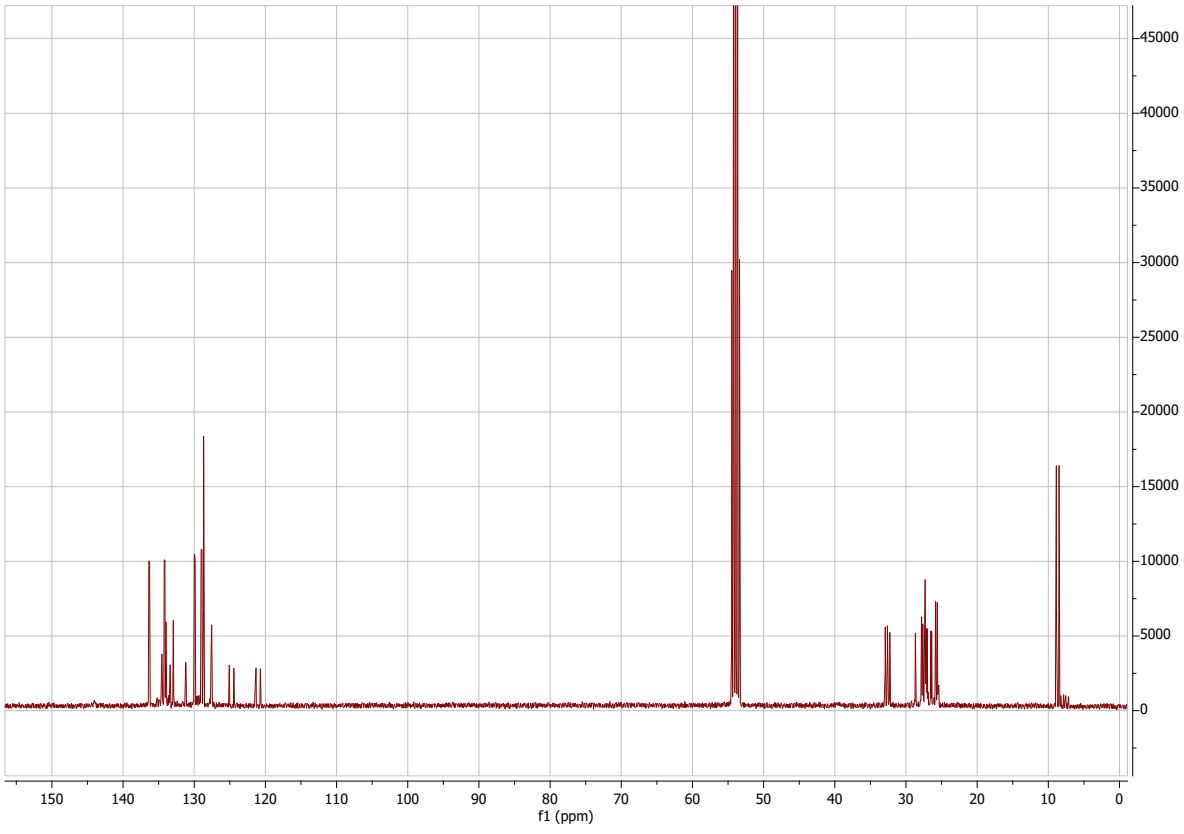


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **6**

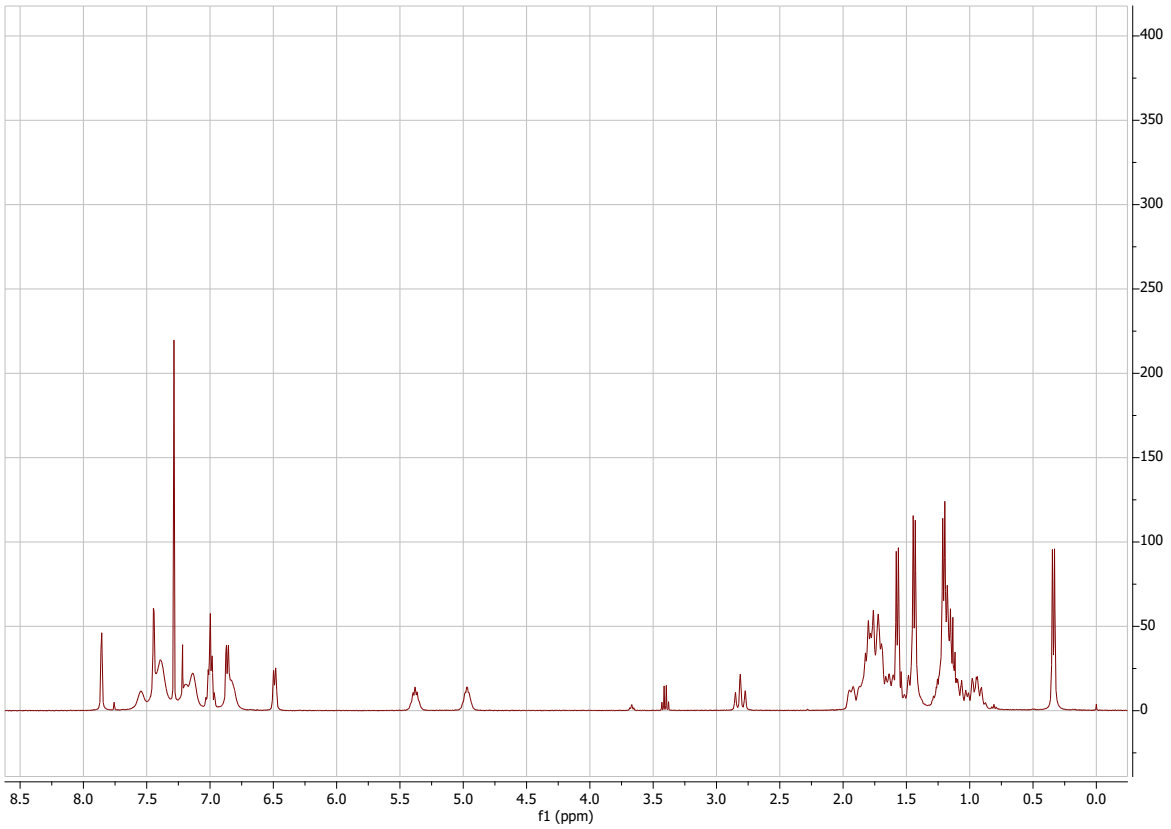


Figure S9. ^{1}H NMR spectrum of **7**

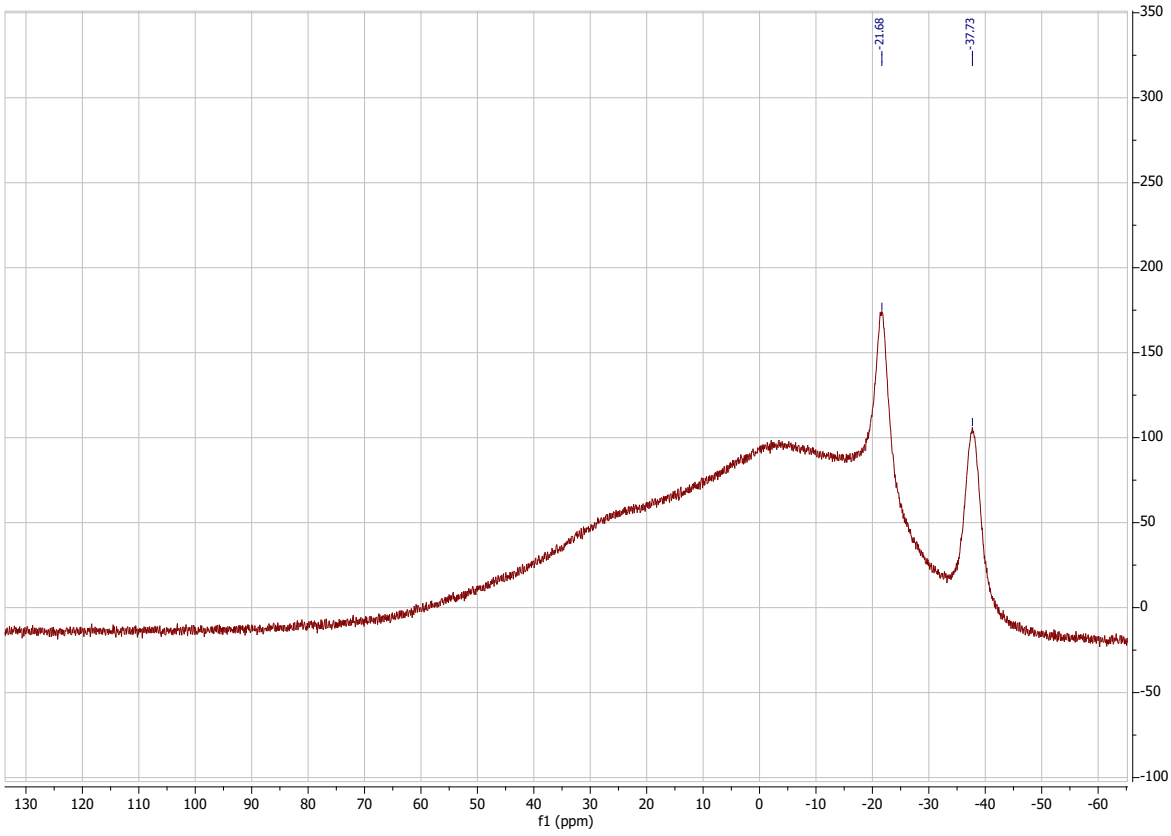


Figure S10. ^{11}B NMR spectrum of **7**

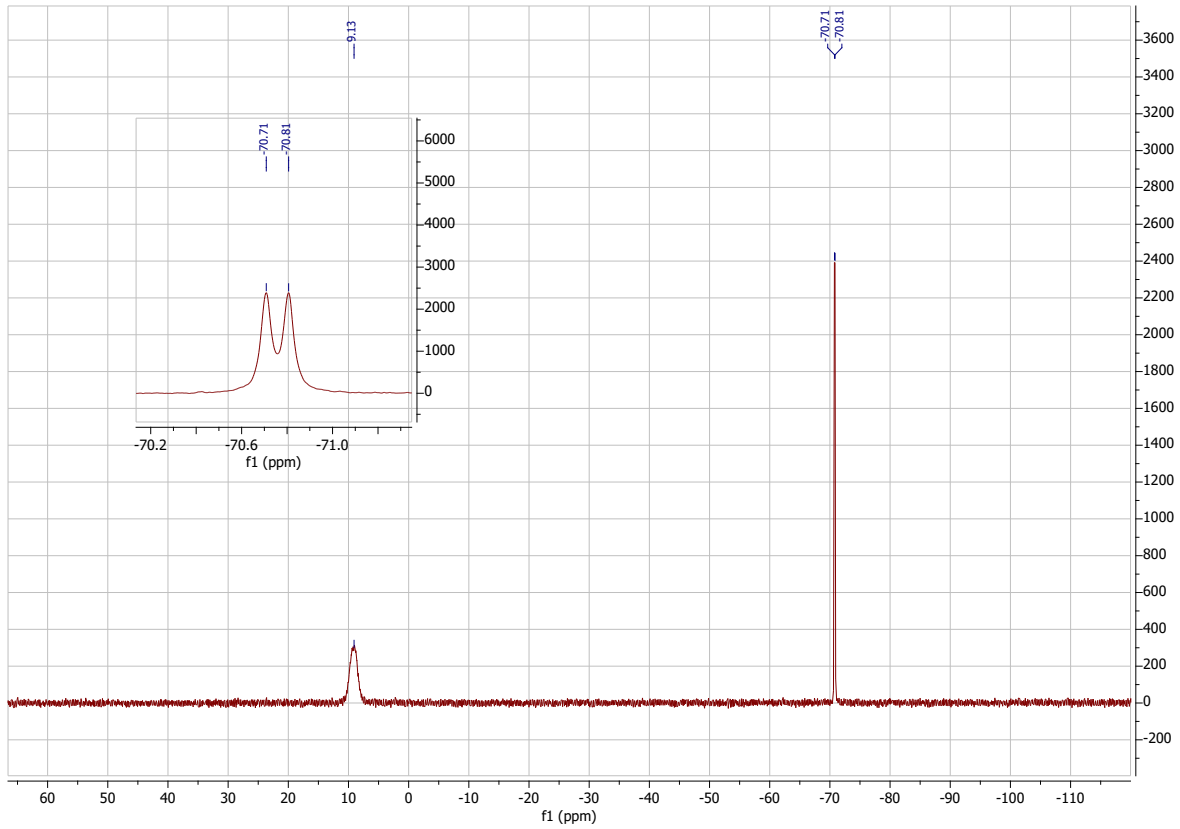


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **7**

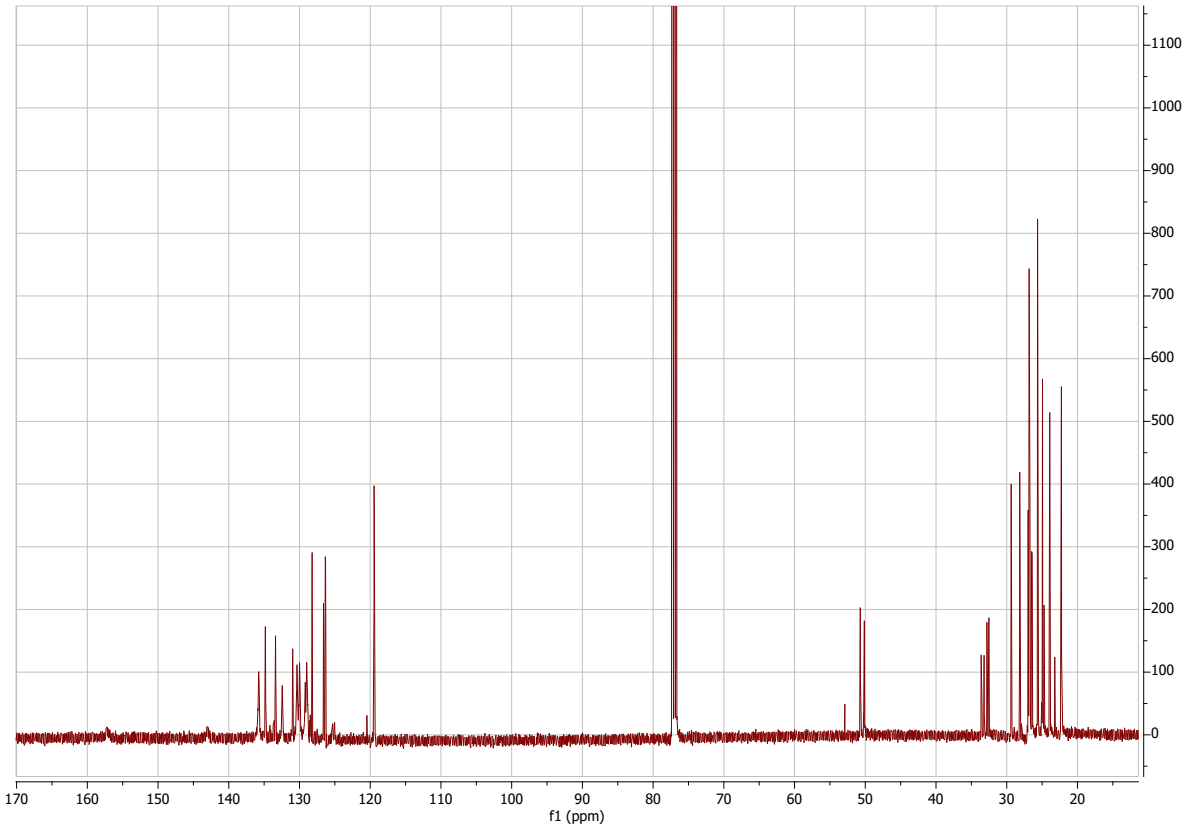


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **7**

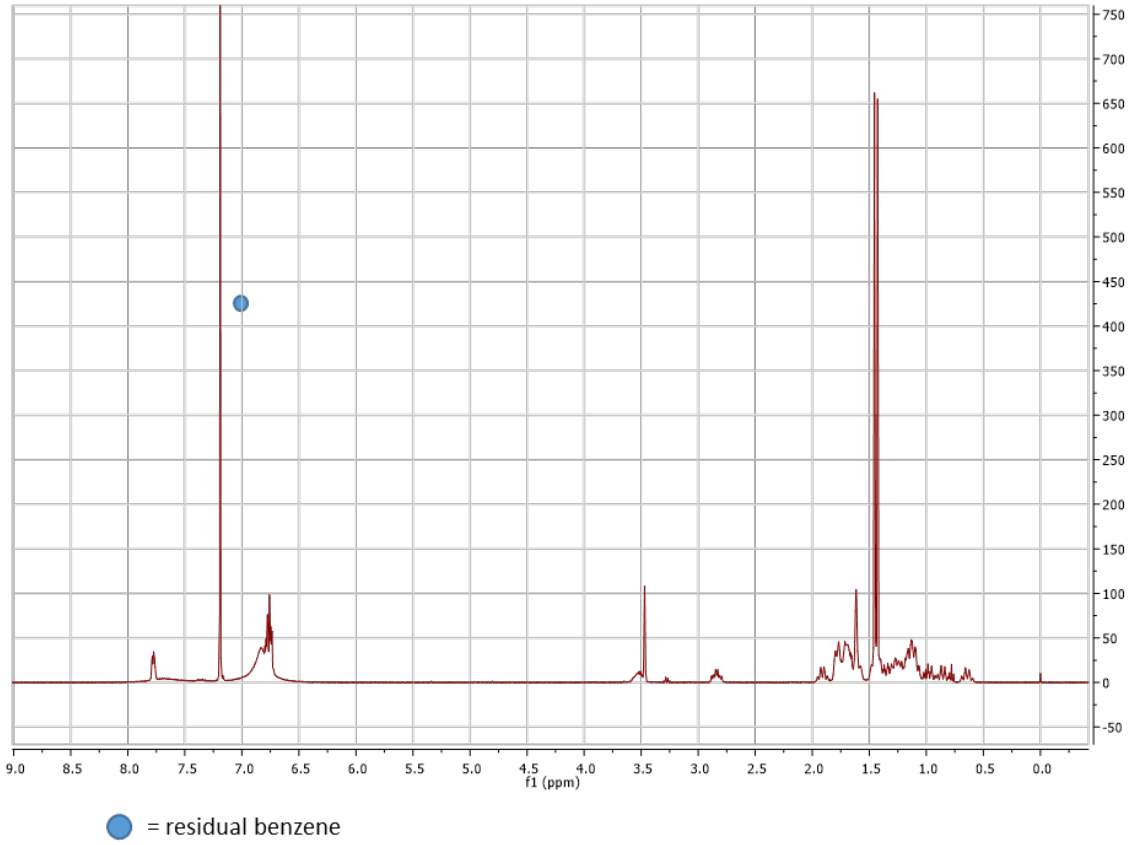


Figure S13. ^{1}H NMR spectrum of **8**

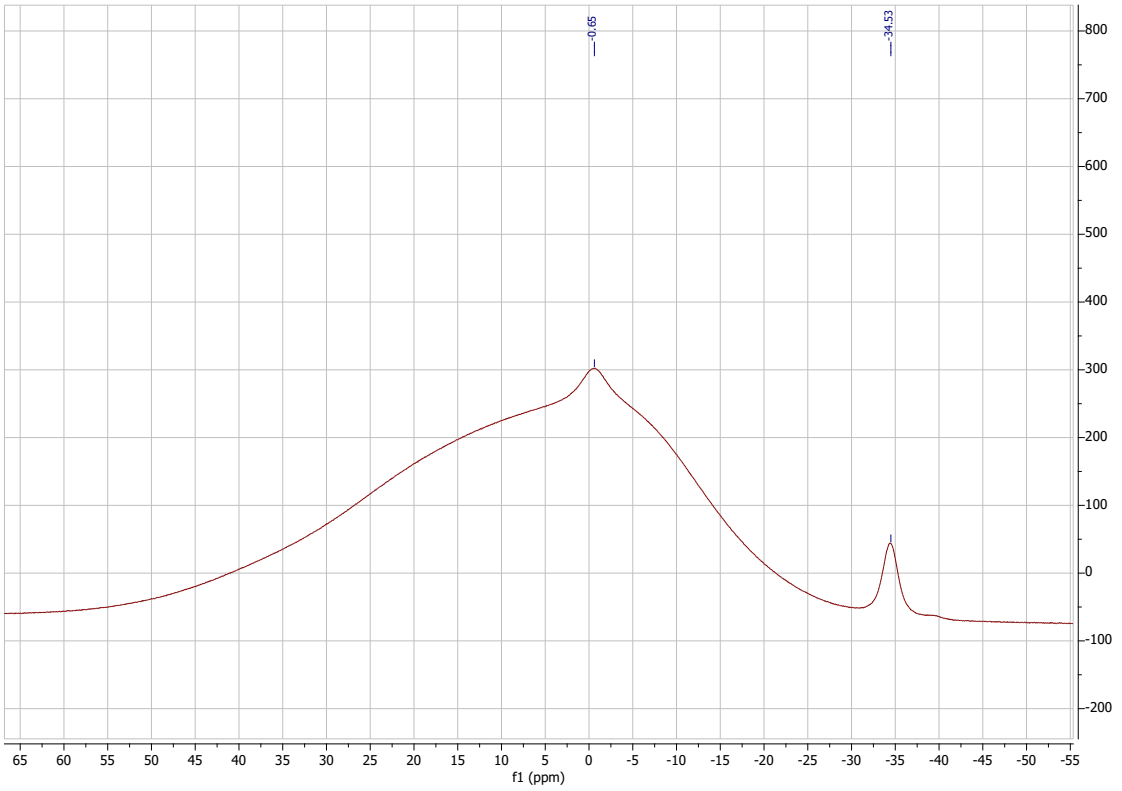


Figure S14. ^{11}B NMR spectrum of **8**

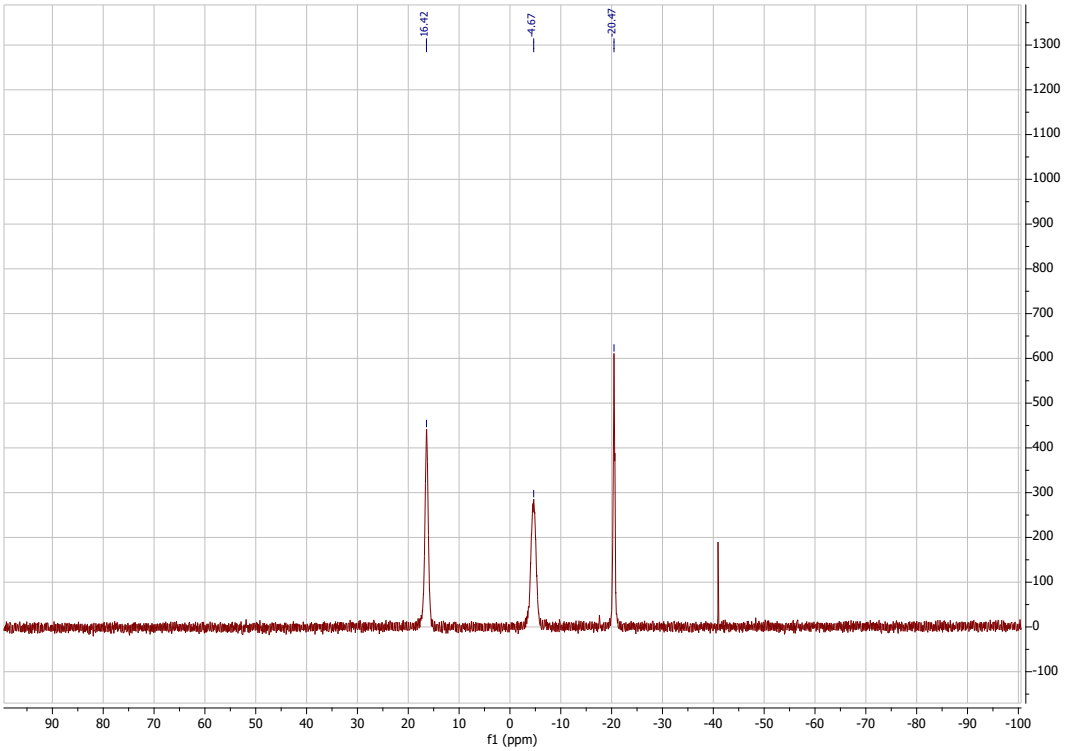


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **8**

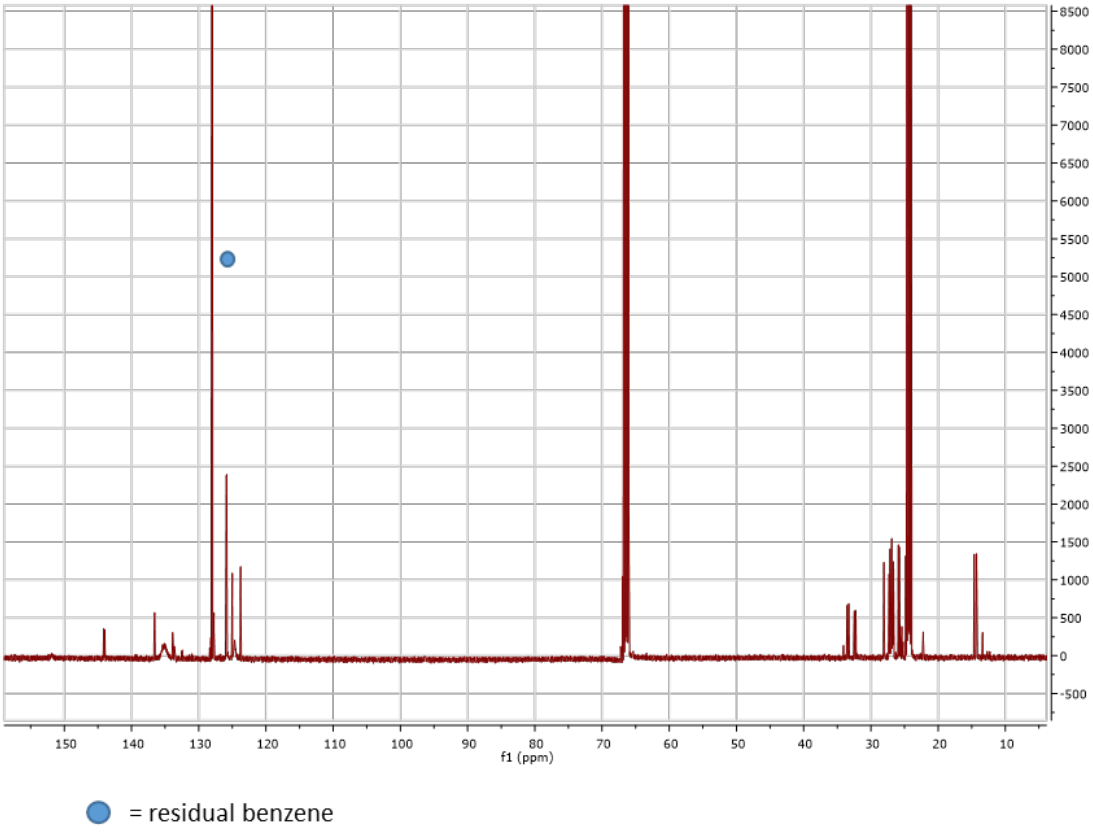


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of **8**

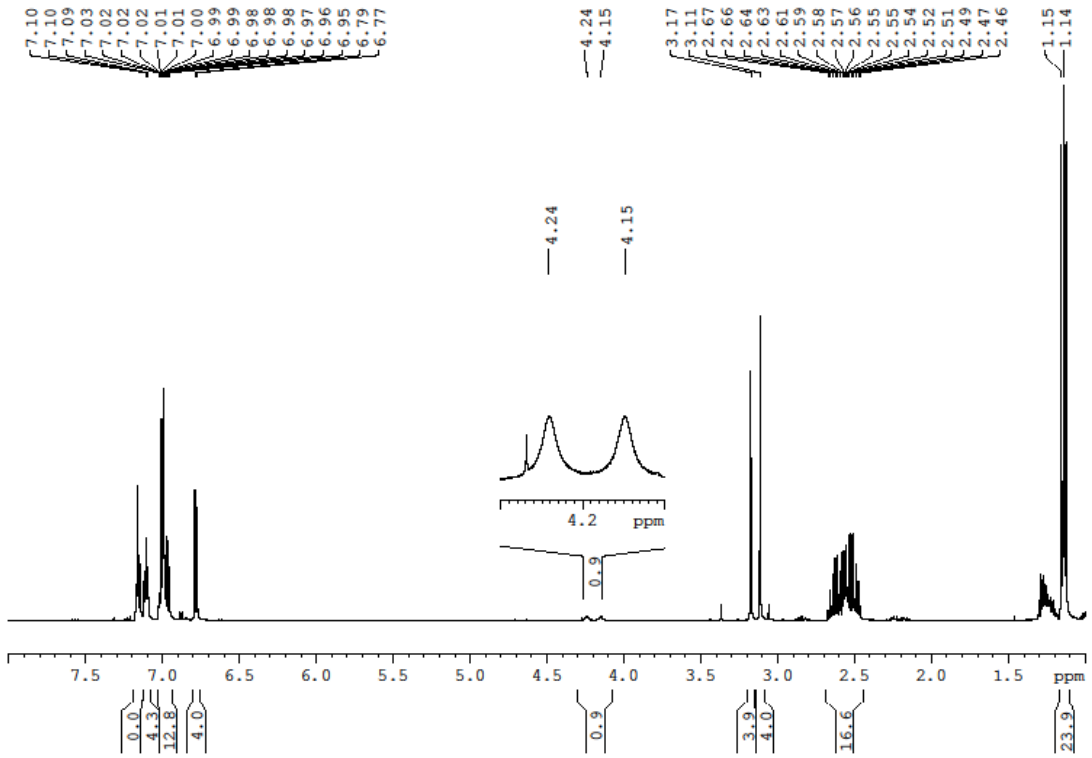


Figure S17. $^{1}H\{^{11}B\}$ NMR spectrum of **10**

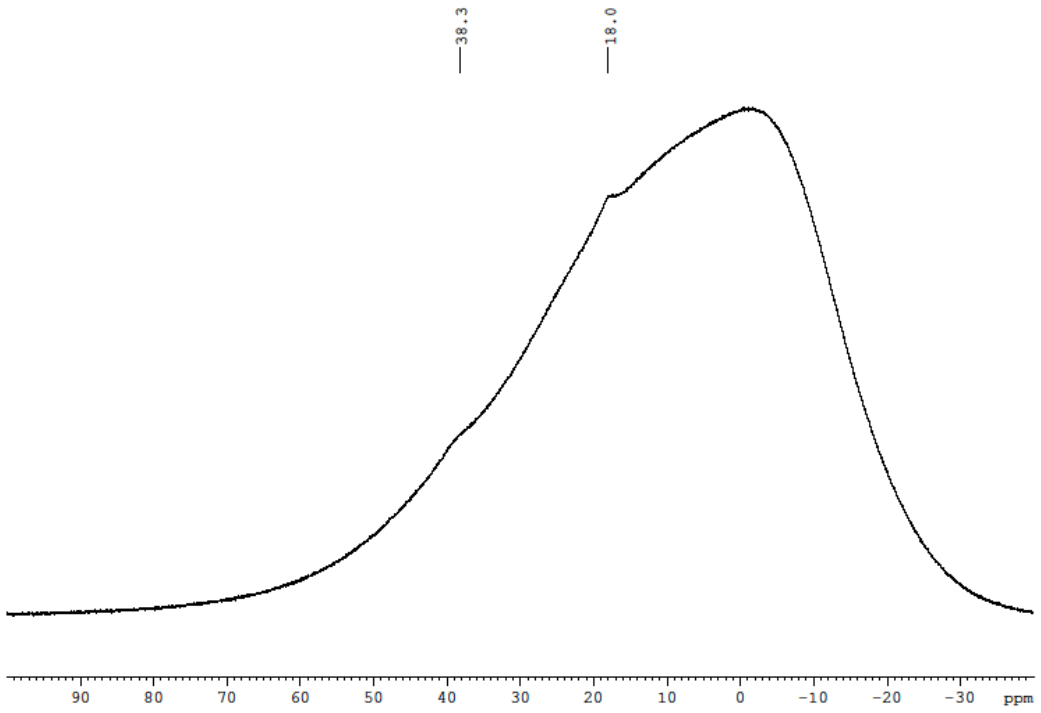


Figure S18. ^{11}B NMR spectrum of **10**

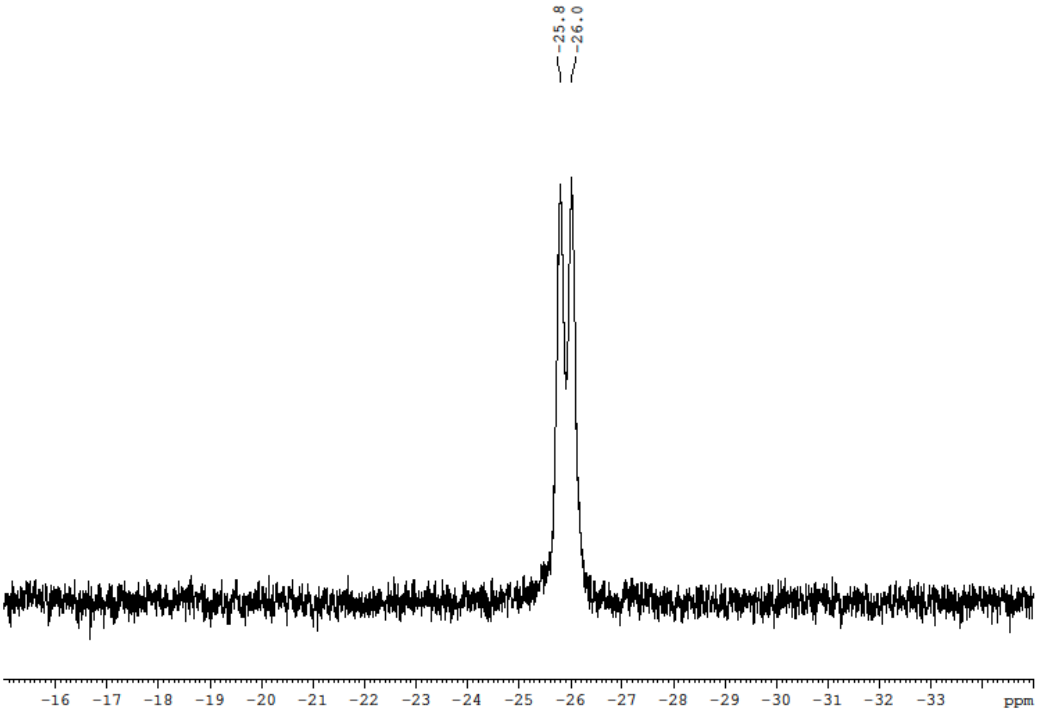


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of **10**

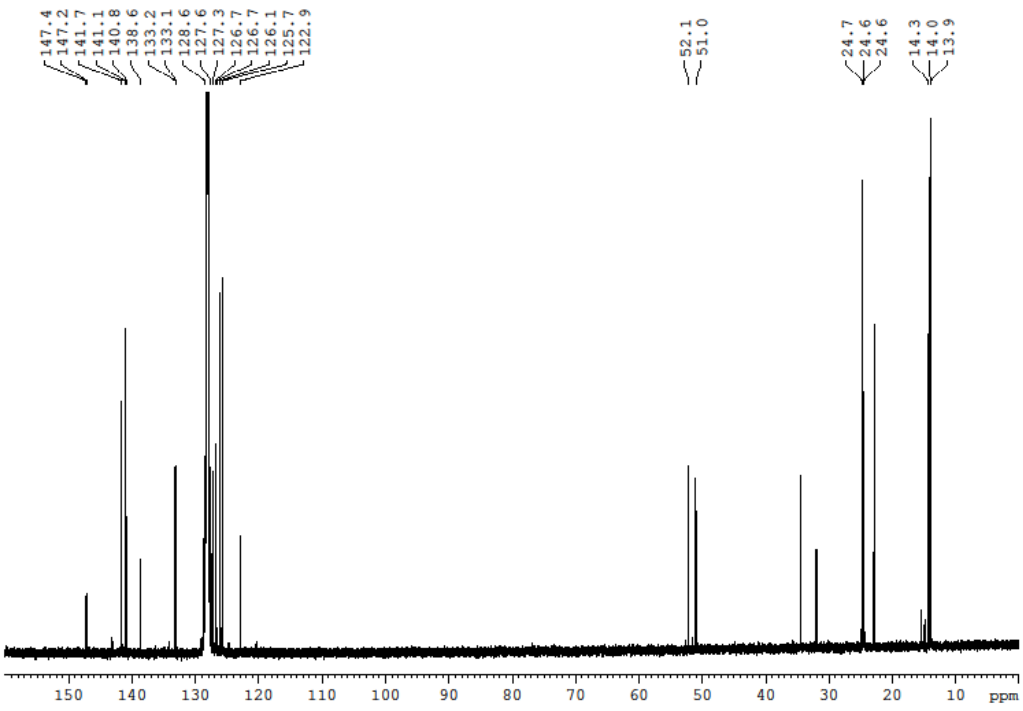


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **10**

Computational details.

All computations were performed using the Gaussian 09 (Revision E.01) software.[4] Geometry optimizations and vibrational frequency calculations were performed using the hybrid DFT-D2 functional ωB97XD,[5] which has been suggested to be a highly promising functional for obtaining reasonably accurate data for general main group thermochemistry, kinetics and non-covalent interactions.[6] The basis set used for optimization and frequency calculations was 6-31G**. All geometry optimizations were performed without symmetry constraints. Transition state geometries were obtained using opt = (ts, noeigentest, calcfc) algorithms.[7] All optimized transition state structures were confirmed as maxima with only one imaginary frequency, and the magnitudes of all frequencies were greater than the residual frequencies due to rotations and translations. Additionally, each transition state established was ensured to be on the preferred reaction path by performing "plus-and-minus-displacement" minimization calculations, which involves the displacement of transition state structures by ca. 0.05 Å or 5° along the imaginary frequency normal mode in both directions,[8-12] and the displaced geometries were subsequently optimized to the nearest minimum. For ionic compounds, energies of van der Waals compounds were used. Zero-point vibrational energies and thermal corrections were computed from frequency calculations with a standard state of 298 K and 1 atm. Single-point energies were computed on the ωB97XD/6-31G(d,p) optimized geometries using the ωB97XD/6-311G++** level of theory combined with the SMD solvation model (SCRF = SMD) for inclusion of the THF or benzene solvent effect.[13] The energies (ΔG) given are corrected for zero-point vibrational energies (ZPVEs). It must be noted here that the calculated barriers for the feasible pathways are seemingly high for the room temperature reactions, and we attribute these unanticipated high barriers to the use of methyl substituents, instead of cyclohexyl substituents, on the chelating phosphines. As a result, the energy reduction due to the London dispersion effect,[14] which establishes the attractive part of the van der Waals potential from the bulky cyclohexyl groups is lost. This effect is greater for the transition states than the starting diborenes, resulting in a slightly exaggerated energ barrier.

Optimized structures, Cartesian coordinates, and energies

REACTION 1

Pathway 1 of reaction 1

As shown in Figure S21, pathway 1 involves in an initial coordination of PPh_2H to diborene **A1**, followed by a 1,3-proton shift and subsequent rearrangement to form the net 1,2-hydrophosphinated product

A6 through phosphine dissociation/association. Compared to the other pathways computed (vide infra), this pathway was found to have an overall lower barrier.

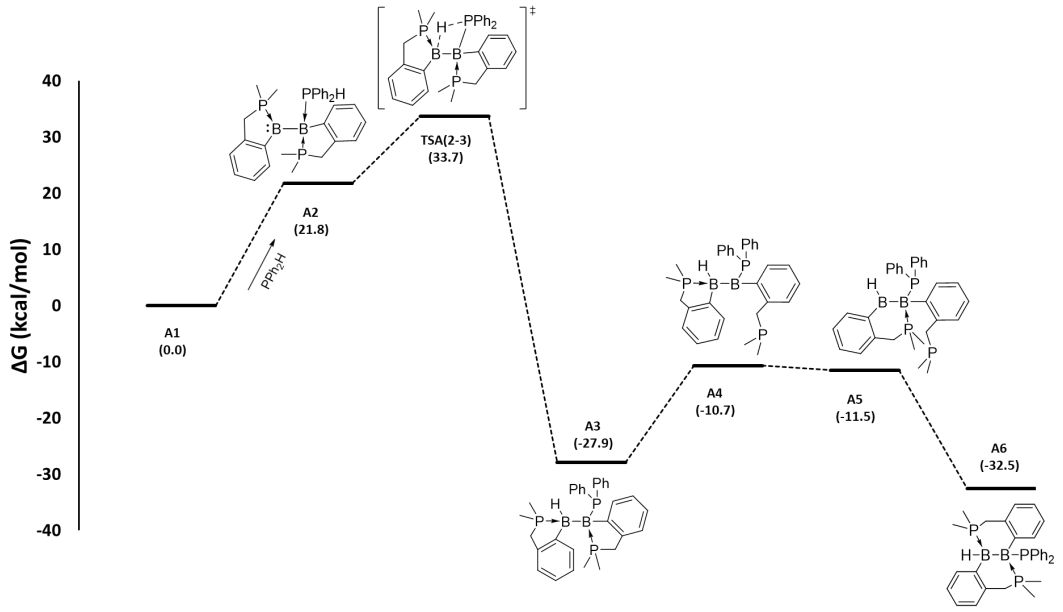
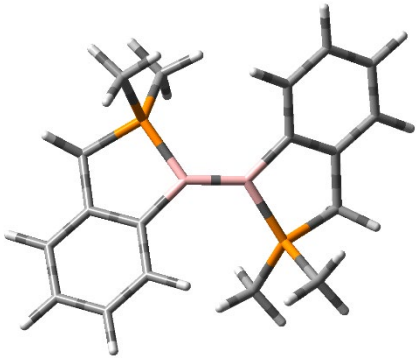


Figure S21. Computed mechanism 1 for 1,2-hydrophosphination of symmetrical diborene **A1**. Transition states (TS) computed for phosphine association and dissociation steps are not included in the free energy profile as the barriers for these steps have energies just above the higher energy intermediate; for example, the TS between **A1** and **A2** possesses a $\Delta G^{\ddagger}$ of 21.9 kcal/mol and the TS between intermediates **A3** and **A4** has a $\Delta G^{\ddagger}$ of –10.7 kcal/mol.

1) Diborene **A1**



Number of imaginary frequencies = 0

E_{total} = -1432.55628806 a.u

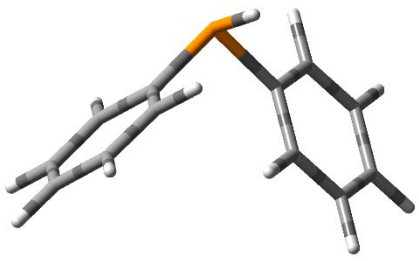
$G_{correction}$ = 0.520448 a.u

Cartesian coordinates:

P	-1.09316400	2.12005700	-0.08013200
B	-0.72334300	0.29759900	0.32628700
C	-3.19479900	0.49881800	-0.31347500
C	-4.50488300	0.04820700	-0.42774100
H	-5.26115000	0.68497700	-0.88144400
C	-2.18318100	-0.30094100	0.27031200

C	-1.33522700	3.33938600	1.26835400
H	-1.72497600	4.28819600	0.88786000
C	-2.75919200	1.86355100	-0.82532500
H	-3.46458400	2.66060900	-0.56951300
H	-2.64887500	1.85804600	-1.91672000
C	-2.57344200	-1.55998700	0.75606800
H	-1.83717300	-2.17658000	1.26809400
C	-3.88043800	-2.02081100	0.63215700
H	-4.14982200	-2.99948800	1.02005300
C	-0.04384000	2.99568100	-1.28846400
H	0.97112900	3.06799800	-0.89083500
C	-4.85220700	-1.21912900	0.03725200
H	-5.87556800	-1.57052400	-0.05094600
P	1.09249000	-2.11949100	-0.08032900
B	0.72374900	-0.29677000	0.32616700
C	3.19521400	-0.49941700	-0.31301200
C	4.50556000	-0.04950500	-0.42714300
H	5.26162400	-0.68689500	-0.88031700
C	2.18383800	0.30110700	0.27013700
C	0.04332700	-2.99402700	-1.28960000
H	0.42729900	-3.99433600	-1.50589100
C	2.75923400	-1.86420300	-0.82437200
H	2.64983400	-1.85939100	-1.91585400
H	3.46400900	-2.66145500	-0.56744800
C	2.57460200	1.56023300	0.75529800
H	1.83850900	2.17750700	1.26674400
C	3.88185500	2.02034300	0.63152800
H	4.15161200	2.99910000	1.01896600
C	1.33245200	-3.33930600	1.26806700
H	0.37887400	-3.51285300	1.77269300
C	4.85340200	1.21787100	0.03731800
H	5.87697100	1.56869300	-0.05074900
H	-0.42804000	3.99598900	-1.50434300
H	-0.00470200	2.40572500	-2.20584700
H	-2.03827400	2.91954400	1.99148200
H	-0.38222400	3.51350600	1.77385400
H	2.03517100	-2.92016400	1.99192100
H	1.72182400	-4.28832600	0.88771600
H	-0.97179200	-3.06624300	-0.89234300
H	0.00475000	-2.40349300	-2.20663000

2) **PPh_2H**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

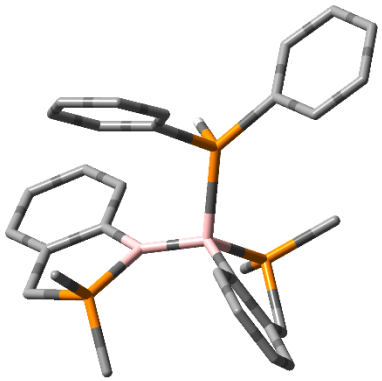
E_{total} = -805.08056 a.u

$G_{correction}$ = 0.15333 a.u

Cartesian coordinates:

P	0.05692000	1.70819700	0.28475900
C	-1.41369600	0.62571400	0.07285000
C	-2.17600700	0.15782800	1.14782100
C	-1.79383100	0.26655800	-1.22567300
C	-3.28899400	-0.65059200	0.93024400
H	-1.89809600	0.42201700	2.16434500
C	-2.89634700	-0.55147800	-1.44293500
H	-1.21942800	0.62875900	-2.07414900
C	-3.64860600	-1.01011400	-0.36434500
H	-3.87105500	-1.00418900	1.77560200
H	-3.17312300	-0.82509800	-2.45623000
H	-4.51348200	-1.64363700	-0.53356300
C	1.43269800	0.48181900	0.14645200
C	2.63201400	0.90907300	-0.42882000
C	1.32817300	-0.84242700	0.58516500
C	3.71185900	0.03687000	-0.55103800
H	2.72116700	1.93072100	-0.78797200
C	2.40259400	-1.71484800	0.45882000
H	0.39661500	-1.19486400	1.01839500
C	3.59785400	-1.27564200	-0.10758400
H	4.63755100	0.38357500	-0.99948400
H	2.30770500	-2.74025000	0.80253500
H	4.43512800	-1.95947400	-0.20655000
H	-0.00306800	1.78292400	1.69993900

3) **TSA(1-2)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*88.8)

E_{total} = -2237.63718033 a.u

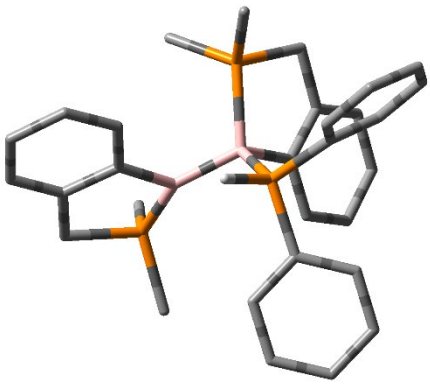
$G_{correction}$ = 0.510621 a.u

Cartesian coordinates:

P	0.21550900	-1.78973700	-2.03549900
B	-0.08782500	-0.83173700	-0.39042700
C	0.36171400	-3.29563400	0.14462100
C	0.65489600	-4.37289000	0.97414900
H	0.62965500	-5.38658400	0.58153300
C	0.37906400	-1.97328300	0.62856500
C	-0.03838400	-3.45996000	-1.30965000
H	-1.10389400	-3.70072700	-1.39965800
H	0.53249500	-4.23294700	-1.83429100
C	0.71681700	-1.77226100	1.97234300
H	0.74179600	-0.75994800	2.37013800
C	1.00798000	-2.84976000	2.80888000
H	1.26155200	-2.67437700	3.85052500
C	0.97656200	-4.14997800	2.31247800
H	1.20720500	-4.98865400	2.96216300
P	-2.68163000	-0.54062300	1.17979000
B	-1.56502700	-0.17410800	-0.26862000
C	-3.77722200	1.00522400	-0.72705800
C	-4.63314600	1.83694400	-1.42780300
H	-5.64865100	1.99206100	-1.06775700
C	-2.43936200	0.76523800	-1.15456200
C	-4.20590000	0.28192000	0.54011400
H	-4.62470900	0.96613500	1.28608700
H	-4.97061500	-0.47553000	0.33123900
C	-2.03797100	1.44261500	-2.32608200
H	-1.02010600	1.31464900	-2.69239900
C	-2.90167300	2.27612400	-3.03388300
H	-2.54929300	2.77604200	-3.93301300
C	-4.20475000	2.48094700	-2.59455000
H	-4.87800300	3.13334000	-3.14136100
H	0.81524700	1.65032100	-1.36637100
P	1.30598500	0.85976900	-0.30930700
C	-0.91649800	-1.58812900	-3.44386300
H	-1.91856400	-1.42469600	-3.04211100
H	-0.63528300	-0.71258200	-4.03193700
H	-0.89589300	-2.47415900	-4.08346100
C	1.90178900	-1.83031300	-2.75999700
H	2.61420700	-2.04927300	-1.96044900
H	1.98997400	-2.58532100	-3.54566900
H	2.14883400	-0.84886200	-3.17346800
C	-2.40928000	0.11053700	2.88130500
H	-3.26821400	-0.08496700	3.53163600
H	-1.52344000	-0.37315200	3.30181100
H	-2.21824300	1.18387600	2.82810900
C	-3.08804400	-2.29342700	1.55456600
H	-3.44087800	-2.77442400	0.64006100
H	-2.17236200	-2.79652100	1.87958400
H	-3.84750300	-2.38222200	2.33749900
C	0.88995100	1.90698100	1.11389000
C	-0.31979800	2.61131700	1.11446000
C	1.70433900	1.93287900	2.25039500
C	-0.69737500	3.33906200	2.24303200
H	-0.95442900	2.60543300	0.23466100

C	1.31521100	2.64939300	3.37565100
H	2.64869900	1.39564100	2.25430200
C	0.11129100	3.35340500	3.37351200
H	-1.63148900	3.89242800	2.23202500
H	1.95490800	2.66466400	4.25242700
H	-0.18921300	3.91697800	4.25138400
C	3.10908900	1.12096500	-0.58305100
C	3.61373300	2.08143400	-1.46615100
C	3.99997300	0.24149400	0.04393900
C	4.98179100	2.17500800	-1.69928500
H	2.93377500	2.76589400	-1.96628400
C	5.36997300	0.34667800	-0.17659200
H	3.61213000	-0.53327300	0.70250400
C	5.86226100	1.31185100	-1.05073500
H	5.36264200	2.92637100	-2.38422100
H	6.05201500	-0.33325600	0.32429100
H	6.92976300	1.38944100	-1.23086800

4) Intermediate **A2**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2237.637022 a.u

$G_{correction}$ = 0.512811 a.u

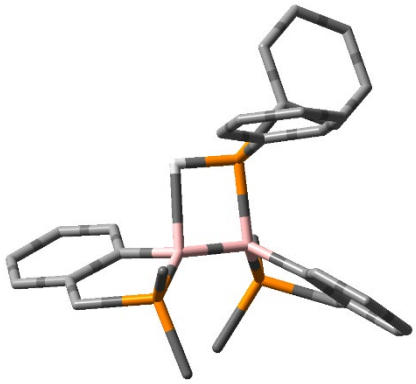
Cartesian coordinates:

P	0.20187200	-1.70309100	1.79588500
B	-0.06128800	-0.14697100	0.60342000
C	1.25161500	0.57089900	2.73494100
C	1.80172000	1.50516800	3.61205000
H	2.27102100	1.17098800	4.53427600
C	0.62398800	0.97311600	1.53985300
C	1.32568300	-0.91967000	3.02106400
H	1.05038300	-1.16756900	4.05141000
H	2.34006800	-1.30303900	2.85230500
C	0.59986100	2.34600200	1.25298200
H	0.14202500	2.68086400	0.32644100
C	1.15447400	3.27933400	2.12214600
H	1.11802900	4.33649700	1.87586500

C	1.75253500	2.86128000	3.30912800
H	2.17777700	3.58753300	3.99492700
P	-2.84829100	1.31235700	0.35162400
B	-1.61811100	-0.00858400	0.00544600
C	-3.87776200	-0.89441000	-0.78403000
C	-4.74361500	-1.85059700	-1.26986800
H	-5.79822900	-1.60968000	-1.39445400
C	-2.48373800	-1.15029200	-0.58724500
C	-4.32677600	0.50493300	-0.40395100
H	-4.64065600	1.08120800	-1.28254100
H	-5.17033200	0.49768800	0.29527100
C	-2.05768600	-2.45957600	-0.92499600
H	-1.00842200	-2.73122100	-0.80808800
C	-2.93701100	-3.42384000	-1.42309000
H	-2.55890000	-4.41409400	-1.66959800
C	-4.28239800	-3.13659400	-1.60194700
H	-4.96887100	-3.88678900	-1.98084800
H	0.19742200	-1.19886400	-1.95372000
P	0.90841100	-0.35851300	-1.08435700
C	-1.34510700	-2.11627900	2.65035800
H	-1.74112900	-1.20053700	3.09256900
H	-2.05855700	-2.46536600	1.89910900
H	-1.18537700	-2.87498300	3.42090400
C	0.95952900	-3.30110900	1.33146200
H	1.89865900	-3.12429400	0.80153900
H	1.15461000	-3.90435400	2.22222100
H	0.27637100	-3.84543800	0.67611000
C	-2.79817400	3.01564100	-0.36982100
H	-3.73333100	3.55485900	-0.18646900
H	-1.97391600	3.58028000	0.07449200
H	-2.62397000	2.94048500	-1.44484900
C	-3.27054200	1.75878400	2.09888100
H	-3.57204600	0.84890800	2.62320600
H	-2.36813000	2.15199700	2.57749700
H	-4.06880800	2.50516200	2.16932600
C	1.07192800	1.24011500	-1.92529100
C	-0.06561000	1.81945400	-2.49864500
C	2.28048700	1.94123700	-1.92168400
C	0.00946500	3.10071200	-3.03980200
H	-1.00150600	1.26984600	-2.48545300
C	2.34711500	3.21942400	-2.46390500
H	3.17109700	1.49562900	-1.49146800
C	1.20993100	3.80262200	-3.01847000
H	-0.87475700	3.54752800	-3.48367200
H	3.28752000	3.76064300	-2.44960600
H	1.26467100	4.79988700	-3.44387500
C	2.57395200	-1.12287100	-1.12268200
C	2.91294800	-2.14865500	-2.00914600
C	3.47519300	-0.77120700	-0.10786300
C	4.13948500	-2.79679700	-1.89764500
H	2.21407100	-2.44476800	-2.78691900
C	4.70412200	-1.41403000	-0.00377600
H	3.20477000	0.00429100	0.60632700

C	5.03708900	-2.42860700	-0.89827400
H	4.39666500	-3.58879600	-2.59384900
H	5.39991100	-1.12750000	0.77850800
H	5.99278000	-2.93562600	-0.81291100

5) **TSA(2-3)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*955.3)

E_{total} = -2237.61822 a.u

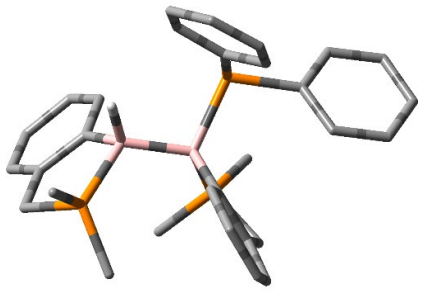
$G_{correction}$ = 0.509821 a.u

Cartesian coordinates:

P	0.20232800	1.47570400	2.05434600
B	0.11060400	0.09500700	0.64815100
C	-0.90833100	-0.79472100	2.87874700
C	-1.36269400	-1.79333200	3.73927000
H	-1.67956600	-1.53707500	4.74748000
C	-0.47668300	-1.09197900	1.57125000
C	-0.86144700	0.66158100	3.30897800
H	-0.47166600	0.79335000	4.32352600
H	-1.85737000	1.12155900	3.28085700
C	-0.54262800	-2.43372000	1.16697000
H	-0.24097000	-2.69112500	0.15580000
C	-1.00289000	-3.43223400	2.01742600
H	-1.04494900	-4.46058300	1.67027000
C	-1.41122300	-3.11514700	3.31145500
H	-1.76480900	-3.89177100	3.98249400
P	2.65774300	-1.54381300	-0.35008800
B	1.50646700	-0.07535600	-0.30844500
C	3.81828000	0.76925800	-1.04096700
C	4.75065400	1.74042000	-1.35659700
H	5.76800500	1.44995100	-1.61251800
C	2.48091300	1.09551300	-0.67731600
C	4.14086600	-0.71427500	-1.06826600
H	4.28675100	-1.07332000	-2.09402100
H	5.04774900	-0.96382200	-0.50685500
C	2.15843100	2.47102700	-0.68179800

H	1.13761500	2.77598300	-0.45762600
C	3.09457400	3.44797100	-1.02051000
H	2.80155400	4.49541800	-1.02079500
C	4.39852700	3.09678300	-1.34714000
H	5.13471400	3.85631400	-1.58937200
H	0.35330200	0.66701200	-1.78007100
P	-0.87274100	0.55721900	-0.97735400
C	1.86715100	1.55775400	2.78201500
H	2.16685000	0.53938900	3.03978700
H	2.55499300	1.94064700	2.02467700
H	1.88484200	2.18815700	3.67459700
C	-0.37475000	3.19968900	1.89314500
H	-1.33383800	3.21226300	1.36956100
H	-0.48939500	3.65882700	2.87863700
H	0.35179400	3.77247200	1.31420800
C	2.34187100	-3.01910500	-1.39853500
H	3.19384700	-3.70557300	-1.38260300
H	1.45216000	-3.54526000	-1.04454100
H	2.15619300	-2.69124300	-2.42304600
C	3.16490900	-2.33189200	1.23525600
H	3.57426000	-1.55753300	1.88820600
H	2.27508100	-2.75233000	1.71221100
H	3.91053400	-3.11988800	1.09106300
C	-1.43114300	-1.04249400	-1.68310400
C	-0.68482500	-1.69321100	-2.66778500
C	-2.59507700	-1.64830500	-1.20513400
C	-1.08934700	-2.93032700	-3.15829200
H	0.22835800	-1.23095800	-3.03023700
C	-2.99657900	-2.88959900	-1.68892900
H	-3.18806500	-1.15493300	-0.44181200
C	-2.24310800	-3.53495100	-2.66384300
H	-0.50326800	-3.42296400	-3.92837600
H	-3.89664800	-3.35336900	-1.29813500
H	-2.55585200	-4.50284800	-3.04343500
C	-2.51578400	1.46747000	-0.99275400
C	-2.96714300	2.16753600	-2.11521200
C	-3.23101500	1.58165400	0.20546000
C	-4.11216600	2.95388900	-2.04454200
H	-2.41958800	2.09635900	-3.05198700
C	-4.37868800	2.36737800	0.27779600
H	-2.89674900	1.03067400	1.08344400
C	-4.81949000	3.05766200	-0.84785400
H	-4.45652700	3.48794500	-2.92510800
H	-4.93029000	2.43761100	1.21087700
H	-5.71135700	3.67399100	-0.79438600

6) Intermediate **A3**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2237.727069 a.u

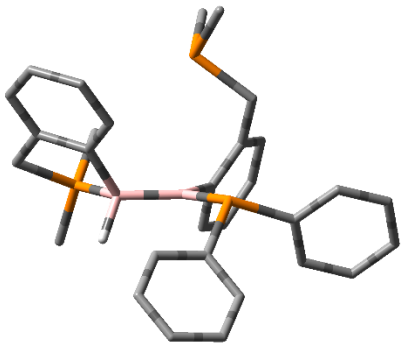
$G_{correction}$ = 0.516972 a.u

Cartesian coordinates:

P	-0.40111800	-1.82038400	1.02809400
B	-0.08140700	-0.13427900	0.04062200
C	0.66016300	0.11386700	2.53620400
C	1.02885900	0.85005100	3.66076300
H	1.15119500	0.35329500	4.62046800
C	0.47821100	0.73063900	1.28302800
C	0.47511700	-1.39297500	2.58855200
H	-0.07016700	-1.73151200	3.47537900
H	1.44882600	-1.89836300	2.58374100
C	0.71941700	2.11125700	1.20221300
H	0.59890700	2.60945900	0.24358200
C	1.10232900	2.84796500	2.31924000
H	1.28546800	3.91475900	2.22669400
C	1.24665400	2.22103900	3.55644500
H	1.53427400	2.79414900	4.43252100
P	-2.67976500	1.59322900	0.52891600
B	-1.54792500	0.52220000	-0.67862800
C	-4.00194000	-0.38465500	-0.70803400
C	-4.97989000	-1.33624800	-0.99567500
H	-5.98973000	-1.21134200	-0.61098800
C	-2.68001300	-0.52546100	-1.16941200
C	-4.31796800	0.84451100	0.12883400
H	-4.91821500	1.56634100	-0.43775400
H	-4.88097500	0.60454300	1.03759400
C	-2.39550600	-1.64406200	-1.96807300
H	-1.38467300	-1.77064100	-2.35059100
C	-3.36848000	-2.59473900	-2.26294800
H	-3.11752000	-3.45473000	-2.87796000
C	-4.66382800	-2.44950600	-1.76732700
H	-5.42281100	-3.19417200	-1.98675400
H	-1.28580200	1.36159600	-1.52153800
P	1.19723600	-0.54611100	-1.45047900

C	-2.11194600	-2.25372700	1.51144300
H	-2.64095000	-1.37225100	1.87512100
H	-2.65203000	-2.63389200	0.64188200
H	-2.09317300	-3.01363200	2.29749300
C	0.24642300	-3.41653600	0.42667100
H	1.32336600	-3.34556000	0.26682900
H	0.02797300	-4.21337900	1.14213700
H	-0.23488300	-3.64402100	-0.52790200
C	-2.77306900	3.37324600	0.14340000
H	-3.57005300	3.87152600	0.70133000
H	-1.81251400	3.83050000	0.39409000
H	-2.93998900	3.49138600	-0.92907100
C	-2.53600300	1.57611800	2.35425300
H	-2.45635800	0.55246400	2.72375200
H	-1.62885100	2.10719500	2.65136800
H	-3.40936000	2.05363300	2.80708000
C	1.78488700	1.14654100	-1.89556500
C	1.03718100	1.85828200	-2.84425800
C	2.90444300	1.77517100	-1.33950800
C	1.36884400	3.16413300	-3.18969600
H	0.18100100	1.38173800	-3.31134200
C	3.24844400	3.07587900	-1.69672600
H	3.51908000	1.24966500	-0.61771800
C	2.47625300	3.78122500	-2.61385200
H	0.76628100	3.69682400	-3.91962300
H	4.12222700	3.54016600	-1.24886000
H	2.74024700	4.79874800	-2.88596300
C	2.71063600	-1.30651400	-0.68521700
C	3.30963800	-2.36788200	-1.37679600
C	3.25125400	-0.95460700	0.56002600
C	4.39565400	-3.05967500	-0.84529500
H	2.90363600	-2.65904500	-2.34177800
C	4.33527900	-1.64371700	1.09683400
H	2.81847100	-0.13158300	1.11772700
C	4.90927800	-2.70197300	0.39754600
H	4.83862600	-3.88060200	-1.40126600
H	4.73435600	-1.34907800	2.06317500
H	5.75354800	-3.24067600	0.81678900

7) **TSA(3-4)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*27.5)

E_{total} = -2237.69481870 a.u

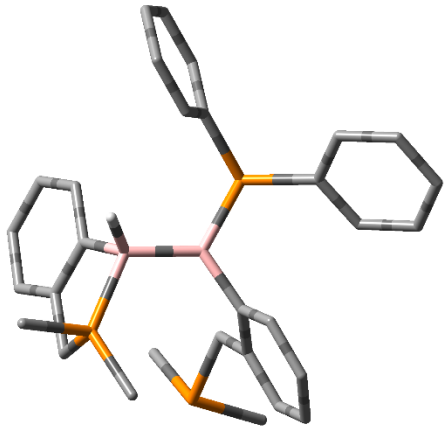
$G_{correction}$ = 0.510896 a.u

Cartesian coordinates:

P	-1.55961500	-2.11053400	-1.84671800
B	0.17539100	0.10914900	0.40772200
C	0.41906600	-2.52427200	0.10117700
C	0.56672600	-3.77805400	0.69837300
H	0.55939200	-4.66418900	0.06803200
C	0.40494000	-1.36787400	0.90823500
C	0.22394700	-2.43018200	-1.39068400
H	0.57859900	-3.34130700	-1.88653700
H	0.80288900	-1.59690800	-1.80051900
C	0.58809300	-1.52836100	2.29079100
H	0.59921500	-0.64387400	2.92614000
C	0.76494700	-2.77930500	2.87336600
H	0.91680300	-2.86646200	3.94512800
C	0.73926800	-3.91550700	2.07213000
H	0.86289200	-4.90100500	2.50986900
P	-2.50421500	0.09060500	2.00938300
B	-1.20130000	1.00436600	0.86797000
C	-3.63207100	1.52467400	0.12254400
C	-4.63397400	1.89713500	-0.76896800
H	-5.66990600	1.92961000	-0.43968500
C	-2.27866600	1.46156700	-0.26828100
C	-3.93160600	1.14954900	1.56286000
H	-3.91520100	2.03129700	2.21651300
H	-4.89658500	0.65024900	1.69219000
C	-1.98605500	1.77837100	-1.59933700
H	-0.96101900	1.70653300	-1.95484900
C	-2.98209000	2.16061500	-2.49454000
H	-2.72222700	2.39658800	-3.52244800
C	-4.30964900	2.22207500	-2.08258300
H	-5.08888100	2.51029500	-2.78138900
H	-0.88220500	1.95104900	1.57699900
P	1.47741300	0.84527100	-0.77570700
C	-2.18670900	-3.85400300	-1.77271000
H	-2.13462000	-4.20478800	-0.73733300
H	-3.23264100	-3.89102100	-2.08947200
H	-1.60179200	-4.53417800	-2.40189500
C	-1.36279300	-1.89886100	-3.67324900
H	-0.86916500	-0.94174200	-3.86374000
H	-0.77493700	-2.70191400	-4.13084000
H	-2.34759300	-1.86643500	-4.14695500
C	-2.31541100	0.11019700	3.82301600
H	-3.25352600	-0.15127700	4.31912200
H	-1.54814000	-0.61225700	4.11012700
H	-1.99982500	1.10663200	4.13995300
C	-2.99042000	-1.61395400	1.59184600
H	-3.16686600	-1.65644000	0.51397300
H	-2.17239900	-2.29623500	1.83546000
H	-3.89376700	-1.90624700	2.13391000

C	1.90002900	2.53988500	-0.20425100
C	0.89652600	3.51321500	-0.11207900
C	3.21949200	2.91331000	0.07252900
C	1.20500800	4.81410100	0.26829400
H	-0.13430800	3.26004000	-0.33451500
C	3.52401100	4.21892600	0.44763700
H	4.01771200	2.18260200	-0.00222700
C	2.51961100	5.17448400	0.55168200
H	0.41066700	5.55092300	0.33776900
H	4.55540500	4.48492000	0.65907800
H	2.75775700	6.19240700	0.84400800
C	3.01687500	-0.13419700	-0.57432600
C	3.62019700	-0.67188100	-1.71462300
C	3.58502200	-0.41145800	0.67631700
C	4.75775600	-1.46957800	-1.61358300
H	3.18925000	-0.46584700	-2.69039100
C	4.72303200	-1.20166100	0.78011900
H	3.12908100	-0.00290200	1.57261100
C	5.31029900	-1.73436100	-0.36571200
H	5.21127600	-1.88156700	-2.50968300
H	5.15078800	-1.40683000	1.75644400
H	6.19728200	-2.35497600	-0.28362000

8) Intermediate **A4**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2237.69513 a.u

$G_{correction}$ = 0.51032 a.u

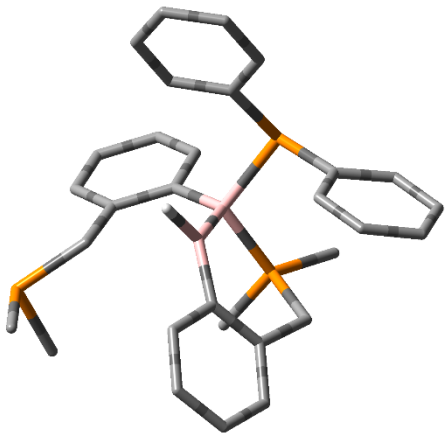
Cartesian coordinates:

P	3.60441600	-1.54615000	1.50264500
B	-0.39732700	-0.08509300	-0.42848100
C	1.21351000	-2.10039700	-0.04098500
C	1.70687800	-3.34268100	-0.44582900
H	2.56368300	-3.77586100	0.06111800
C	0.11798200	-1.54017900	-0.72703000

C	3.59862600	-3.01632500	2.63633200
H	2.83234400	-2.92588900	3.41375800
C	1.78502900	-1.34782800	1.14371500
H	1.20976500	-1.58744200	2.04929000
H	1.63903500	-0.27034700	0.99174300
C	-0.47457200	-2.26857800	-1.76594700
H	-1.34250300	-1.85742300	-2.27644600
C	0.02325900	-3.50574300	-2.15847800
H	-0.44845400	-4.04953900	-2.97118500
C	3.74216900	-0.21618400	2.78456900
H	4.73265500	-0.25417600	3.24633700
C	1.12689900	-4.04001500	-1.50279300
H	1.53323200	-5.00072300	-1.80310600
P	1.85693800	0.94840000	-2.30881800
B	0.32256500	1.30461900	-1.13425600
C	2.55436700	2.18840000	-0.09484400
C	3.31562400	2.96143900	0.78226300
H	4.40129400	2.90811900	0.74721900
C	1.14617100	2.24367500	-0.08867600
C	2.03053600	2.25155800	-3.57416200
H	2.99810200	2.19426700	-4.07921800
C	3.19946900	1.25369000	-1.10366900
H	4.09327600	1.67817400	-1.57135100
H	3.49113300	0.29585600	-0.65158100
C	0.53903700	3.10255500	0.83676400
H	-0.54456800	3.17816400	0.85843700
C	1.29414900	3.86508800	1.72105300
H	0.79614200	4.52351400	2.42681200
C	2.20669400	-0.61594900	-3.17600900
H	1.38601200	-0.85690300	-3.85471900
C	2.68607100	3.79661800	1.69825200
H	3.27718600	4.39846100	2.38149500
H	2.98389400	-0.32064200	3.56802200
H	3.61937200	0.76317600	2.31360900
H	3.42557500	-3.94276300	2.08375200
H	4.57736000	-3.09682300	3.11820900
H	2.29468400	-1.42470900	-2.44760500
H	3.13661900	-0.53068500	-3.74430900
H	1.22820100	2.15636000	-4.30941100
H	1.93117400	3.21966200	-3.07794500
H	-0.48500200	1.92342400	-1.79989700
P	-1.76542900	0.07955000	0.87838500
C	-2.80050200	1.53419900	0.46026100
C	-3.20458200	2.39278900	1.48772800
C	-3.19709900	1.82755800	-0.85074000
C	-3.97785500	3.51840100	1.21367400
H	-2.90281600	2.17989000	2.50901100
C	-3.97160200	2.94834900	-1.12669100
H	-2.88911500	1.17218000	-1.65889000
C	-4.36101000	3.79774300	-0.09389700
H	-4.27909100	4.17754800	2.02182700
H	-4.26616400	3.16207400	-2.14942100
H	-4.96026800	4.67691900	-0.30959400

C	-2.88368200	-1.36826900	0.69229100
C	-2.37872800	-2.63838500	1.00089400
C	-4.21615700	-1.26211800	0.28319900
C	-3.17312400	-3.77115200	0.87230800
H	-1.35085600	-2.74541100	1.33418900
C	-5.01532400	-2.39706600	0.17051100
H	-4.63669300	-0.28908700	0.05135400
C	-4.49669400	-3.65545200	0.45626000
H	-2.75511100	-4.74631900	1.10202300
H	-6.04854400	-2.29282800	-0.14710700
H	-5.11986900	-4.53926900	0.36212700

9) Intermediate **A5**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2237.70004455 a.u

$G_{correction}$ = 0.513044 a.u

Cartesian coordinates:

B	0.02537600	-0.36480900	0.84294300
B	0.00834100	0.42676500	-0.66406400
P	0.08479300	-1.04094800	-1.94031300
C	-1.26558700	1.33428500	-1.12179000
C	-1.15021600	2.14829100	-2.26128100
H	-0.18407700	2.21135100	-2.75722600
C	-2.20810900	2.89751500	-2.76441400
H	-2.06871400	3.51157500	-3.64915900
C	-3.43563500	2.85879600	-2.11731200
H	-4.27527800	3.44020400	-2.48563400
C	-3.58208300	2.07124400	-0.98111700
H	-4.54084400	2.05721600	-0.46961500
C	-2.73497400	0.47875000	0.77807100
H	-2.14266700	-0.44394500	0.72036900
C	-2.52630400	1.30397500	-0.47743800
C	0.07451200	-1.92003500	1.09059800

C	-0.37690400	-2.40045100	2.33163900
H	-0.64193200	-1.67545400	3.09673700
C	-0.51194700	-3.75749600	2.60050600
H	-0.88077000	-4.09273800	3.56482200
C	-0.15915900	-4.68150500	1.62297700
H	-0.25366800	-5.74595500	1.81459300
C	0.31906900	-4.24002900	0.39311500
H	0.60434000	-4.96748800	-0.36243700
C	0.43720200	-2.87830300	0.11586000
C	0.99084000	-2.46406200	-1.23133400
H	0.95604200	-3.29835600	-1.93974200
H	2.03903000	-2.15944800	-1.13622700
C	0.81663200	-0.76321100	-3.58789900
H	0.30150500	0.07385600	-4.06496800
C	-1.58880700	-1.67999400	-2.27118800
H	-2.01513000	-2.04126700	-1.33304300
H	1.87114800	-0.50513200	-3.47395400
H	0.72486200	-1.65434100	-4.21410900
H	-2.21562200	-0.86872300	-2.64734300
H	-1.56098700	-2.49952900	-2.99344800
H	-2.35551000	1.02844000	1.64804500
P	-4.48030500	-0.03368400	1.19022200
C	-4.07334400	-1.12418300	2.63284700
H	-3.28462200	-1.84808400	2.39881600
H	-3.74547000	-0.50774700	3.47474800
H	-4.97032400	-1.66596000	2.94518000
C	-4.72111200	-1.32650400	-0.11630400
H	-3.94864000	-2.10251400	-0.07184100
H	-5.69919700	-1.80025700	0.00130300
H	-4.68974500	-0.84966700	-1.10007100
P	1.71897000	1.48456200	-0.81756000
H	0.01584300	0.29042900	1.85264800
C	1.73362900	2.50134300	0.71960500
C	2.93773300	2.79394300	1.37171800
C	0.55968900	3.09486200	1.20082600
C	2.96523800	3.63280400	2.48116700
H	3.86489800	2.35512300	1.01464700
C	0.58921300	3.93778600	2.30683200
H	-0.38782600	2.89381200	0.71145900
C	1.79045800	4.20789300	2.95552400
H	3.91076700	3.83705700	2.97473600
H	-0.33452600	4.38225900	2.66513600
H	1.81108700	4.86343300	3.82060800
C	3.02650300	0.22531600	-0.45568000
C	3.89441400	-0.13127000	-1.49343500
C	3.14865500	-0.44953700	0.76749700
C	4.82002200	-1.16259800	-1.33765300
H	3.84430400	0.41130700	-2.43421600
C	4.07278300	-1.47437800	0.93010900
H	2.51134200	-0.16528500	1.60058500
C	4.90396200	-1.84260400	-0.12744300
H	5.47988200	-1.42745400	-2.15826500
H	4.13930000	-1.99277500	1.88141800

H	5.62251300	-2.64649300	-0.00179500

10) Product **A6**

(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2237.73555365 a.u

$G_{correction}$ = 0.51799 a.u

Cartesian coordinates:

B	-0.28957600	-0.19569100	-0.70804200
H	0.33884800	0.11792600	1.68775300
B	0.48609900	-0.72378400	0.81537600
P	1.01289600	-0.84612600	-2.03354400
C	1.26394100	3.92082000	-1.14440600
H	0.54182400	4.28011800	-1.87273700
C	3.34774300	4.20457100	0.03595600
H	4.24685000	4.77931700	0.23698200
P	-0.70031100	-2.00548600	1.60180700
C	2.40894100	4.66830000	-0.88029000
H	2.56970800	5.61071200	-1.39545100
C	3.12744200	2.99543100	0.68951200
H	3.85401900	2.61965200	1.40411100
C	1.97566600	2.25831500	0.43092500
H	1.82141100	1.31979300	0.94704900
C	-1.65715500	2.12290800	0.41510200
C	-1.23871300	2.43800400	1.71309400
H	-0.18203900	2.57387200	1.91797600
C	-2.16049700	2.57589200	2.74771200
H	-1.81241900	2.82190000	3.74697200
C	-3.51977600	2.39233700	2.50808500
H	-4.23775300	2.49257100	3.31659300
C	-3.95222700	2.09298200	1.21867300
H	-5.00998700	1.95431900	1.01599900
C	-3.03136200	1.97363200	0.18287500
H	-3.38030900	1.74015200	-0.81894800
C	1.98220800	-1.33555100	0.87955200
C	2.80643000	-1.08753800	1.98874800

H	2.42467100	-0.44384000	2.77854800
C	4.08537500	-1.62169000	2.10719400
H	4.68853500	-1.40126200	2.98327700
C	4.58991300	-2.43288100	1.09609100
H	5.58679600	-2.85581200	1.17215700
C	3.80635900	-2.68856400	-0.02348500
H	4.19986300	-3.30987500	-0.82500800
C	1.72130400	-2.41645800	-1.39198800
H	0.87161100	-3.08613900	-1.21522600
H	2.34422500	-2.87822600	-2.16523200
C	2.51973000	-2.15683900	-0.13390600
P	-0.51427400	1.79717700	-0.99748100
C	1.02246000	2.70367300	-0.49363600
C	2.46921500	0.22687400	-2.25994500
H	2.92386500	0.43730900	-1.29145700
C	0.54851200	-1.26945200	-3.75570100
H	0.23534800	-0.36837200	-4.28791600
C	-1.79409800	-0.75198100	-1.06462400
C	-2.30671300	-0.61387000	-2.36780000
H	-1.68814300	-0.13469400	-3.11898900
C	-3.58882900	-1.00187000	-2.73782700
H	-3.92288500	-0.86445900	-3.76203100
C	-4.44063700	-1.54717800	-1.78552700
H	-5.44623500	-1.85986200	-2.04902300
C	-3.99134800	-1.66096200	-0.47734900
H	-4.66203200	-2.04987000	0.28514600
C	-2.70554000	-1.25661500	-0.10654700
C	-2.36702900	-1.32510600	1.36776000
H	-3.11149700	-1.90954400	1.91710300
H	-2.34352100	-0.31656000	1.80033700
C	-0.46044900	-2.23073600	3.39585900
H	0.55680700	-2.58985900	3.57292600
C	-0.75991200	-3.70275400	0.92984100
H	-1.12644000	-3.65914500	-0.09847500
H	3.19868900	-0.26919700	-2.90597400
H	2.16275500	1.17526700	-2.70664300
H	1.40821300	-1.70575300	-4.27196500
H	-0.27836500	-1.98214100	-3.75786400
H	-0.57307700	-1.25915400	3.88232000
H	-1.17857400	-2.93815900	3.81865700
H	0.24543700	-4.13207200	0.94031300
H	-1.42921000	-4.33718400	1.51662000

Pathway 2 of reaction 1

Figure S22 shows the computed free energy profile for the conceived mechanism 2 for the 1,2-hydrophosphination of diborene **A1**. This mechanism involves (i) an initial PPh_2H coordination, (ii) dissociation of a chelating phosphine, (iii) 1,3-proton shift, and (iv) rearrangements via chelating phosphine dissociation/association. The overall barrier of this mechanism was found to be 8.3 kcal/mol higher in energy than that of mechanism 1.

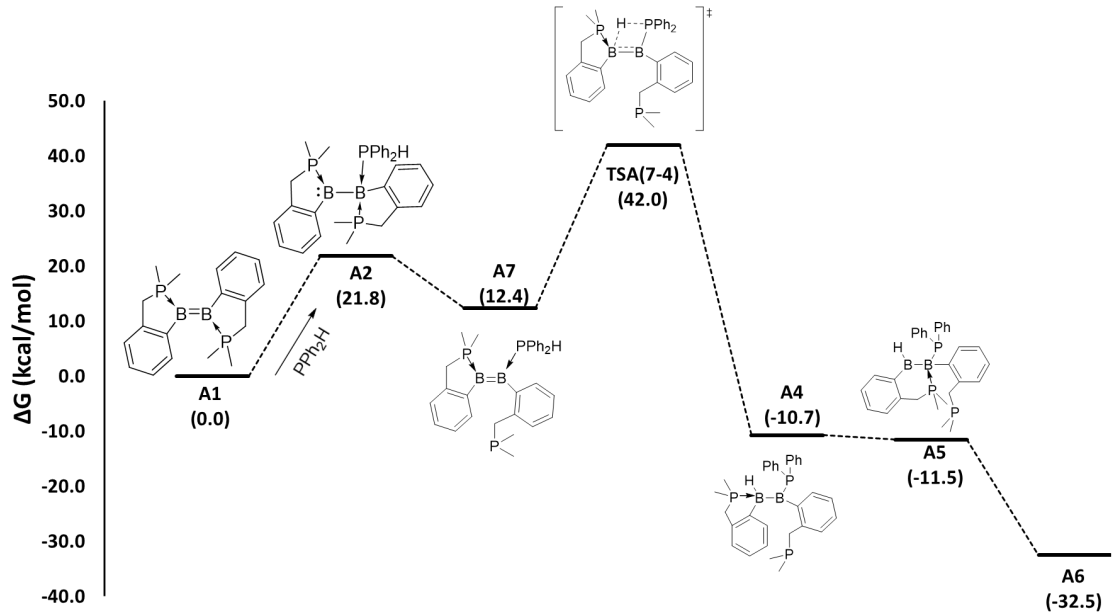


Figure S22. Computed mechanism 2 for 1,2-hydrophosphination of symmetrical diborene **A1**.

Note: Details of species **A1, A2, A5** and **A6** are provided above in Pathway 1 of reaction 1.

11) Intermediate **A7**

(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2237.65218133 a.u

$G_{correction}$ = 0.50961 a.u

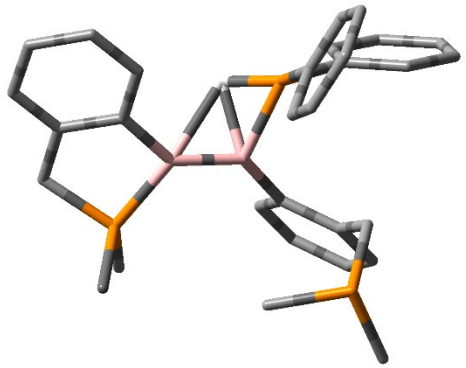
Cartesian coordinates:

P	-2.29913300	-2.46549100	0.63396200
B	-1.81896300	-0.73847900	-0.02188700
C	-3.98132600	-1.47055600	-1.17238500
C	-5.12693000	-1.28826200	-1.93876700
H	-5.79667300	-2.12562100	-2.12167500
C	-3.08595000	-0.40413400	-0.90677400
C	-1.07960400	-3.82023100	0.63857900

H	-1.53749400	-4.77011100	0.92651100
C	-3.62181300	-2.83113100	-0.59057300
H	-3.20691200	-3.49237600	-1.36132500
H	-4.48173600	-3.34323000	-0.14730300
C	-3.42415500	0.84960900	-1.44383700
H	-2.80142600	1.71358300	-1.22650100
C	-4.56395900	1.03256600	-2.22000100
H	-4.79345300	2.01686400	-2.61846800
C	-3.06943000	-2.56209100	2.29057600
H	-2.30956400	-2.31496300	3.03636500
C	-5.42037000	-0.03549400	-2.47279900
H	-6.31737800	0.10724100	-3.06734300
P	3.48376500	-2.67992500	-1.20007000
B	-0.39996300	-0.18410800	0.33578600
C	1.75917800	-1.61196200	0.87066000
C	2.57397500	-2.27064400	1.79324400
H	3.39883600	-2.88560600	1.44224300
C	0.65671800	-0.84649300	1.32402700
C	1.99014300	-1.73362600	-0.62211700
H	1.10651900	-2.19891000	-1.07812700
H	2.03888200	-0.73132500	-1.06455800
C	0.44433700	-0.77612200	2.70972300
H	-0.39971500	-0.19304300	3.07032200
C	1.26693500	-1.42910700	3.62605200
H	1.07042600	-1.34845700	4.69149100
C	2.33678700	-2.18347000	3.16345100
H	2.98533300	-2.70802200	3.85878700
H	-3.47554000	-3.55717000	2.49352400
H	-3.86895300	-1.82006400	2.34593000
H	-0.64007600	-3.91033600	-0.35672300
H	-0.28147500	-3.56721100	1.34136300
C	3.27371600	-2.35948300	-3.01510300
H	3.11829500	-1.29517900	-3.22505300
H	4.16342000	-2.69882000	-3.55269000
H	2.41614200	-2.92134600	-3.39522200
C	4.79777000	-1.41974500	-0.84419900
H	4.90671700	-1.29359200	0.23622200
H	5.75591800	-1.76022500	-1.24713700
H	4.55190400	-0.44595200	-1.28039900
P	0.04367800	1.47718000	-0.44182600
H	-0.46378100	1.63570100	-1.74635000
C	-0.62839400	2.95890900	0.41145900
C	-0.08120300	4.23044700	0.21929900
C	-1.72989500	2.79460000	1.25198900
C	-0.63724200	5.32976800	0.86342700
H	0.78444300	4.36056200	-0.42389100
C	-2.28766400	3.89938900	1.88897300
H	-2.13362700	1.79405500	1.39647400
C	-1.74159600	5.16470700	1.69691600
H	-0.20659300	6.31531600	0.71775700
H	-3.14670600	3.76966600	2.53941800
H	-2.17461300	6.02501100	2.19773000
C	1.80805700	1.85012800	-0.67143700

C	2.34008800	2.11874900	-1.93483000
C	2.65523000	1.81275700	0.44230400
C	3.70340700	2.35760300	-2.08391400
H	1.69000200	2.13953300	-2.80507400
C	4.01449200	2.05596800	0.28945700
H	2.25124900	1.58142500	1.42314300
C	4.53961400	2.33034300	-0.97150200
H	4.11165800	2.56473000	-3.06775500
H	4.66774700	2.02231400	1.15504900
H	5.60268700	2.51407300	-1.08863200

12) **TSA(7-4)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*1055.0)

E_{total} = -2237.60511161 a.u

$G_{correction}$ = 0.50891 a.u

Cartesian coordinates:

P	2.78876200	-2.09104400	0.20577600
B	1.78255000	-0.45087100	0.39218100
C	4.25191600	-0.02043800	0.91799900
C	5.38052000	0.76356900	1.11820200
H	6.32406400	0.29720300	1.39125400
C	3.00280600	0.54573000	0.55424000
C	4.29034700	-1.52970700	1.09317300
H	4.18875200	-1.80888800	2.14924000
H	5.20998500	-1.98353300	0.71156200
C	2.96822400	1.94100300	0.38705700
H	2.05624500	2.42134600	0.05378100
C	4.09465000	2.73020800	0.60568900
H	4.02965700	3.80543400	0.46791400
C	5.30315100	2.14739400	0.97005900
H	6.18578000	2.76051800	1.12333000
B	0.18940400	-0.38081000	0.40092400
P	-0.44145800	1.39188400	0.84121300
H	0.57011400	0.68148200	1.73583100
C	-0.89844400	-1.53158400	0.47822000

C	-0.81481000	-2.46929300	1.52049800
C	-2.02328900	-1.61788700	-0.37627000
C	-1.76277200	-3.46942000	1.71211800
H	0.01388600	-2.38390600	2.21900900
C	-2.98212400	-2.61380500	-0.16745700
C	-2.85785500	-3.54262800	0.85966000
H	-1.65809900	-4.17227800	2.53382700
H	-3.85185500	-2.65184200	-0.81914900
H	-3.61964800	-4.30333400	1.00121900
C	-0.52394100	2.66389200	-0.46604600
C	0.05608400	2.38178900	-1.70550900
C	-1.09094300	3.92400300	-0.24016700
C	0.04172200	3.33490700	-2.71852500
H	0.52242400	1.41062600	-1.86040600
C	-1.10568500	4.87106800	-1.25642000
H	-1.53408900	4.15303400	0.72457600
C	-0.54045800	4.57913300	-2.49721100
H	0.48601200	3.10348300	-3.68113900
H	-1.55791900	5.84209100	-1.08050300
H	-0.55008100	5.32411200	-3.28625800
C	-2.05065000	1.30130200	1.66980900
C	-2.12576700	0.71084500	2.93608000
C	-3.23366400	1.69223800	1.03456600
C	-3.35571200	0.51535100	3.55138100
H	-1.21606300	0.39205200	3.43663000
C	-4.46231000	1.50813300	1.65995300
H	-3.19609000	2.13667500	0.04496900
C	-4.52829500	0.91709600	2.91753400
H	-3.39822800	0.04893600	4.53042300
H	-5.37199200	1.81859100	1.15545500
H	-5.48844600	0.76756100	3.40078200
C	2.24497900	-3.69229100	0.88292500
H	2.08356600	-3.59508900	1.95777400
H	1.29517600	-3.97338900	0.42269000
H	2.99449900	-4.46511200	0.69356100
C	3.34979300	-2.47709300	-1.49096900
H	3.76638400	-1.56754000	-1.92952400
H	4.11213400	-3.26083900	-1.48181400
H	2.49891400	-2.79863900	-2.09445400
C	-2.21684300	-0.65996600	-1.52125800
H	-3.28294100	-0.45043700	-1.66751100
H	-1.74190900	0.30272700	-1.31589900
P	-1.58592200	-1.16645000	-3.21454000
C	-2.51527900	-2.74678900	-3.48986800
H	-2.15385600	-3.21048300	-4.41239700
H	-2.39218000	-3.45629800	-2.66546500
H	-3.58080400	-2.53577400	-3.61942300
C	0.06511900	-1.89173100	-2.79630700
H	-0.01476200	-2.66126400	-2.02035500
H	0.49797200	-2.32893000	-3.70162200
H	0.73007600	-1.10590900	-2.42909800

Pathway 3 of reaction 1

Figure S23 shows the computed free energy profile for the conceived mechanism 3 for the 1,2-hydrophosphination of diborene **A1**. This mechanism involves (i) starting with the stable isomer of diborene **A1** (**A8**), (ii) dissociation of a chelating phosphine, (iii) PPh_2H coordination, (iv) 1,3-proton shift, and (v) association of the dangling phosphine. The overall barrier of this mechanism was found to be 10.8 kcal/mol higher in energy than that of mechanism 1.

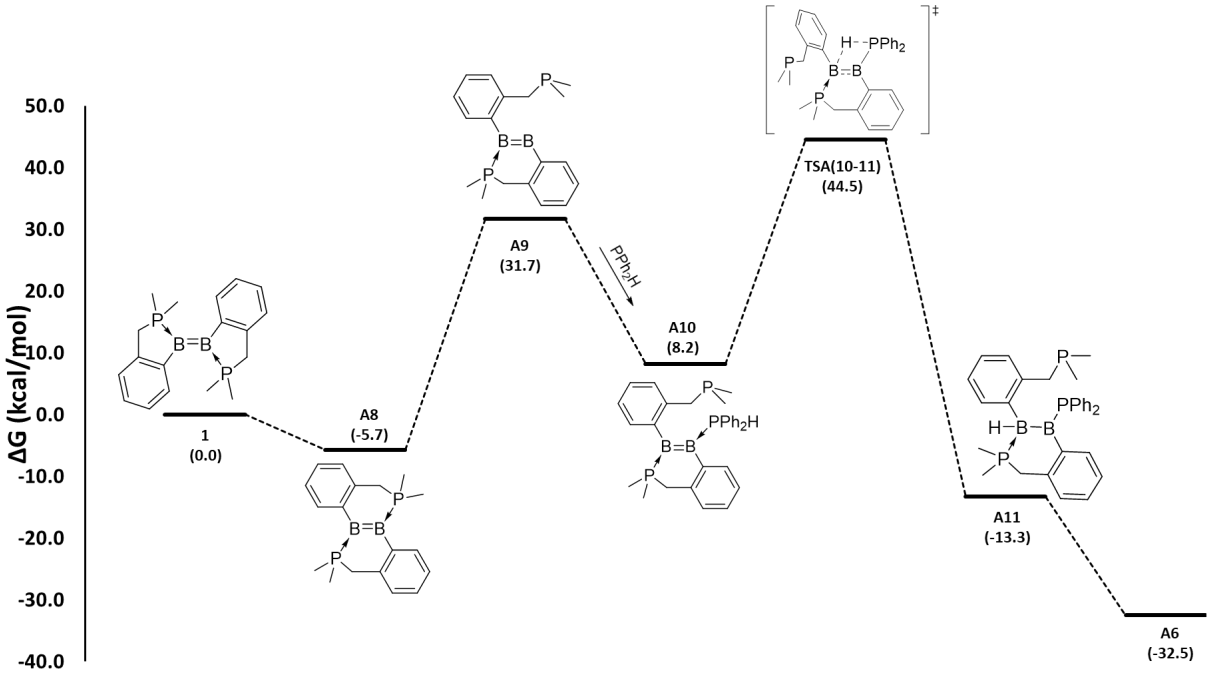
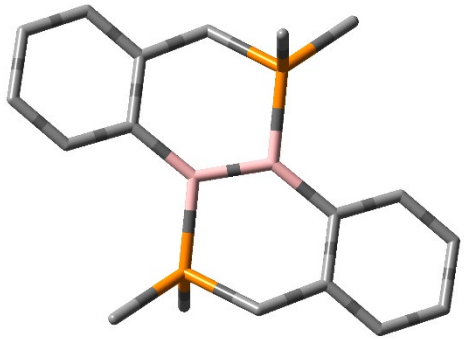


Figure S23. Computed mechanism 3 for 1,2-hydrophosphination of symmetrical diborene **A1**.

Note: Details of species **A1** and **A6** are provided above in Pathway 1 of reaction 1.

13) Intermediate **A8**



(Hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

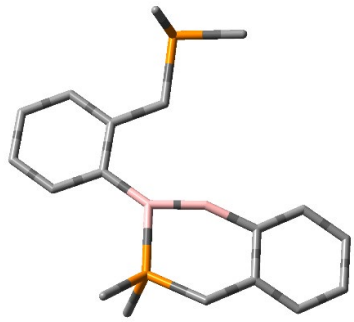
E_{total} = -1432.56900814 a.u

$G_{correction}$ = 0.33333 a.u

Cartesian coordinates:

B	-0.54578100	-0.57185400	-0.01483400
B	0.54577900	0.57184800	0.01485700
P	0.44919700	-2.18158500	-0.10297800
P	-0.44919500	2.18158200	0.10297200
C	2.11999600	0.51017300	0.05267200
C	2.94775600	1.59802200	-0.28267000
H	2.49026600	2.54040300	-0.56780100
C	4.33560900	1.51966600	-0.29247900
H	4.92463200	2.39146900	-0.56363200
C	4.96473100	0.32418400	0.03399700
H	6.04711400	0.24315700	0.02395600
C	4.18124400	-0.77565800	0.36844500
H	4.66182400	-1.71705100	0.62610900
C	2.00861800	-1.91609400	0.80865400
H	1.69981500	-1.81103000	1.85810300
H	2.62267100	-2.82030700	0.73315800
C	2.79023400	-0.69413500	0.38210700
C	0.96466000	-2.65829600	-1.79520900
H	1.50765900	-1.81513500	-2.22709000
C	-0.14947400	-3.76837300	0.60179900
H	-0.99538600	-4.14022400	0.01910200
C	-2.12000000	-0.51017600	-0.05265400
C	-2.94776500	-1.59801900	0.28269700
H	-2.49028000	-2.54039800	0.56783900
C	-4.33561800	-1.51965800	0.29250000
H	-4.92464500	-2.39145600	0.56366000
C	-4.96473500	-0.32417700	-0.03399100
H	-6.04711700	-0.24314700	-0.02395500
C	-4.18124300	0.77565800	-0.36844900
H	-4.66181800	1.71705000	-0.62612500
C	-2.79023300	0.69413100	-0.38210400
C	-2.00861200	1.91608200	-0.80866500
H	-2.62266300	2.82029700	-0.73318500
H	-1.69980400	1.81100200	-1.85811100
C	0.14948700	3.76835700	-0.60182600
H	0.99539800	4.14021200	-0.01913100
C	-0.96466400	2.65832000	1.79519400
H	-1.50766800	1.81516700	2.22708400
H	1.60491800	-3.54550400	-1.78818700
H	0.07689700	-2.85145700	-2.40192500
H	0.64516900	-4.51992100	0.58592800
H	-0.47687400	-3.61245700	1.63234100
H	0.47689100	3.61242400	-1.63236300
H	-0.64515300	4.51991000	-0.58596900
H	-0.07690300	2.85148700	2.40191100
H	-1.60491900	3.54553000	1.78815500

14) Intermediate **A9**



(Hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -1432.50633895 a.u

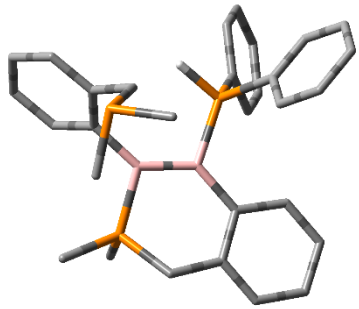
$G_{correction}$ = 0.32797 a.u

Cartesian coordinates:

B	0.12993600	0.83977200	-0.20527900
B	0.94961600	-0.43513100	-0.19456100
P	1.69802600	1.90510700	-0.18315600
P	-3.50055600	-2.21101900	0.23961900
C	2.21599800	-1.25860900	-0.06008600
C	2.35981100	-2.61981400	0.23760700
H	1.47729500	-3.24441900	0.33873600
C	3.62093600	-3.17677400	0.41657700
H	3.71564300	-4.23344500	0.64659200
C	4.76064500	-2.38477200	0.30922800
H	5.74416900	-2.81812900	0.45772600
C	4.63411200	-1.03039400	0.00597200
H	5.52328400	-0.41161000	-0.08769800
C	3.24267000	0.97796600	-0.62496000
H	3.26421300	1.01164900	-1.72201700
H	4.08604800	1.58253900	-0.27351200
C	3.37996800	-0.46429200	-0.18650300
C	2.01858300	2.71587900	1.42992200
H	2.23223700	1.93932200	2.16720400
C	1.81151800	3.30225200	-1.37100600
H	1.05100700	4.05060800	-1.13942300
C	-1.31483500	1.37331700	0.04037200
C	-1.63346700	2.74026100	0.06508500
H	-0.85198700	3.47409000	-0.11955200
C	-2.92027000	3.20268500	0.31286300
H	-3.12390600	4.26942500	0.32335600
C	-3.93977700	2.28816500	0.54443000
H	-4.95168200	2.62821000	0.74188400
C	-3.65656600	0.92567100	0.52333500
H	-4.45696300	0.21776600	0.72301400
C	-2.36778100	0.45193800	0.27555200
C	-2.06076200	-1.02984000	0.27716400

H	-1.46855400	-1.27160000	1.17176500
H	-1.41593100	-1.25891200	-0.58523000
H	2.85465000	3.41919000	1.37659200
H	1.11355300	3.24446800	1.73948700
H	2.79792800	3.77377900	-1.32735500
H	1.62845500	2.92428400	-2.37892600
C	-4.00507400	-1.99731300	-1.53106700
H	-4.76130500	-2.74156800	-1.79506400
H	-4.44409200	-1.00476100	-1.66249400
H	-3.15560300	-2.09465200	-2.21586200
C	-2.51928400	-3.77765100	0.09352500
H	-3.19270800	-4.61148400	-0.12287000
H	-1.76200200	-3.72355300	-0.69697700
H	-2.02211700	-3.98777900	1.04482600

15) Intermediate **A10**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2237.65942748 a.u

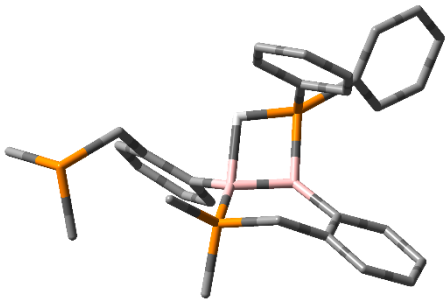
$G_{correction}$ = 0.51065 a.u

Cartesian coordinates:

B	-1.24565300	-0.67909800	-0.56130800
B	0.18502000	-0.81094700	0.08940500
P	-2.02351400	-2.40483300	-0.37945300
P	-3.37629700	2.38045900	1.63403700
C	0.85152900	-1.99842100	0.89097300
C	2.22207700	-2.03625100	1.21794300
H	2.85977100	-1.20016200	0.93828800
C	2.81372600	-3.09526100	1.89635200
H	3.87783400	-3.06926500	2.11294700
C	2.04251800	-4.18093900	2.29348200
H	2.48944400	-5.02182700	2.81407500
C	0.67859400	-4.16699400	2.01957600
H	0.05912300	-5.00039000	2.34445400
C	-1.42155600	-3.12367100	1.18202100
H	-1.88088100	-2.50492600	1.96632500
H	-1.81683900	-4.13933100	1.29259000
C	0.08466300	-3.10271300	1.34404900

C	-1.53862900	-3.60911400	-1.67170000
H	-0.44811900	-3.66665200	-1.68073000
C	-3.84394100	-2.55674000	-0.29842900
H	-4.27417400	-2.06788000	-1.17654200
C	-2.05165100	0.40650600	-1.39319000
C	-2.52226900	0.08150200	-2.68039800
H	-2.28400600	-0.89812500	-3.09123200
C	-3.25600600	0.96222600	-3.46424400
H	-3.59117400	0.66356300	-4.45344000
C	-3.54890400	2.23119200	-2.97441800
H	-4.12065600	2.93580800	-3.57053900
C	-3.10037400	2.58751800	-1.70978300
H	-3.33075400	3.57511700	-1.31679300
C	-2.36051500	1.70385300	-0.91473800
C	-1.93766700	2.16874000	0.46033400
H	-1.42775100	3.13800300	0.40168700
H	-1.24806900	1.44593800	0.90243300
H	-1.95966100	-4.59905600	-1.47295300
H	-1.88048900	-3.26031900	-2.64888000
H	-4.16232100	-3.60224900	-0.26877300
H	-4.20883600	-2.03976700	0.59170000
C	-3.93634900	0.61471400	1.70582300
H	-4.69531800	0.49471900	2.48401200
H	-4.38334500	0.35527300	0.74218800
H	-3.09855600	-0.06503600	1.89882500
C	-2.40993900	2.45459300	3.21782900
H	-3.09304900	2.44745400	4.07184000
H	-1.71357100	1.61392200	3.31285600
H	-1.83795300	3.38635900	3.25328500
P	1.24349200	0.68306300	-0.38477400
H	0.41881400	1.67138000	-0.94295000
C	2.09590400	1.55175000	0.99044600
C	3.24830500	2.32486700	0.83435900
C	1.52767200	1.41310400	2.26043100
C	3.81386200	2.96409900	1.93336600
H	3.71476400	2.42045500	-0.14089600
C	2.09057100	2.05879600	3.35545900
H	0.65192500	0.78092600	2.38366800
C	3.23369700	2.83594700	3.19235400
H	4.71279900	3.55879700	1.80606000
H	1.64139000	1.94521600	4.33674400
H	3.67886300	3.33380500	4.04801900
C	2.48993700	0.49895500	-1.70658600
C	2.84740900	1.59057000	-2.50483400
C	3.06553100	-0.74977500	-1.95299500
C	3.79322600	1.44270800	-3.51379800
H	2.38014900	2.55855400	-2.34343400
C	4.01429000	-0.89378200	-2.96021900
H	2.76280400	-1.60899400	-1.36284900
C	4.38224700	0.20105400	-3.73689800
H	4.06482500	2.29420900	-4.12943600
H	4.46211800	-1.86534400	-3.14200600
H	5.12108200	0.08552300	-4.52358200

16) **TSA(10-11)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*1044.8)

E_{total} = -2237.60341178 a.u

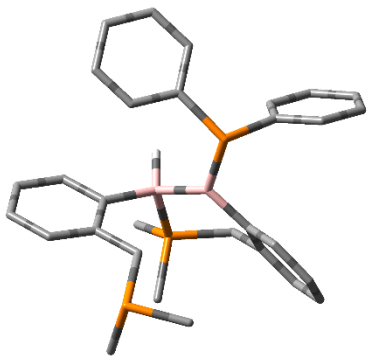
$G_{correction}$ = 0.508412 a.u

Cartesian coordinates:

B	-0.82391700	-0.13599600	-0.57550100
B	0.77135500	-0.15971600	-0.92889900
P	-1.26682100	-2.00189600	-0.40692400
P	-4.90583700	-0.07588400	1.12583900
C	1.68445100	-1.28949800	-1.50281800
C	2.76757900	-1.06112100	-2.36298300
H	3.02516200	-0.03849800	-2.62592900
C	3.51506700	-2.10891400	-2.89005400
H	4.34373000	-1.89982600	-3.56001000
C	3.19931200	-3.42297700	-2.55917400
H	3.77392200	-4.24739400	-2.96948500
C	2.14267400	-3.67523400	-1.68930900
H	1.90600600	-4.70020300	-1.41303500
C	0.30827000	-2.91489500	-0.14701700
H	0.64648400	-2.61612000	0.85474900
H	0.07755800	-3.98519400	-0.10731600
C	1.39317500	-2.62710900	-1.15816600
C	-1.82924000	1.04613800	-0.94415800
C	-1.55919200	1.74664400	-2.13537700
C	-2.23606100	2.90849900	-2.49660200
H	-1.98931600	3.41411300	-3.42540800
C	-3.20577500	3.42552500	-1.64956800
H	-3.72244700	4.34847800	-1.89493600
C	-3.50392600	2.75232500	-0.46941600
H	-4.23794600	3.17440100	0.21121200
C	-2.85800700	1.56421200	-0.11847200
C	-3.27586800	0.86784400	1.14879100
H	-3.38429700	1.58575800	1.97122300
H	-2.50248700	0.16097300	1.46462400
P	1.25055300	1.06984700	0.39735500
H	-0.26628900	1.01531800	0.66640000
H	-0.78672200	1.36109300	-2.79272000
C	2.82012900	2.05887500	0.28502600

C	3.63269600	2.40118200	1.37081400
C	3.14680600	2.54155600	-0.98469500
C	4.76127200	3.19182000	1.18102000
H	3.39139300	2.03410400	2.36432900
C	4.28132300	3.32282400	-1.17849100
H	2.49711500	2.30209200	-1.82519600
C	5.08988600	3.64967500	-0.09344300
H	5.39014000	3.44856600	2.02821200
H	4.53030000	3.68286300	-2.17207800
H	5.97378300	4.26287600	-0.23886100
C	1.59572500	-0.01127600	1.84997500
C	0.67340400	-0.13687100	2.89273600
C	2.73431500	-0.82331400	1.85650600
C	0.87699500	-1.05842300	3.91469700
H	-0.22169100	0.48024600	2.89273300
C	2.93950200	-1.74599700	2.87866700
H	3.45197400	-0.74803400	1.04471200
C	2.00978300	-1.86993800	3.90738800
H	0.15166700	-1.14093300	4.71858600
H	3.82209200	-2.37790800	2.86319400
H	2.16630400	-2.59499500	4.69989900
C	-1.98908200	-2.76982700	-1.90314500
H	-1.24381400	-2.68737500	-2.69865200
H	-2.22629600	-3.82471300	-1.73963900
H	-2.88570800	-2.22960100	-2.21143200
C	-2.24287700	-2.60070200	1.01913000
H	-1.74761300	-2.25912500	1.93244100
H	-3.26197900	-2.21129600	1.01719200
H	-2.27694600	-3.69360400	1.02083500
C	-6.14712800	1.29749700	1.04500600
H	-7.14847800	0.85823200	1.05959700
H	-6.05174900	1.94209300	1.92332500
H	-6.04415600	1.90416100	0.14115000
C	-5.03102200	-0.63225500	-0.63890600
H	-4.73564200	0.15136900	-1.34271500
H	-4.41494000	-1.51669900	-0.81443100
H	-6.06984900	-0.91526500	-0.83239200

17) Intermediate **A11**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2237.69875771 a.u

$G_{correction}$ = 0.511558 a.u

Cartesian coordinates:

B	-0.53358900	-0.21536400	-0.10526700
H	-0.27096100	1.27407000	1.70446700
B	0.45920500	0.50530400	1.08884900
C	-2.35967100	3.41036200	-0.65597600
H	-3.37284600	3.02444100	-0.60806100
C	-0.83555100	5.27063100	-0.42981600
H	-0.65599100	6.31808700	-0.20837600
P	0.66966600	-0.88337000	2.42046300
C	-2.12652400	4.75473400	-0.37917600
H	-2.96055400	5.40022000	-0.11984700
C	0.22247800	4.43464400	-0.77578800
H	1.23638400	4.81967200	-0.82003300
C	-0.01207600	3.09606300	-1.06457900
H	0.82604500	2.46237800	-1.33749500
C	-3.17056300	0.33313500	-0.73968100
C	-3.51514400	0.60067500	0.59381700
H	-2.83911100	1.18609000	1.21195000
C	-4.71284700	0.13518500	1.12479500
H	-4.96490400	0.35102000	2.15882700
C	-5.58232600	-0.61419700	0.33496500
H	-6.51378200	-0.98483200	0.75150300
C	-5.25306000	-0.88395100	-0.98876100
H	-5.92767300	-1.46451600	-1.61027900
C	-4.05671800	-0.40983600	-1.52238800
H	-3.80381700	-0.62352600	-2.55633000
C	1.89121300	1.17647500	0.76589300
C	2.32722600	2.25104000	1.55502100
H	1.67031100	2.61141300	2.34299100
C	3.54542800	2.88855700	1.34508500
H	3.84282000	3.72030200	1.97731100
C	4.37001500	2.45908300	0.31273600
H	5.32140600	2.94766200	0.12547100
C	3.96524400	1.39690100	-0.48929700
H	4.60646600	1.07673800	-1.30680800
C	2.30841300	-0.38103800	-1.19234100
H	1.76049100	-1.13680000	-0.62011200
C	2.74714400	0.74510800	-0.27436200
P	-1.51944000	0.78974400	-1.43042600
C	-1.30181700	2.55804600	-0.98697800
C	-0.86052200	-1.76153800	-0.15247900
C	-0.95031400	-2.44191900	-1.37760400
H	-0.83871800	-1.87817100	-2.29977200
C	-1.15592400	-3.81540300	-1.44549200
H	-1.20629300	-4.31050000	-2.41006700
C	-1.30664100	-4.54663400	-0.27276900
H	-1.47634200	-5.61807800	-0.31165700

C	-1.23340900	-3.89910600	0.95621800
H	-1.34939900	-4.47029900	1.87379400
C	-1.00629800	-2.52544200	1.02796700
C	-0.87833800	-1.86771700	2.38596500
H	-0.89365100	-2.60863600	3.19065700
H	-1.69664500	-1.15864900	2.56196500
C	0.89422800	-0.28908400	4.12828100
H	1.81331300	0.30174300	4.16792100
C	2.01174700	-2.08674200	2.15014400
H	1.78873800	-2.65955900	1.24704500
H	0.05775700	0.36334600	4.38874800
H	0.95750600	-1.11127400	4.84557100
H	2.94806200	-1.54427400	1.99752600
H	2.11367400	-2.77434100	2.99336400
H	1.59374800	0.00620200	-1.93387800
P	3.62834400	-1.26410900	-2.16921700
C	2.55911200	-2.62373700	-2.83586900
H	1.96368100	-3.11215900	-2.05634500
H	1.87570700	-2.21442900	-3.58551000
H	3.18488900	-3.37312200	-3.32837200
C	4.46669700	-2.17250400	-0.78735600
H	3.76305200	-2.76142900	-0.18945600
H	5.22836800	-2.84398800	-1.19275300
H	4.96444100	-1.44921500	-0.13522500

REACTION 2

Pathway 1 of reaction 2

As shown in Figure S24, pathway 1 involves (i) an initial coordination of PPh_2H to diborene **B1**, (ii) bromide shift from one boron to another through dissociation and association steps, and (iii) a 1,2-proton shift. Among other pathways computed (vide infra), this pathway was found to have an overall lower barrier. To understand the bromide shift step, we used a highly truncated model diborene **B1'** to locate the transition state for a direct shift of the bromide (Figure S25). Calculations showed a very high barrier for this direct shift. Therefore, the stepwise association and dissociation pathway as shown in Figure S24 was proposed. To ascertain if the bromide shift occurs first before all other steps, including PPh_2H coordination, a direct bromide shift through a single transition state was located. However, this step has a very high barrier (Figure S26). This finding also supports a stepwise dissociation and association path, as shown in Figure S24, for the bromide shift.

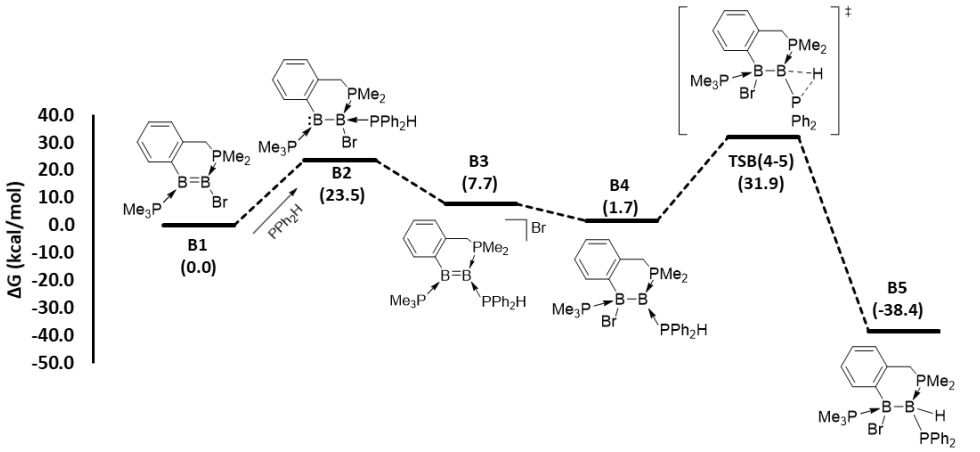
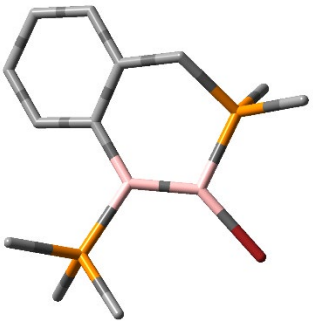


Figure S24. Computed mechanism 1 for 1,1-hydrophosphination of the unsymmetrical diborene **B1**. The transition state computed for phosphine association step (**B1** to **B2**) is not included in the free energy profile as the barrier for this step has an energy just above that of the higher energy intermediate ($\Delta G^{\ddagger}$ = 23.9 kcal/mol).

18) Diborene **B1**



Number of imaginary frequencies = 0

E_{total} = -3773.96205317 a.u

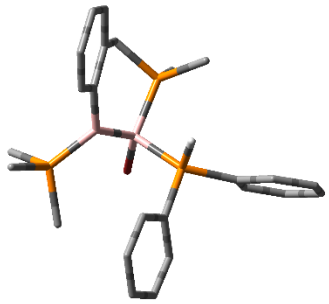
$G_{correction}$ = 0.263219 a.u

Cartesian coordinates:

B	1.01247900	-0.32331100	-0.01240800
B	-0.25426500	0.59056700	-0.09926100
P	0.51677200	-2.14005200	-0.09807900
P	0.01035700	2.47347400	-0.16469300
C	-1.75230300	0.06412400	-0.02757300
C	-2.80786900	0.84616000	0.48115200
H	-2.60118700	1.85607100	0.82830400
C	-4.11419000	0.38511400	0.60219000
H	-4.88216900	1.03929900	1.00549900
C	-4.42843900	-0.91319200	0.22185100
H	-5.43995600	-1.29460200	0.31751100
C	-3.41332700	-1.72496000	-0.27457400
H	-3.64231500	-2.74621900	-0.57166700
C	-1.07287500	-2.19672800	-0.98669300
H	-0.82249800	-1.88882500	-2.01067500
H	-1.44592900	-3.22555300	-1.02448200
C	-2.10698900	-1.25826300	-0.40384800
Br	2.96613200	-0.08394800	0.27845800

C	0.25922600	-3.00222900	1.49389300
H	-0.00218600	-4.05418600	1.34849200
H	1.17273300	-2.92837300	2.08836200
H	-0.54848900	-2.49226000	2.02386000
C	1.65063300	-3.21850800	-1.03560300
H	1.69834000	-2.86790500	-2.06899200
H	2.64945900	-3.12718300	-0.60187400
H	1.32793700	-4.26231900	-1.01342200
C	1.65025100	2.96485400	-0.78860100
H	2.42669600	2.57886600	-0.12720200
H	1.80265600	2.51863000	-1.77318600
H	1.71643800	4.05395900	-0.85802000
C	-1.13922600	3.35879700	-1.28353200
H	-2.17313100	3.15133900	-1.00288300
H	-0.96060200	4.43721400	-1.25884400
H	-0.98370300	2.98858800	-2.29953900
C	-0.12072600	3.39066500	1.41934600
H	-1.10803200	3.23885500	1.86051600
H	0.62624900	2.98881000	2.10791300
H	0.05203800	4.46136500	1.27618000

19) **TSB(1-2)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*21.25)

E_{total} = -4579.03978312 a.u

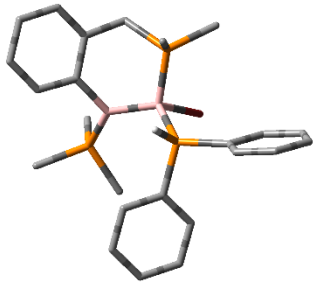
$G_{correction}$ = 0.447368 a.u

Cartesian coordinates:

B	-0.22749200	-0.48195600	0.69617000
P	-0.44434700	-2.42031700	0.57896000
B	-1.61261200	0.19811600	0.11916400
P	1.16405000	-0.01085200	-0.69018000
C	-2.85862300	-1.99158400	-0.61178000
C	-2.61093500	-0.59951700	-0.79863900
C	-3.67780000	-2.72075200	-1.47184100
H	-3.82920600	-3.78364200	-1.29074600
C	-3.29219600	-0.02198600	-1.89832300
H	-3.11677900	1.02922800	-2.11407900
C	-4.13939000	-0.73932300	-2.73093800
H	-4.63283100	-0.23625500	-3.55897700
C	-4.33246400	-2.10610700	-2.53416900

H	-4.97492800	-2.68136000	-3.19300500
C	-2.24319000	-2.68759600	0.57859600
H	-2.47008000	-3.75866900	0.60021400
H	-2.58938000	-2.22125900	1.51148300
Br	0.66213600	0.00074500	2.51461200
P	-2.17243100	1.76680900	0.92323300
H	0.66224300	-0.50905300	-1.90302300
C	2.90342200	-0.61922600	-0.79759700
C	3.58293100	-0.92179000	0.38741100
C	3.52050000	-0.87605300	-2.02701100
C	4.87045700	-1.45112900	0.33895700
H	3.09349200	-0.74738600	1.34279100
C	4.80268800	-1.41059400	-2.07163400
H	2.99824200	-0.65167300	-2.95375500
C	5.48014100	-1.69585100	-0.88718300
H	5.39373400	-1.67738100	1.26269200
H	5.27667700	-1.60214800	-3.02923300
H	6.48058700	-2.11534600	-0.92328100
C	1.29150000	1.76484000	-1.00061800
C	0.38315100	2.38557500	-1.86390300
C	2.24891900	2.52540900	-0.32746000
C	0.44646700	3.76395900	-2.05722900
H	-0.36872300	1.79165100	-2.37155300
C	2.29658800	3.90295600	-0.51191000
H	2.95151300	2.04221200	0.34501900
C	1.39743800	4.52083400	-1.37904300
H	-0.25227900	4.24554100	-2.73378400
H	3.03574500	4.49340400	0.01928100
H	1.44189200	5.59518000	-1.52802800
C	0.17508300	-3.26299000	-0.92081500
H	1.24659200	-3.08978100	-1.04860300
H	-0.01073500	-4.33752700	-0.84803200
H	-0.36692300	-2.86999000	-1.78437800
C	0.27636700	-3.33184300	1.98060000
H	-0.07632900	-2.88414200	2.91124000
H	0.00118800	-4.38837600	1.93905300
H	1.36375500	-3.22995000	1.94786600
C	-3.50357800	2.71119800	0.08381400
H	-3.88933500	3.49854100	0.73761400
H	-3.10955100	3.16055400	-0.83063400
H	-4.31531200	2.03108000	-0.18433400
C	-0.92474100	3.05091100	1.32602900
H	-0.60046000	3.55344400	0.41388300
H	-1.34344000	3.78505000	2.02082600
H	-0.06230400	2.56834400	1.78943400
C	-2.91809000	1.49538500	2.59593400
H	-3.23612300	2.42314700	3.08494700
H	-3.77271400	0.82200700	2.48967400
H	-2.15943100	0.99472400	3.20365500

20) Intermediate **B2**



Number of imaginary frequencies = 0

E_{total} = -4579.04003855 a.u

$G_{correction}$ = 0.446838 a.u

Cartesian coordinates:

B	-0.22173200	-0.47796300	0.54990800
P	-0.57520900	-2.37426900	0.29851300
B	-1.55937500	0.32151600	-0.00906200
P	1.20681900	-0.01225400	-0.72725700
C	-3.10158800	-1.76952200	-0.46983200
C	-2.74904200	-0.41428900	-0.73931300
C	-4.11421900	-2.42566200	-1.16788700
H	-4.33518900	-3.46557000	-0.93280500
C	-3.52937000	0.20621300	-1.74617400
H	-3.27947000	1.22539900	-2.03068500
C	-4.56574200	-0.43289800	-2.41131600
H	-5.12788700	0.10287100	-3.17227900
C	-4.86457100	-1.76664200	-2.13558400
H	-5.65904100	-2.28292100	-2.66492900
C	-2.36056700	-2.51758300	0.61357200
H	-2.66205000	-3.56803300	0.67655600
H	-2.50816700	-2.03667300	1.59059000
Br	0.60801300	-0.26036400	2.48463900
P	-1.98789200	1.89388400	0.86604100
H	0.75767800	-0.41840500	-1.99281700
C	2.89619500	-0.75622400	-0.76057400
C	3.47764500	-1.20880900	0.42840800
C	3.56586500	-0.95890200	-1.97263100
C	4.71973900	-1.83947900	0.40173200
H	2.95162300	-1.06863700	1.36947700
C	4.80289100	-1.59154100	-1.99566800
H	3.11966900	-0.61423200	-2.90240700
C	5.38170800	-2.03159500	-0.80643100
H	5.16740500	-2.18434000	1.32847900
H	5.31670900	-1.74159100	-2.93999400
H	6.34723400	-2.52706300	-0.82483100
C	1.50070900	1.75963100	-0.93414900
C	0.67221500	2.50756000	-1.77651500
C	2.52196700	2.38717400	-0.21943700
C	0.87138800	3.88044300	-1.89861600

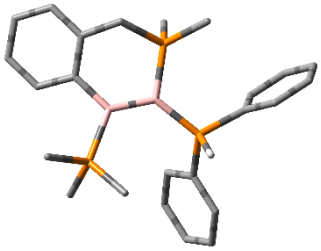
H	-0.13535500	2.01585100	-2.30748900
C	2.70669400	3.76101600	-0.33468600
H	3.16829600	1.80424900	0.42980700
C	1.88321800	4.50650400	-1.17553000
H	0.23170200	4.46182400	-2.55476100
H	3.49543500	4.24835000	0.22878800
H	2.03382700	5.57722500	-1.27075900
C	-0.30680400	-3.03883800	-1.38065100
H	0.75456300	-2.99988700	-1.63912100
H	-0.65193600	-4.07455900	-1.43109200
H	-0.88593800	-2.43837600	-2.08534500
C	0.32667400	-3.49954700	1.41096600
H	0.21032500	-3.14691500	2.43707600
H	-0.04517500	-4.52220800	1.31284100
H	1.39035800	-3.46691000	1.15992100
C	-3.15761400	3.06538400	0.06561700
H	-3.40991400	3.88387600	0.74636300
H	-2.70245700	3.47173600	-0.84065100
H	-4.07113600	2.53341000	-0.21007200
C	-0.62287800	2.98539000	1.41775000
H	-0.19951900	3.52218400	0.56830500
H	-0.99951000	3.70486800	2.15044000
H	0.15529600	2.37743900	1.88208000
C	-2.85415900	1.59228300	2.47442800
H	-3.11824400	2.51359500	3.00592700
H	-3.75902100	1.01194100	2.27407500
H	-2.18294200	0.98564600	3.08841300

21) Bromide ion

E_{total} = -2571.78580790 a.u

$G_{correction}$ = -0.016176 a.u

22) Intermediate **B3**



Number of imaginary frequencies = 0

E_{total} = -2007.13405071 a.u

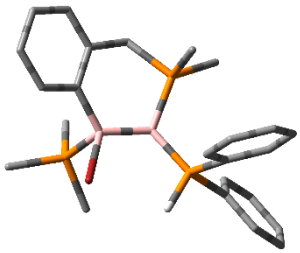
$G_{correction}$ = 0.450444 a.u

Cartesian coordinates:

B	-0.16185900	-0.43967900	-0.47174000
B	-1.58140200	0.24709300	-0.36157900
P	-0.30577700	-2.28018700	-0.10034900
P	-1.89784400	2.05835300	-1.01366200
C	-2.89131000	-0.48063900	0.16283000
C	-3.91984100	0.21014000	0.82499300
H	-3.83383900	1.28339000	0.97434800
C	-5.04849800	-0.42161900	1.33494300
H	-5.81297800	0.15652800	1.84373700
C	-5.18681100	-1.79595100	1.19148000
H	-6.06193100	-2.30630800	1.57901200
C	-4.18221200	-2.51647200	0.55414300
H	-4.28484300	-3.59281700	0.44557300
C	-1.99351800	-2.72960000	-0.62723500
H	-2.01129400	-2.58188300	-1.71414500
H	-2.16002100	-3.79326500	-0.43076400
C	-3.04829700	-1.88250400	0.04996900
C	-0.19996500	-2.77676700	1.65322100
H	-0.43361300	-3.83792000	1.77545800
H	0.80936900	-2.58714100	2.02522400
H	-0.91249800	-2.17937900	2.22590200
C	0.78392100	-3.45516000	-0.97225400
H	0.80045700	-3.22585900	-2.03962800
H	1.80054400	-3.38759100	-0.57972100
H	0.41476400	-4.47395600	-0.82809800
C	-0.63372200	2.65809900	-2.18138700
H	0.29363400	2.88391200	-1.65125900
H	-0.44669000	1.89727000	-2.94196300
H	-0.98677400	3.57218600	-2.66522900
C	-3.44637200	2.11504400	-1.97473200
H	-4.28821200	1.83242500	-1.34081800
H	-3.60898800	3.11503600	-2.38379600
H	-3.38033200	1.39446300	-2.79317700
C	-2.02129900	3.40540700	0.21432300
H	-2.80795000	3.19778900	0.94120100
H	-1.06854900	3.49271400	0.74173600
H	-2.24066600	4.35032900	-0.28976900
P	1.52327300	0.31916500	-0.71881400
H	1.87421200	0.75281700	-2.01743500
C	2.89025300	-0.81913900	-0.36329200
C	3.14843200	-1.18642500	0.96100600
C	3.62413800	-1.39245200	-1.40302500
C	4.12081100	-2.14051000	1.23786400
H	2.59779600	-0.72018000	1.77379000
C	4.59779000	-2.34648500	-1.12070000
H	3.43381800	-1.10680100	-2.43363900
C	4.84031700	-2.72499100	0.19669600
H	4.32409900	-2.42148500	2.26563900
H	5.16602800	-2.79274900	-1.92955300
H	5.59870400	-3.46906000	0.41513300
C	1.84221400	1.83340300	0.24039400

C	2.79977000	2.75194700	-0.20212700
C	1.16805000	2.05196500	1.44353800
C	3.07334200	3.88650300	0.55219200
H	3.32970900	2.58447500	-1.13618200
C	1.45390100	3.18538100	2.20118500
H	0.41357300	1.34002000	1.76776800
C	2.40180900	4.10175000	1.75448500
H	3.81050500	4.60229200	0.20510100
H	0.93628200	3.35166600	3.14017400
H	2.61976900	4.98650200	2.34328600

23) Intermediate **B4**



Number of imaginary frequencies = 0

E_{total} = -4579.07596733 a.u

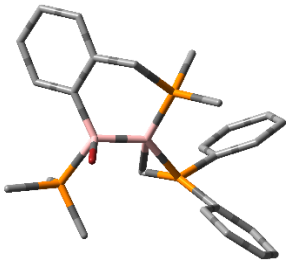
$G_{correction}$ = 0.445525 a.u

Cartesian coordinates:

Br	-1.35042100	-0.25860600	2.44454400
B	0.03595500	-0.24712700	-0.45549400
P	-0.05946000	0.91454500	-1.85806300
B	-1.47520100	-0.40512500	0.32211100
P	1.57925300	-0.22376100	0.50078100
P	-1.98182200	-2.31118200	0.21345900
C	-2.82747400	0.89689000	-1.57736100
C	-2.74185500	0.44373300	-0.23917400
C	-3.95397100	1.60042600	-2.01643500
H	-3.99264300	1.94615200	-3.04696100
C	-3.83101000	0.74850700	0.59506900
H	-3.77817200	0.44732000	1.63665600
C	-4.95210000	1.43948100	0.15204500
H	-5.76434300	1.65109500	0.84141300
C	2.29804600	1.43508800	0.85807100
C	-5.01945000	1.86871900	-1.16787300
H	-5.88357600	2.41592600	-1.53206400
C	-1.72064300	0.67276900	-2.59058300
H	-1.84783600	1.34725200	-3.44401300
H	-1.73076900	-0.35174400	-2.97851500
C	3.03892800	-1.19351200	-0.06868200
C	0.01277700	2.73991700	-1.58943300
H	0.99502300	3.01038500	-1.19235900
C	1.11826600	0.70893600	-3.25068300
H	0.96094000	1.45958900	-4.03091200

C	1.54346700	2.27258400	1.68992800
H	0.64762600	1.88255000	2.16867700
C	3.41128400	1.95131300	0.19312500
H	4.00454600	1.31209600	-0.45451200
C	2.93512800	-1.93442100	-1.24411300
H	1.98825200	-1.90933800	-1.78153000
C	-3.51248200	-2.81228000	1.07981200
H	-3.39926100	-2.55615300	2.13573500
H	-3.71601300	-3.88075600	0.97321600
H	-4.34802900	-2.23561500	0.67497800
C	-0.68543300	-3.41102300	0.86204300
H	0.22773700	-3.23409500	0.28901600
H	-0.97821600	-4.46103300	0.79014800
H	-0.50401500	-3.14010100	1.90471200
C	-2.23334200	-2.82379800	-1.51723900
H	-1.31583100	-2.58606800	-2.06128300
H	-3.06237300	-2.25035300	-1.94072800
H	-2.45037800	-3.89167700	-1.59609600
C	4.22980600	-1.23068200	0.66431000
H	4.32112600	-0.65281900	1.58036300
C	3.76926800	3.28922200	0.35799200
H	4.63278500	3.68532900	-0.16755900
C	4.01215500	-2.69415700	-1.69531900
H	3.92617000	-3.26348200	-2.61579000
C	5.30205800	-1.99477300	0.21943300
H	6.22359600	-2.02169300	0.79257300
C	1.91566500	3.59788100	1.86788100
H	1.32918100	4.23814400	2.51914100
C	5.19493900	-2.72447700	-0.96402500
H	6.03443000	-3.31877600	-1.31147200
C	3.02499000	4.11181500	1.19599900
H	3.30359200	5.15301000	1.32503600
H	-0.74202200	2.99961300	-0.84386600
H	-0.17470100	3.29787000	-2.51255600
H	2.13728800	0.80671400	-2.86450300
H	1.00816700	-0.29253600	-3.67226400
H	1.36500800	-0.73731100	1.79177400

24) **TSB(4-5)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*809.69)

E_{total} = -4579.02417330 a.u

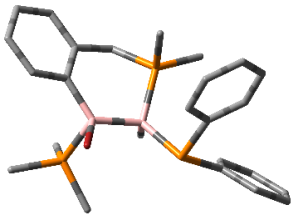
$G_{correction}$ = 0.444549 a.u

Cartesian coordinates:

B	0.01420700	0.18155600	0.00324700
B	1.62775600	-0.28687700	0.29932300
P	-0.04743000	0.99566800	-1.71271200
C	2.73771300	0.79321100	-0.16031100
C	3.74680300	1.27868300	0.68067200
H	3.85749200	0.87241600	1.68162800
C	4.63290200	2.28487000	0.30452100
H	5.39352600	2.62452100	1.00117900
C	4.53583200	2.84846800	-0.95908400
H	5.21687600	3.63394000	-1.27073500
C	3.54945000	2.38987100	-1.82618500
H	3.46555200	2.82377100	-2.81969000
C	1.62657000	0.92300400	-2.44884300
H	1.79598900	-0.12776200	-2.70736900
H	1.65835600	1.52269100	-3.36377000
C	2.66635100	1.37977500	-1.44896200
P	-1.55923200	-0.09851000	0.89901700
H	-0.65979000	0.43767300	1.96742200
C	-2.68198000	1.36171300	1.03183400
C	-3.61898500	1.65679500	0.03326400
C	-2.53989400	2.27281500	2.08413800
C	-4.38415000	2.81897400	0.08454200
H	-3.75957200	0.96460700	-0.79145500
C	-3.30370700	3.43245300	2.14132200
H	-1.80846800	2.07267800	2.86338300
C	-4.22911600	3.71354600	1.13843100
H	-5.10289400	3.02480100	-0.70306700
H	-3.17674700	4.12121400	2.97122500
H	-4.82270700	4.62132300	1.17989200
C	-2.69849300	-1.34356300	0.03624500
C	-4.06760200	-1.52572300	0.26778900
C	-2.02652300	-2.25678400	-0.78009800
C	-4.75553500	-2.56295700	-0.35244600
H	-4.60296000	-0.84128100	0.92104000
C	-2.71808400	-3.28391100	-1.41763200
H	-0.94492500	-2.16701800	-0.89403500
C	-4.08471800	-3.43891100	-1.20633100
H	-5.81994600	-2.68872200	-0.17556000
H	-2.18376700	-3.97566800	-2.06259300
H	-4.62377700	-4.24843900	-1.68911100
C	-1.19043100	0.29024200	-2.94960400
H	-0.89610600	-0.74102800	-3.15306900
H	-2.20028400	0.27463900	-2.53403000
H	-1.18019300	0.87317700	-3.87478000
C	-0.46072200	2.77405700	-1.64852800
H	-1.43496200	2.90033700	-1.17028400
H	0.29565000	3.27446400	-1.03976300
H	-0.47661200	3.21567600	-2.64906400

Br	1.97181200	-2.08294600	-0.89129100
P	1.94164800	-1.12919500	2.04981100
C	1.81143200	-0.02663100	3.50175500
H	1.97969800	-0.58944000	4.42368100
H	2.54355100	0.77963100	3.43205200
H	0.81429500	0.41711600	3.52066900
C	0.74646800	-2.46384900	2.36388800
H	1.02585200	-3.02153500	3.26140500
H	-0.25164000	-2.03636500	2.47888900
H	0.74476100	-3.11990800	1.49148400
C	3.57380000	-1.93283600	2.21798900
H	4.37079300	-1.18805100	2.20013300
H	3.62497800	-2.49960600	3.15104400
H	3.70567300	-2.59943800	1.36364300

25) Product **B5**



Number of imaginary frequencies = 0

E_{total} = -4579.14323545 a.u

$G_{correction}$ = 0.448595 a.u

Cartesian coordinates:

Br	1.53113600	0.01345600	-2.35830000
B	-0.15123900	-0.49296700	0.35046200
H	-0.24872700	-1.49159400	1.04915300
P	-0.15062300	0.84534600	1.71632000
B	1.48775400	-0.40414500	-0.31786100
P	-1.65841300	-0.51196100	-0.92683000
P	2.07927900	-2.27646000	-0.36943200
C	2.60239700	0.72539300	1.83722300
C	2.66684000	0.41025100	0.45977200
C	3.67037600	1.36462000	2.47436100
H	3.58849100	1.60400900	3.53198200
C	3.83872800	0.79575600	-0.21359200
H	3.89879000	0.61260900	-1.28203700
C	4.90379200	1.41994900	0.42400600
H	5.78837700	1.69481900	-0.14290400
C	-2.15344800	1.27454400	-1.00298800
C	4.82566400	1.70219600	1.78288000
H	5.64582700	2.19507300	2.29560100
C	1.36378800	0.44494900	2.66662300
H	1.38988000	1.01596100	3.60049100
H	1.27765100	-0.61579700	2.93187100
C	-3.10612500	-1.22861800	-0.02254500

C	0.04953900	2.58821400	1.22815200
H	-0.90313700	2.98431200	0.87120100
C	-1.51284200	0.85139400	2.92928300
H	-1.35523600	1.61723300	3.69358500
C	-1.39431100	2.13157300	-1.81341400
H	-0.55630300	1.73050600	-2.37415700
C	-3.21252600	1.83288000	-0.27460400
H	-3.83426100	1.19632200	0.34769900
C	-3.04653900	-1.85183800	1.22778400
H	-2.10230800	-1.89282700	1.75905100
C	3.66764000	-2.55375800	-1.22116700
H	3.58916300	-2.12940500	-2.22436100
H	3.90654000	-3.61828100	-1.27986200
H	4.45812200	-2.02584400	-0.68234000
C	0.87528600	-3.35069900	-1.20717000
H	-0.05419000	-3.36254600	-0.63408900
H	1.25848600	-4.36735800	-1.32099800
H	0.66613300	-2.90971900	-2.18463400
C	2.32645400	-2.97279500	1.29842000
H	1.37126400	-2.98489800	1.82696000
H	3.02744400	-2.33400800	1.84275000
H	2.72610000	-3.98825500	1.24585400
C	-4.34540400	-1.22143900	-0.68385800
H	-4.41896300	-0.75805300	-1.66438000
C	-3.49193800	3.19645400	-0.33947900
H	-4.31991300	3.60154700	0.23530800
C	-4.17657800	-2.43144400	1.80300000
H	-4.09785300	-2.91077900	2.77472800
C	-5.47832800	-1.78061000	-0.10693200
H	-6.42514100	-1.74887200	-0.63774700
C	-1.66868800	3.49345900	-1.87300300
H	-1.05689200	4.13391800	-2.50133900
C	-5.39862200	-2.39179900	1.14326300
H	-6.28043000	-2.83754300	1.59290500
C	-2.71792400	4.03573700	-1.13517400
H	-2.93354100	5.09849400	-1.18593600
H	0.78082200	2.64925900	0.42057200
H	0.40093700	3.17680700	2.08016300
H	-2.44904500	1.04853700	2.40242700
H	-1.58744700	-0.12910500	3.40408900

Bromide shift path for reaction 2 using a highly truncated system

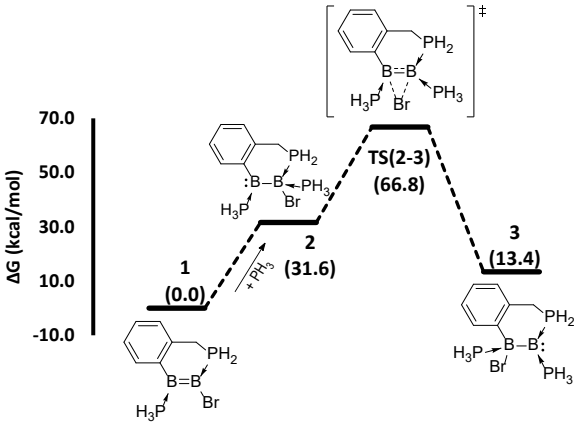
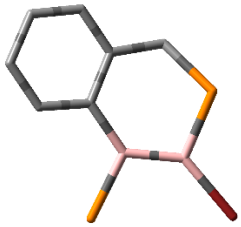


Figure S25. Computed direct bromide shift route using the highly truncated unsymmetrical diborene **B1'**.

26) Diborene **B1'**



(Hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -3577.35935509 a.u

$G_{correction}$ = 0.126327 a.u

Cartesian coordinates:

C	-3.89287000	1.17706500	-0.36114400
C	-2.53313000	1.43128000	-0.22686800
C	-1.59147200	0.42538700	0.05188600
C	-2.10765700	-0.88387500	0.20301000
C	-3.46967100	-1.14108500	0.06415300
C	-4.37088400	-0.11999300	-0.21951200
H	-4.57723900	1.99048700	-0.58332400
H	-2.19201800	2.45638800	-0.36418900
C	-1.20986600	-2.03691400	0.60350900
H	-3.83586500	-2.15810500	0.18568200
H	-5.42831800	-0.33700600	-0.32952000
H	-1.00704200	-1.98017300	1.68108900
B	-0.04399800	0.71184400	0.13563200
B	1.16431300	-0.27328000	0.01613200
H	-1.68738600	-3.00053000	0.40713200
P	0.45763100	-2.01802200	-0.14619200
Br	3.11589400	-0.09187000	-0.11966000
P	0.55941200	2.50468500	0.26207200

H	1.95869100	2.56253800	0.30866300
H	0.19964100	3.29986100	1.37356200
H	0.27665500	3.45046900	-0.75108200
H	1.10634100	-3.08472000	0.50734400
H	0.32633700	-2.58769400	-1.43447300

27) Phosphine **PH_3**

Number of imaginary frequencies = 0

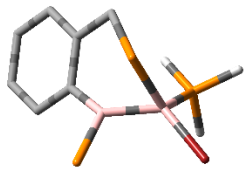
E_{total} = -343.12012242 a.u

$G_{correction}$ = 0.004296 a.u

Cartesian coordinates:

P	0.00000000	0.00000000	0.12695900
H	0.00000000	1.19545600	-0.63479400
H	-1.03529600	-0.59772800	-0.63479400
H	1.03529600	-0.59772800	-0.63479400

28) Intermediate **B2'**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -3920.45078609 a.u

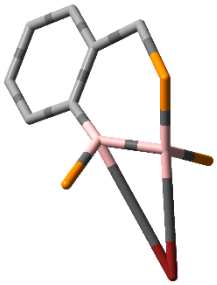
$G_{correction}$ = 0.151508 a.u

Cartesian coordinates:

C	-3.82365500	0.90577800	1.22391300
C	-2.47485300	1.20673500	1.06821300
C	-1.66237200	0.48973200	0.17923800
C	-2.24854400	-0.56680700	-0.55761700
C	-3.60490900	-0.85699200	-0.39969800
C	-4.39232300	-0.13199200	0.48954200
H	-4.43148100	1.47772900	1.91906900
H	-2.04375100	2.01250700	1.65942500
C	-1.37443800	-1.29920200	-1.53273400
H	-4.04943100	-1.66063000	-0.98221200
H	-5.44398400	-0.37428400	0.60917000
H	-1.16769300	-2.33519300	-1.22705200

B	-0.14483400	0.73215000	-0.12944100
B	1.05442500	-0.46411500	0.00478000
H	-1.85578400	-1.37230900	-2.51558500
P	0.34778300	-0.40508200	-1.80440000
Br	2.97953800	-0.04569900	0.38938400
P	0.57672000	2.46165700	-0.28358600
P	0.54245000	-1.88139300	1.17719800
H	0.78509400	-1.58787100	2.52608800
H	-0.82415400	-2.19461200	1.17429400
H	1.15169600	-3.14460500	1.06266100
H	0.54244000	-1.20153700	-2.99672200
H	1.46859500	0.45862300	-2.21766300
H	1.50648000	2.51643800	-1.34194800
H	1.33932800	3.05625000	0.74150300
H	-0.32688800	3.49754900	-0.57949700

29) **TSB(2'-3')**



(Hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*70.0)

E_{total} = -3920.38580015 a.u

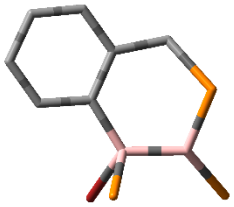
$G_{correction}$ = 0.151778 a.u

Cartesian coordinates:

C	-3.14540800	-2.40535400	-0.09640500
C	-1.90718500	-1.96925200	0.35274000
C	-1.54118700	-0.61528600	0.31702700
C	-2.48545900	0.32443500	-0.18786200
C	-3.73616500	-0.12922300	-0.61738700
C	-4.06516800	-1.47838600	-0.58102000
H	-3.39502200	-3.46134500	-0.06875900
H	-1.19007200	-2.69388500	0.72791000
C	-2.23291400	1.83372200	-0.26980400
H	-4.46364300	0.58686200	-0.99168800
H	-5.03932300	-1.80582500	-0.93067200
H	-2.27256900	2.16127400	-1.31625400
B	-0.22776100	0.03551900	0.82493600
B	0.70819700	1.06472700	-0.01521100
H	-3.02111500	2.38848500	0.25406400
P	-0.54639300	2.34407700	0.36214900
Br	3.14838500	-0.73625100	-0.35733800

P	0.74052300	-0.06293700	2.43514700
P	0.90257000	0.54507100	-1.83933300
H	0.74881800	-0.81442100	-2.10442100
H	-0.09657400	1.09860200	-2.69458800
H	2.05115200	0.96345000	-2.50849700
H	-0.52319500	3.70046300	-0.10199800
H	-0.67632100	2.51999700	1.74835900
H	1.29193800	1.21188100	2.66018000
H	1.90824900	-0.82302700	2.19961300
H	0.31242300	-0.52207200	3.71179200

30) Intermediate **B3'**



(Hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -3920.47882293 a.u

$G_{correction}$ = 0.150963 a.u

Cartesian coordinates:

C	-3.40801400	-1.41952900	0.09752300
C	-2.02282400	-1.38993300	0.17849500
C	-1.27160700	-0.21924900	-0.01567800
C	-1.98706100	0.95425800	-0.33868700
C	-3.38482800	0.92336500	-0.40970300
C	-4.09784700	-0.24667700	-0.18946800
H	-3.94420600	-2.35053400	0.25399800
H	-1.48922300	-2.31596000	0.38191400
C	-1.32460400	2.27544400	-0.70444900
H	-3.92213400	1.83683400	-0.65323400
H	-5.18172700	-0.24247400	-0.25163500
H	-1.02540800	2.25242600	-1.75835600
B	0.32780600	-0.27737100	0.18116100
B	1.24463800	1.12675600	0.23594400
H	-2.03183900	3.10083600	-0.57394200
P	0.21735000	2.61422600	0.22728000
Br	1.22499800	-1.81262300	-0.86310900
P	0.66368300	-0.92335000	2.10730000
P	2.98368000	1.23230800	-0.25997900
H	3.40277700	0.58447600	-1.44725600
H	3.44298000	2.54812700	-0.46639800
H	4.05115900	0.76305200	0.56096000
H	0.75093900	3.78935000	-0.34846000
H	-0.32799300	3.20799200	1.40819700
H	0.22834100	0.00138500	3.07185700

H	2.04079000	-0.95999300	2.36714300
H	0.27841700	-2.13446800	2.75128300

Pathway involving the bromide shift before PPh_2H coordination for the reaction 2

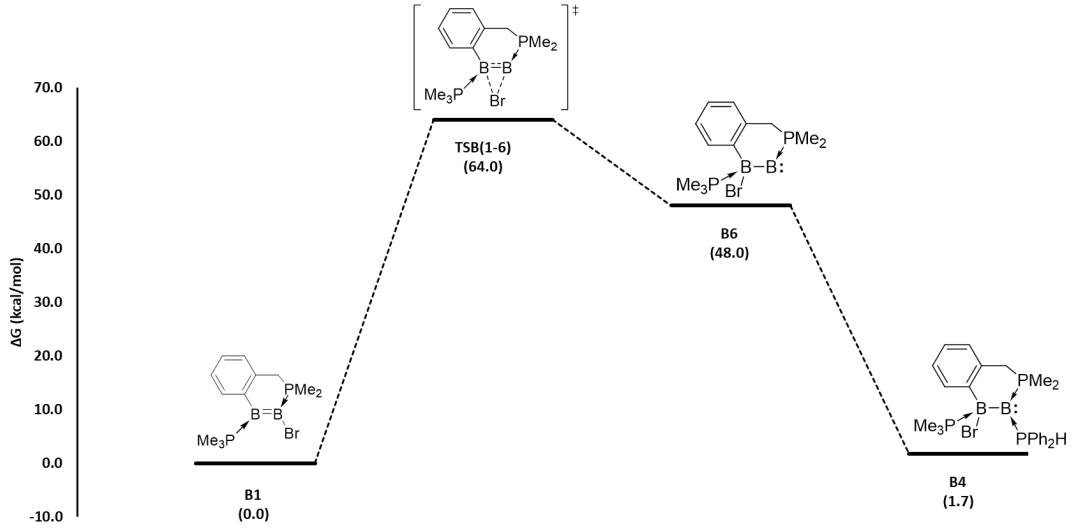
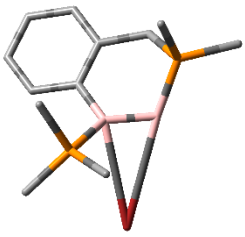


Figure S26. Computed direct bromide shift step as a first step prior to coordination of PPh_2H and all other steps using diborene **B1**.

<u>Note:</u> Details of species **B1** and **B4** are provided above in pathway 1 of reaction 2.

31) **TSB(1-6)**



(Hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*59.8)

E_{total} = -3773.84461821 a.u

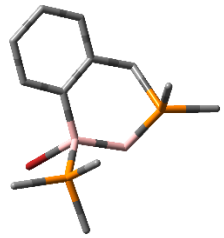
$G_{correction}$ = 0.263401 a.u

Cartesian coordinates:

C	-1.79176600	-3.42766400	-0.64886000
C	-0.77507700	-2.49635600	-0.47925100
C	-1.01419900	-1.11224800	-0.44508800
C	-2.35306900	-0.68884600	-0.63526100
C	-3.37309800	-1.62896800	-0.78938900
C	-3.10427800	-2.99260400	-0.78991300
H	-1.56067900	-4.48804300	-0.66935200
H	0.24561100	-2.85458100	-0.38552000

C	-2.74215900	0.76781000	-0.78992600
H	-4.39675300	-1.28795300	-0.92368800
H	-3.91267000	-3.70657800	-0.90959000
H	-2.62628800	1.05939000	-1.84071600
B	0.13368600	-0.07313100	-0.10452800
B	-0.17094700	1.41051400	-0.49250100
H	-3.79443400	0.92257700	-0.52578400
P	-1.77173000	2.03171400	0.14685700
C	-2.30966200	1.92732600	1.90349100
H	-1.66280700	2.54563400	2.53080200
H	-3.34478500	2.25985900	2.02688200
H	-2.21760300	0.88471900	2.21542900
C	-2.44636800	3.63856500	-0.40366800
H	-1.93630000	4.45027700	0.12154500
H	-2.25671600	3.74753200	-1.47301100
H	-3.51945600	3.70809400	-0.20407300
Br	2.99638700	0.63003600	-1.38118300
P	1.46475100	-0.59041200	1.19288400
C	0.50228500	-1.27416900	2.60210500
H	1.16937600	-1.56276400	3.41855100
H	-0.20086700	-0.52117700	2.96627200
H	-0.06580200	-2.14661800	2.27184600
C	2.68900200	-1.90011000	0.86483900
H	3.31966800	-2.02130500	1.75026900
H	2.18281900	-2.84550400	0.65854100
H	3.27829100	-1.57749900	0.00370900
C	2.33718700	0.82009600	1.93843400
H	2.95752300	0.47175900	2.76845600
H	2.94659800	1.27177800	1.15181200
H	1.59990800	1.53572700	2.31298500

32) Intermediate **B6**



(Hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -3773.87518544 a.u

$G_{correction}$ = 0.262945 a.u

Cartesian coordinates:

C	0.34128700	3.40297200	0.96560400
C	-0.34947400	2.26522100	0.56302800
C	0.28417100	1.18559000	-0.06858600
C	1.65880600	1.32797000	-0.35299600

C	2.35283500	2.47198700	0.04616600
C	1.70530400	3.50392800	0.71582500
H	-0.18514300	4.21328400	1.46125300
H	-1.42486000	2.22143500	0.71259400
C	2.39287400	0.26127500	-1.13684700
H	3.41283100	2.56069800	-0.17872400
H	2.25897700	4.38548700	1.02369300
H	2.01107400	0.20953100	-2.16275200
B	-0.52402600	-0.17219200	-0.43721500
B	0.40571500	-1.41127900	-1.17041200
H	3.46809400	0.45789600	-1.19333600
P	2.13684100	-1.40881200	-0.37602600
C	2.90635300	-1.12805900	1.30347000
H	2.81715900	-2.02883100	1.91670400
H	3.96802400	-0.87699600	1.20933600
H	2.38955600	-0.30312100	1.79733600
C	3.35817800	-2.56807500	-1.10058100
H	3.27530100	-3.54107000	-0.60726100
H	3.12599700	-2.69579400	-2.15834100
H	4.38036100	-2.19880400	-0.97617600
Br	-2.22769000	0.32308600	-1.58337900
P	-1.45016300	-0.93990600	1.11382400
C	-0.37592500	-1.33354300	2.53524900
H	-0.96338700	-1.73070200	3.36678800
H	0.37452200	-2.06808100	2.23944900
H	0.13470800	-0.42207900	2.85536400
C	-2.80753900	0.03509400	1.84811100
H	-3.39736700	-0.58027700	2.53236900
H	-2.39254000	0.88696800	2.39103600
H	-3.43458200	0.40216600	1.03288900
C	-2.21324400	-2.51845300	0.62013600
H	-2.78999000	-2.96122700	1.43557400
H	-2.85792800	-2.31370900	-0.23762700
H	-1.43202300	-3.21210100	0.29778000

Pathway 2 of reaction 2

Figure S27 shows the computed free energy profile for the conceived mechanism 2 for 1,1-hydrophosphination of diborene **B1**. This mechanism involves (i) an initial PPh_2H coordination, (ii) dissociation of bromide (no bromide shift), (iii) 1,2-proton shift, and (iv) association of the dissociated bromide to the other boron. The overall barrier of this mechanism was found to be 6.2 kcal/mol higher in energy than that of mechanism 1.

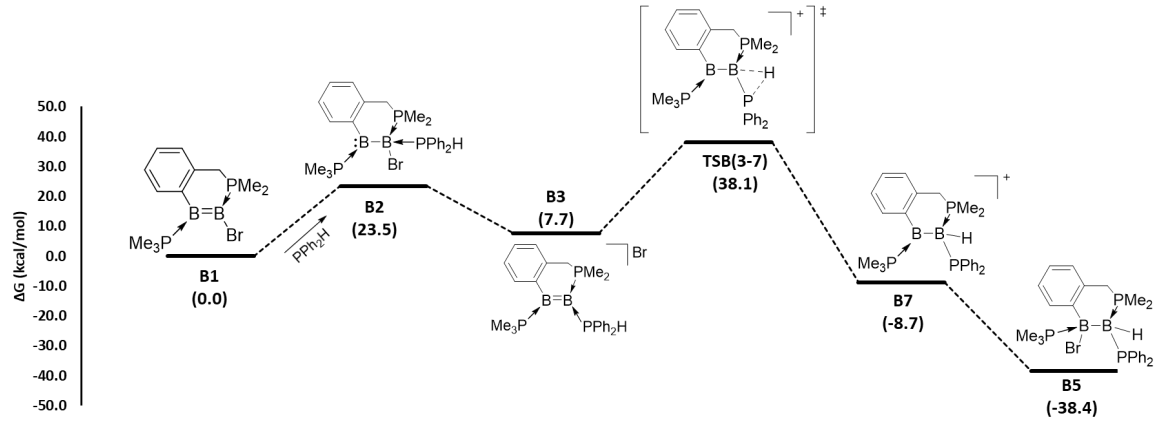
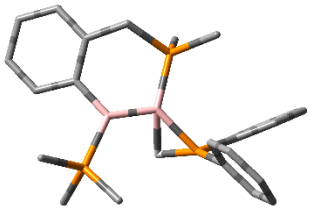


Figure S27. Computed mechanism 2 for 1,1-hydrophosphination of the unsymmetrical diborene **B1**.

Note: Details of species **B1-B3**, **B7** are provided above in pathway 1 of reaction 2.

33) **TSB(3-7)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*1174.8)

E_{total} = -2007.07200715 a.u

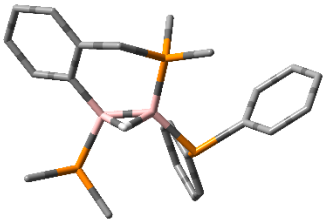
$G_{correction}$ = 0.444420 a.u

Cartesian coordinates:

B	0.24525700	-0.13114800	0.09850300
B	1.65731300	0.54335300	-0.22593400
P	0.45641100	-1.70837300	1.13594400
P	1.79543500	2.31980700	-1.03822600
C	3.04492600	-0.14491700	0.12124100
C	4.20054600	0.09586100	-0.64185600
H	4.16152800	0.80166900	-1.46632700
C	5.40983800	-0.55005500	-0.41454900
H	6.27057700	-0.32903800	-1.03695200
C	5.50344000	-1.48097100	0.61078900
H	6.43808700	-1.99527600	0.80651800
C	4.38059200	-1.75453500	1.38428700
H	4.45157400	-2.48609300	2.18449100
C	2.00447000	-1.45751300	2.06412200
H	1.79724900	-0.63800400	2.76372800
H	2.22869200	-2.34845700	2.65867900
C	3.16718900	-1.10749000	1.15566100
P	-1.43360700	0.33508800	-0.65538700

H	-0.16156000	0.21572100	-1.50486100
C	-2.35255100	-1.18264700	-1.04926900
C	-3.41305900	-1.61407400	-0.24553500
C	-1.95714800	-1.96642800	-2.13920400
C	-4.05537500	-2.81845000	-0.51990000
H	-3.74313400	-1.00667900	0.59213000
C	-2.59421700	-3.17431600	-2.40220000
H	-1.14753300	-1.63403400	-2.78302700
C	-3.64342800	-3.60380000	-1.59224800
H	-4.87953800	-3.14176100	0.10731300
H	-2.27986400	-3.77430100	-3.24978500
H	-4.14397800	-4.54259300	-1.80330300
C	-2.50330700	1.43217600	0.33693400
C	-3.77013900	1.81246600	-0.11845500
C	-2.02042500	1.92294100	1.55050100
C	-4.55446500	2.65930500	0.65593000
H	-4.14866300	1.43446000	-1.06385000
C	-2.80832300	2.77416400	2.31946500
H	-1.02283900	1.63887400	1.88202000
C	-4.07459300	3.14156600	1.87274000
H	-5.54075200	2.94736000	0.30775600
H	-2.43384300	3.15234200	3.26513000
H	-4.68859300	3.80633300	2.47090300
C	0.28556500	3.32752100	-0.91503100
H	-0.51342300	2.87923500	-1.50956900
H	-0.04890800	3.38176200	0.12253800
H	0.48847400	4.33538800	-1.28694600
C	2.18776800	2.34199500	-2.82250700
H	3.13081200	1.83267700	-3.02480300
H	1.39177600	1.82626300	-3.36507900
H	2.25388400	3.37310500	-3.17923300
C	3.07742100	3.31918200	-0.21434200
H	3.14168500	4.30635500	-0.67851800
H	2.81579500	3.43438600	0.83999000
H	4.04556400	2.82087000	-0.27503600
C	-0.85714400	-1.99384200	2.36159200
H	-1.03685200	-1.07556200	2.92474000
H	-1.77584500	-2.26947600	1.83823300
H	-0.57939000	-2.79654700	3.04902000
C	0.63207500	-3.26186000	0.20580200
H	-0.28262600	-3.44422300	-0.36368400
H	1.47039700	-3.16187100	-0.48702200
H	0.81686500	-4.09942300	0.88320500

34) Intermediate **B7**



Number of imaginary frequencies = 0

E_{total} = -2007.15236130 a.u

$G_{correction}$ = 0.450192 a.u

Cartesian coordinates:

B	-0.01548300	-0.39553300	-0.58741400
B	-1.55799600	0.09357600	-0.52196700
P	0.03562900	-2.25122200	-0.05615100
P	-2.03790700	1.88206700	-1.17526800
C	-2.75009000	-0.76919600	0.07741800
C	-3.82550600	-0.15647000	0.73820900
H	-3.87696400	0.92657800	0.80405300
C	-4.83846200	-0.88297600	1.35458300
H	-5.64818800	-0.36547300	1.85804200
C	-4.80605600	-2.27074800	1.32142100
H	-5.59118600	-2.85235700	1.79194600
C	-3.74621900	-2.91081000	0.68929900
H	-3.70900600	-3.99656600	0.67247500
C	-1.58298700	-2.93352700	-0.56049100
H	-1.61345800	-2.85730600	-1.65567300
H	-1.61827700	-3.99752900	-0.30892400
C	-2.72640900	-2.18180800	0.08028900
C	0.15310500	-2.40731100	1.74868600
H	0.08319500	-3.45767200	2.04144000
H	1.11159200	-2.00348200	2.08101000
H	-0.66399700	-1.84719400	2.20778600
C	1.28677900	-3.36814800	-0.75621400
H	1.36289900	-3.22047400	-1.83487700
H	2.26063000	-3.16651300	-0.30644100
H	1.00046200	-4.40288800	-0.55003100
C	-2.13035300	3.13618500	0.13983900
H	-2.86419500	2.85777000	0.89746300
H	-1.14998700	3.22537900	0.61420000
H	-2.41319500	4.09728300	-0.29672000
C	-0.88480600	2.57146100	-2.40029400
H	-0.64101700	1.82679800	-3.16000500
H	-1.35543100	3.43608400	-2.87556800
H	0.03714500	2.88817400	-1.91127800
C	-3.65007300	1.87041800	-2.02439500
H	-3.57772800	1.23769800	-2.91232800
H	-4.42517800	1.46301300	-1.37453200
H	-3.92084600	2.88437900	-2.32855700
P	1.56069400	0.63607700	-1.02539500
C	2.95302800	-0.45546900	-0.50793000
C	3.29216800	-0.70534500	0.82728500

C	3.68200800	-1.09246400	-1.51731000
C	4.30726100	-1.60290000	1.14419400
H	2.77307800	-0.18096400	1.62496100
C	4.69689100	-1.99297400	-1.20160000
H	3.45437100	-0.88220200	-2.55857700
C	5.00439200	-2.25760300	0.12964500
H	4.56100600	-1.78521100	2.18362100
H	5.25193000	-2.48078100	-1.99622800
H	5.79627900	-2.95635600	0.37791900
C	1.54174500	1.93529400	0.28560700
C	2.18649300	3.14574100	0.00348400
C	0.91892700	1.78808100	1.53236400
C	2.20987700	4.17846900	0.93752400
H	2.67555200	3.27977800	-0.95763400
C	0.94484700	2.81675700	2.46931100
H	0.39339800	0.86652500	1.76677300
C	1.58869700	4.01604000	2.17179000
H	2.71351100	5.10975200	0.70037200
H	0.46265800	2.68269300	3.43247100
H	1.60705800	4.81849700	2.90160700
H	-0.93650600	-0.46567200	-1.62592700

Pathway 3 of reaction 2

Figure S28 shows the computed free energy profile for the conceived mechanism 3 for 1,1-hydrophosphination of diborene **B1**. This mechanism involves (i) an initial PPh_2H coordination, (ii) dissociation of the chelating phosphine, (iii) 1,3-proton shift, (iv) 1,2-hydride shift from one boron to another, along with a bromide dissociation, and (v) association of the dissociated bromide to the other boron. The overall barrier of this mechanism was found to be 11.3 kcal/mol higher in energy than that of mechanism 1.

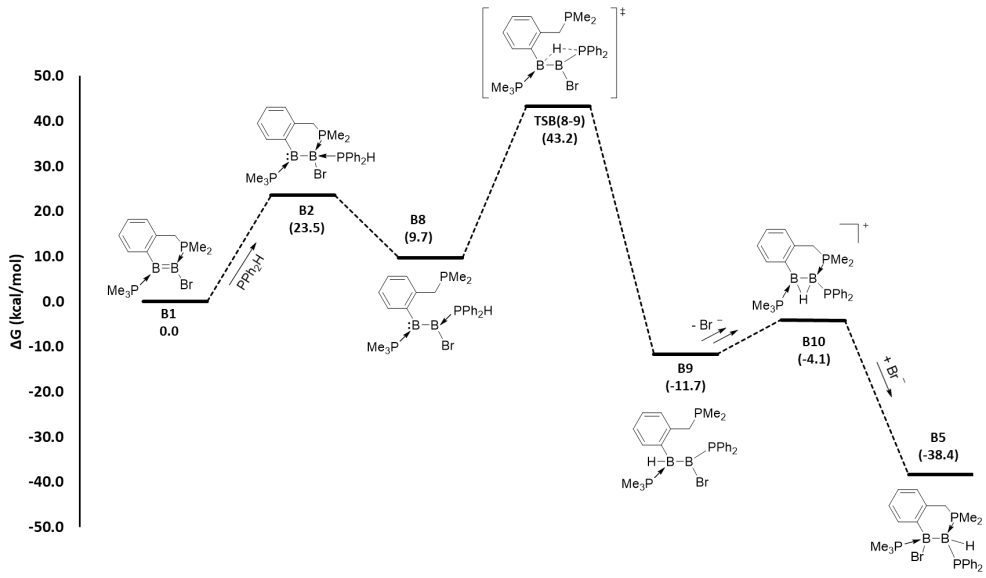
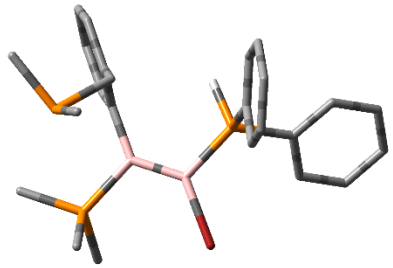


Figure S28. Computed mechanism 3 for 1,1-hydrophosphination of the unsymmetrical diborene **B1**.

Note: Details of species **B1**, **B2**, and **B5** are provided above in pathway 1 of reaction 2.

35) Intermediate **B8**



Number of imaginary frequencies = 0

E_{total} = -4579.06083844 a.u

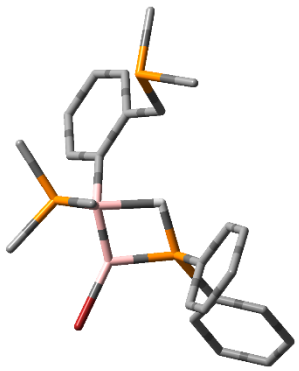
$G_{correction}$ = 0.441689 a.u

Cartesian coordinates:

B	-0.94622000	-1.19330300	-0.34208800
B	0.48336100	-1.04193100	0.25647900
P	-3.51091100	1.29336500	0.83937900
C	-1.60385100	-0.44945400	-1.58794000
C	-1.70966300	-1.11276400	-2.82169500
C	-2.25356500	-0.51355700	-3.95344500
H	-2.31132100	-1.06326400	-4.88850500
C	-2.70867300	0.79849000	-3.88145900
H	-3.12991200	1.28589600	-4.75559300
C	-2.61257200	1.48486500	-2.67670300
H	-2.96284400	2.51315800	-2.61559700
C	-2.07468800	0.88340800	-1.53365800
C	-2.04698600	1.67253500	-0.24797000
H	-2.01075400	2.75086200	-0.44736700
H	-1.16951500	1.40306700	0.34589500
P	1.54626800	0.29394600	-0.50823800
H	0.96362900	0.70122900	-1.71885600
H	-1.33082900	-2.13010900	-2.89544800
C	3.28401000	-0.09638400	-0.91620300
C	4.18102600	0.89325900	-1.32874200
C	3.71072500	-1.42296700	-0.82122000
C	5.48784400	0.55571400	-1.65973200
H	3.86265400	1.93054100	-1.38173500
C	5.02307100	-1.75447300	-1.14552300
H	3.02399700	-2.18360000	-0.46419400
C	5.90899700	-0.76941400	-1.56886100
H	6.18039700	1.32621000	-1.98287400
H	5.35315800	-2.78473500	-1.06079200
H	6.93248700	-1.02992300	-1.81979800
C	1.62360700	1.87010700	0.40832000
C	1.47630000	3.09792000	-0.23998400
C	1.75652500	1.83132300	1.80066000
C	1.48470300	4.28130400	0.49325800
H	1.33774800	3.13182200	-1.31760900
C	1.76922800	3.01582000	2.52729800
H	1.81906600	0.87188600	2.30698700

C	1.63622400	4.24030000	1.87576700
H	1.36532700	5.23321000	-0.01423400
H	1.87547500	2.98249100	3.60680800
H	1.64074300	5.16298600	2.44747700
Br	1.32988800	-1.95109900	1.83110900
C	-4.84310300	2.19330800	-0.08014900
H	-4.58074000	3.24047700	-0.26876200
H	-5.01119800	1.69725100	-1.03996600
H	-5.77647400	2.16018600	0.48854500
P	-2.04493100	-2.48961400	0.54031500
C	-3.71866500	-2.65312100	-0.16463900
H	-4.27666200	-3.45960200	0.31768900
H	-4.24039800	-1.70349700	-0.02044600
H	-3.64089700	-2.84328800	-1.23756800
C	-1.32318800	-4.16779700	0.48418900
H	-1.24708700	-4.49220100	-0.55590600
H	-0.31738900	-4.10606100	0.90687600
H	-1.92565300	-4.88231800	1.05214000
C	-2.30556700	-2.16997200	2.31747700
H	-2.88609000	-1.24994300	2.41516500
H	-2.83212000	-3.00039200	2.79627400
H	-1.32563300	-2.02991000	2.77932600
C	-3.17144100	2.51042200	2.19495900
H	-4.00160900	2.52537100	2.90639100
H	-2.26870400	2.20456600	2.73163000
H	-3.01881600	3.52359500	1.80739500

36) TSB(8-9)



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*1055.2)

E_{total} = -4579.00029860 a.u

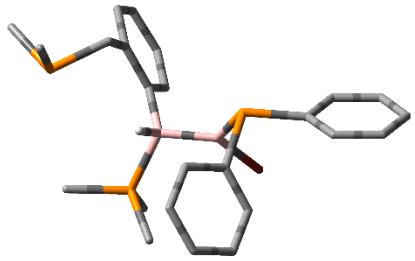
$G_{correction}$ = 0.436498 a.u

Cartesian coordinates:

B	0.63033500	1.05678000	0.48303900
B	-0.98729100	1.18832800	0.63607500
P	4.07300000	-1.31333800	-0.56675400
C	1.58362700	1.63156900	-0.67403900
C	1.54048900	3.02231300	-0.87429600
C	2.32278300	3.66816900	-1.82535500
H	2.25012700	4.74445000	-1.94956100
C	3.17530900	2.92208300	-2.62964900
H	3.78073500	3.40384500	-3.39137500
C	3.23072400	1.54387500	-2.46469900
H	3.86595200	0.95545200	-3.12198800
C	2.46441500	0.88707300	-1.49587100
C	2.56551700	-0.61981200	-1.41838800
H	2.50334600	-1.05427800	-2.42526100
H	1.72121300	-1.02018800	-0.84871300
P	-1.43887200	-0.03150000	-0.68445500
H	0.08327700	-0.02877800	-0.81919600
H	0.85804400	3.60690400	-0.26463500
C	-3.11970300	-0.00325900	-1.45897200
C	-3.74290500	-1.12616300	-2.01064800
C	-3.75800500	1.23751100	-1.52926400
C	-4.98775600	-1.00703000	-2.62024500
H	-3.25944800	-2.09734600	-1.95215700
C	-5.00867600	1.35339600	-2.12589900
H	-3.27316600	2.11231200	-1.10163000
C	-5.62256600	0.23144300	-2.67714700
H	-5.46615200	-1.88304600	-3.04764500
H	-5.50341200	2.31888000	-2.16455900
H	-6.59509000	0.32229000	-3.15089800
C	-1.38124600	-1.73615400	0.00790700
C	-0.55531200	-2.71287500	-0.55700300
C	-2.10197900	-2.04675000	1.16607800
C	-0.43487700	-3.96893900	0.03138200
H	0.00551500	-2.48555100	-1.45980800
C	-1.98101400	-3.30230600	1.75473100
H	-2.72564500	-1.28608200	1.62724000
C	-1.14431200	-4.26390000	1.19238900
H	0.21158000	-4.71681800	-0.41827500
H	-2.53439200	-3.52720400	2.66131900
H	-1.04706700	-5.24008800	1.65692500
Br	-2.25605300	1.65460800	2.05716200
C	5.37431800	-1.11980200	-1.86691300
H	5.03953900	-1.48249400	-2.84504200
H	5.65168100	-0.06669000	-1.95410400
H	6.26632300	-1.67828900	-1.56936300
P	1.58382600	0.64215700	2.12870600
C	3.32627500	1.17347200	2.19408800
H	3.76187000	0.96138100	3.17410100
H	3.89101100	0.64307500	1.42393500
H	3.37502400	2.24633900	1.99334000
C	0.83889800	1.35681600	3.63258900
H	0.82685300	2.44544200	3.54582100
H	-0.19417300	1.02152000	3.72912100

H	1.41983200	1.06295600	4.51104500
C	1.59031300	-1.15644700	2.44030800
H	2.16369300	-1.65439800	1.65543200
H	2.03911600	-1.38661900	3.41022000
H	0.56033100	-1.52184600	2.40594300
C	3.66828900	-3.10901200	-0.79023700
H	4.49764500	-3.72777900	-0.43751800
H	2.78219400	-3.36013800	-0.19809300
H	3.46531900	-3.35545100	-1.83841400

37) Intermediate **B9**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -4579.09720880 a.u

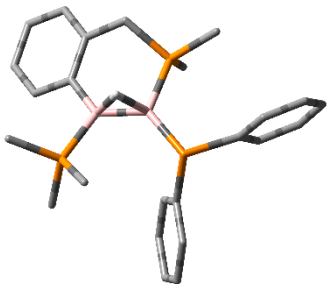
$G_{correction}$ = 0.443561 a.u

Cartesian coordinates:

B	-0.97706900	-0.02924700	0.46538800
B	0.65173000	-0.45305100	0.27467900
P	-4.05210600	1.13726800	-1.38682900
C	-1.89015300	-1.31622600	0.09060400
C	-1.80747000	-2.48474600	0.86603200
C	-2.57900500	-3.61343000	0.61073900
H	-2.48372900	-4.49286900	1.24083700
C	-3.45534600	-3.61011900	-0.46743700
H	-4.06357500	-4.48170800	-0.68944200
C	-3.52330400	-2.48573600	-1.28149200
H	-4.18366100	-2.49241700	-2.14575400
C	-2.75316300	-1.34552600	-1.02790800
C	-2.87472400	-0.18287900	-1.98336600
H	-3.21762600	-0.54011700	-2.96218800
H	-1.90303100	0.29612800	-2.13210400
P	1.49300900	0.08481000	-1.38134200
H	-1.22725800	0.96338900	-0.18850500
H	-1.08492100	-2.52083800	1.67803400
C	3.19273900	-0.61874000	-1.42035400
C	4.30603800	0.15879600	-1.75862100
C	3.37276500	-1.99400400	-1.23358400
C	5.56571700	-0.41790400	-1.88339700
H	4.18928300	1.22649000	-1.91903500
C	4.63217700	-2.57040000	-1.35919000

H	2.52520000	-2.62362800	-0.97895200
C	5.73427400	-1.78453700	-1.68171900
H	6.41741000	0.20395800	-2.14217000
H	4.75231200	-3.63784000	-1.20254900
H	6.71685800	-2.23516800	-1.77949800
C	1.74738800	1.76976800	-0.63960400
C	0.92543300	2.82144000	-1.05657100
C	2.68467200	2.01069000	0.37366700
C	1.03821000	4.08366600	-0.47928000
H	0.19027600	2.64611700	-1.83612600
C	2.81061600	3.27585700	0.93730300
H	3.31012700	1.19603600	0.72689700
C	1.98530700	4.31519500	0.51477600
H	0.39176600	4.88873200	-0.81478000
H	3.54711900	3.44678400	1.71641900
H	2.08103400	5.30135100	0.95829000
Br	1.67863200	-1.38264200	1.64482600
C	-5.65969800	0.25080900	-1.64186300
H	-5.75248100	-0.16334300	-2.65231800
H	-5.73620000	-0.56788400	-0.92130300
H	-6.49084300	0.93907800	-1.46469900
P	-1.36059200	0.66900300	2.22670800
C	-3.00853100	1.43474600	2.32404800
H	-3.17271200	1.90042700	3.29939800
H	-3.10881400	2.17254800	1.52566500
H	-3.76304000	0.66365000	2.15097800
C	-1.30956800	-0.47898200	3.64460800
H	-2.07481000	-1.24727800	3.51288300
H	-0.32969900	-0.96054200	3.67056400
H	-1.48724600	0.05459300	4.58198900
C	-0.16514800	1.97904400	2.63737200
H	-0.13902400	2.70876700	1.82372100
H	-0.41970600	2.47686700	3.57619200
H	0.82738700	1.52892200	2.71709700
C	-4.05224500	2.21177400	-2.89899100
H	-4.81874100	2.98604200	-2.80391300
H	-3.08240800	2.70892000	-2.99256300
H	-4.24121900	1.64125500	-3.81499200

38) Intermediate **B10**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 0

E_{total} = -2007.15236130 a.u

$G_{correction}$ = 0.450192 a.u

Cartesian coordinates:

B	-0.01548300	-0.39553300	-0.58741400
B	-1.55799600	0.09357600	-0.52196700
P	0.03562900	-2.25122200	-0.05615100
P	-2.03790700	1.88206700	-1.17526800
C	-2.75009000	-0.76919600	0.07741800
C	-3.82550600	-0.15647000	0.73820900
H	-3.87696400	0.92657800	0.80405300
C	-4.83846200	-0.88297600	1.35458300
H	-5.64818800	-0.36547300	1.85804200
C	-4.80605600	-2.27074800	1.32142100
H	-5.59118600	-2.85235700	1.79194600
C	-3.74621900	-2.91081000	0.68929900
H	-3.70900600	-3.99656600	0.67247500
C	-1.58298700	-2.93352700	-0.56049100
H	-1.61345800	-2.85730600	-1.65567300
H	-1.61827700	-3.99752900	-0.30892400
C	-2.72640900	-2.18180800	0.08028900
C	0.15310500	-2.40731100	1.74868600
H	0.08319500	-3.45767200	2.04144000
H	1.11159200	-2.00348200	2.08101000
H	-0.66399700	-1.84719400	2.20778600
C	1.28677900	-3.36814800	-0.75621400
H	1.36289900	-3.22047400	-1.83487700
H	2.26063000	-3.16651300	-0.30644100
H	1.00046200	-4.40288800	-0.55003100
C	-2.13035300	3.13618500	0.13983900
H	-2.86419500	2.85777000	0.89746300
H	-1.14998700	3.22537900	0.61420000
H	-2.41319500	4.09728300	-0.29672000
C	-0.88480600	2.57146100	-2.40029400
H	-0.64101700	1.82679800	-3.16000500
H	-1.35543100	3.43608400	-2.87556800
H	0.03714500	2.88817400	-1.91127800
C	-3.65007300	1.87041800	-2.02439500
H	-3.57772800	1.23769800	-2.91232800
H	-4.42517800	1.46301300	-1.37453200
H	-3.92084600	2.88437900	-2.32855700
P	1.56069400	0.63607700	-1.02539500
C	2.95302800	-0.45546900	-0.50793000
C	3.29216800	-0.70534500	0.82728500
C	3.68200800	-1.09246400	-1.51731000
C	4.30726100	-1.60290000	1.14419400
H	2.77307800	-0.18096400	1.62496100
C	4.69689100	-1.99297400	-1.20160000
H	3.45437100	-0.88220200	-2.55857700
C	5.00439200	-2.25760300	0.12964500

H	4.56100600	-1.78521100	2.18362100
H	5.25193000	-2.48078100	-1.99622800
H	5.79627900	-2.95635600	0.37791900
C	1.54174500	1.93529400	0.28560700
C	2.18649300	3.14574100	0.00348400
C	0.91892700	1.78808100	1.53236400
C	2.20987700	4.17846900	0.93752400
H	2.67555200	3.27977800	-0.95763400
C	0.94484700	2.81675700	2.46931100
H	0.39339800	0.86652500	1.76677300
C	1.58869700	4.01604000	2.17179000
H	2.71351100	5.10975200	0.70037200
H	0.46265800	2.68269300	3.43247100
H	1.60705800	4.81849700	2.90160700
H	-0.93650600	-0.46567200	-1.62592700

Pathway for 1,2-hydrophosphination of diborene B1

Although the product obtained experimentally (**6**) was the result of a formal 1,1-hydrophosphination, it remained plausible that an initial 1,2-addition followed by rearrangement could lead to the observed compound. We therefore hoped to gain information on the overall barrier for 1,2-addition. Intriguingly, as shown in Figure S29, the overall barrier of 32.8 kcal/mol found for 1,2-hydrophosphination was only 0.9 kcal/mol higher in energy than that of 1,1-hydrophosphination. These results indicate that 1,2-hydrophosphination can compete with 1,1-hydrophosphination. However, the fact that we only observe the 1,1-hydrophosphinated product from experiments suggests that the bromide dissociation from adduct **B2**, leading to 1,1-hydrophosphination *via* pathway 1, occurs much faster.

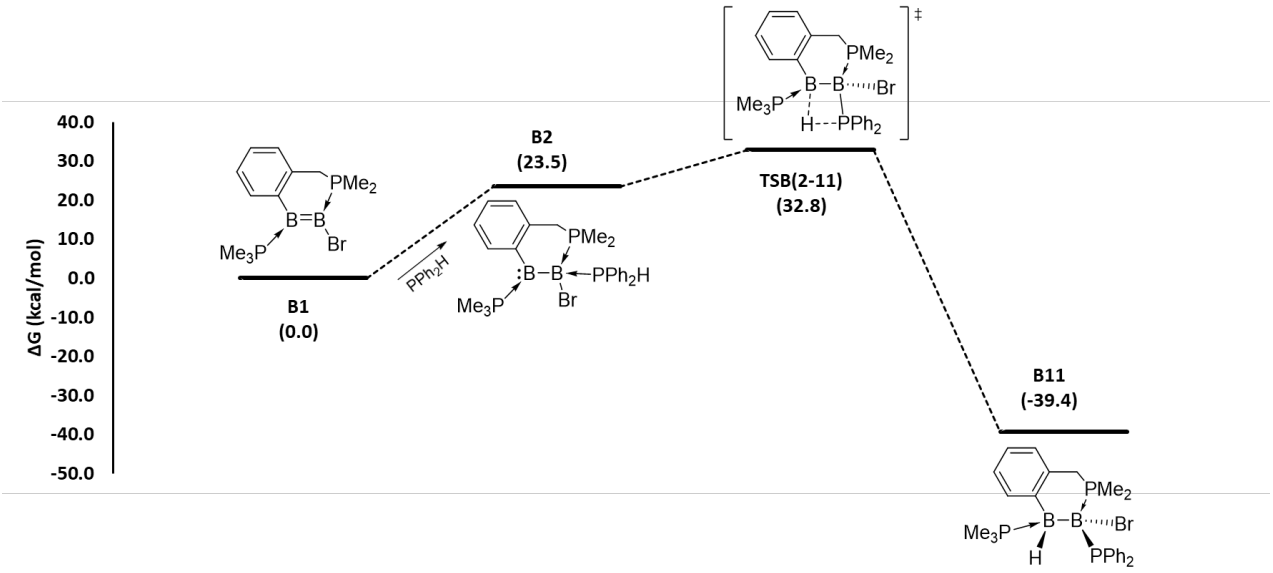
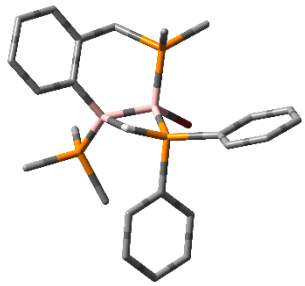


Figure S29. Computed mechanism for 1,2-hydrophosphination of the unsymmetrical diborene **B1**.

Note: Details of species **B1** and **B2** are provided above in pathway 1 of reaction 2.

39) TSB(2-11)



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*970.2)

E_{total} = -4579.02463087 a.u

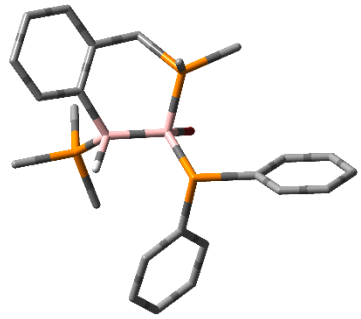
$G_{correction}$ = 0.444323 a.u

Cartesian coordinates:

B	-0.17223000	-0.42737200	0.63870800
P	-0.70924300	-2.29906900	0.66697200
B	-1.40700500	0.43368700	-0.17760700
P	1.05571700	-0.08080800	-0.80377200
C	-3.09153600	-1.59054900	-0.43844600
C	-2.59374400	-0.33953300	-0.89860600
C	-4.09526200	-2.27836200	-1.12392600
H	-4.43645100	-3.23996700	-0.74457400
C	-3.21324400	0.15688200	-2.06912200
H	-2.83705600	1.08895800	-2.48418200
C	-4.24247600	-0.50311100	-2.72405000
H	-4.68202700	-0.06759700	-3.61750000
C	-4.68790200	-1.74021600	-2.25913300
H	-5.47719400	-2.27773800	-2.77508000
C	-2.52554700	-2.20472700	0.82310800
H	-2.95615400	-3.19036100	1.02584400
H	-2.70016900	-1.55498900	1.69148900
Br	0.53909300	0.04511100	2.48583000
P	-1.93680200	2.03125000	0.60938900
H	-0.01164300	0.01633100	-1.78799800
C	2.71455100	-0.95533400	-0.85050800
C	3.11680500	-1.68108000	0.27821400
C	3.46542600	-1.05744200	-2.02604400
C	4.25292100	-2.48521400	0.23177900
H	2.55796600	-1.57965000	1.20699400
C	4.59555500	-1.86599100	-2.07315900
H	3.16461100	-0.49862000	-2.90955800
C	4.99022500	-2.58400200	-0.94506500
H	4.56751900	-3.02842600	1.11819600
H	5.17218200	-1.93713400	-2.99063300
H	5.87218200	-3.21567600	-0.98365300

C	1.60888700	1.65205900	-0.84107000
C	1.16629900	2.52549100	-1.83782000
C	2.51863900	2.10355600	0.11624800
C	1.62993800	3.83480100	-1.87699800
H	0.43557300	2.18077900	-2.56298400
C	2.96682800	3.42207500	0.08700300
H	2.85905700	1.43028800	0.89679500
C	2.52653500	4.28740000	-0.90847000
H	1.28811300	4.50668300	-2.65808900
H	3.66337300	3.77046700	0.84283700
H	2.88216300	5.31273100	-0.93436900
C	-0.37204200	-3.21121900	-0.87256100
H	0.70805000	-3.28717800	-1.02086700
H	-0.81324700	-4.21006000	-0.82552200
H	-0.81484700	-2.66661800	-1.70850500
C	-0.05248700	-3.34350400	2.01038400
H	-0.16158400	-2.81039000	2.95677900
H	-0.57462400	-4.30231200	2.05290800
H	1.01262400	-3.51436100	1.83440400
C	-3.10397200	3.04986000	-0.36877900
H	-3.44853500	3.90755800	0.21576500
H	-2.60725200	3.40363300	-1.27479100
H	-3.96174700	2.43890000	-0.65907500
C	-0.64392200	3.22136500	1.11788000
H	-0.15325000	3.64436800	0.23989200
H	-1.09059100	4.02324100	1.71267700
H	0.10115300	2.69563900	1.71712600
C	-2.85896700	1.81241900	2.19760300
H	-3.15618400	2.75986200	2.65994000
H	-3.74762600	1.20592200	2.00210100
H	-2.20062000	1.26091100	2.87446600

40) Intermediate **B11**



Number of imaginary frequencies = 0

E_{total} = -4579.14869039 a.u

$G_{correction}$ = 0.449884 a.u

Cartesian coordinates:

B	-0.01081500	-0.34191200	0.07666000
P	-0.50923600	-2.19749900	0.27993000
B	-1.47639700	0.45236500	-0.54112200

P	1.39579700	-0.12709100	-1.26737700
C	-3.14846000	-1.60372400	-0.05783400
C	-2.80547400	-0.45510300	-0.80646100
C	-4.31946100	-2.31697100	-0.32793000
H	-4.55137800	-3.20368100	0.25785600
C	-3.68986100	-0.10165300	-1.83914400
H	-3.43486300	0.75307400	-2.46099300
C	-4.86300100	-0.80031900	-2.10251400
H	-5.51676400	-0.48327700	-2.90983500
C	-5.18822200	-1.91313000	-1.33417900
H	-6.09869900	-2.47199300	-1.52684200
C	-2.19760300	-2.14676500	0.98768600
H	-2.50479000	-3.13918900	1.33151400
H	-2.11386600	-1.49416000	1.86522500
Br	0.46987800	0.13075100	2.07875400
P	-2.09232400	1.92180700	0.58589400
H	-1.23240400	1.08983700	-1.55399500
C	2.95198900	-0.99212900	-0.74718200
C	3.32074500	-1.30343800	0.56840200
C	3.80436400	-1.40533700	-1.78046700
C	4.49579500	-2.00100300	0.83831200
H	2.68426500	-0.99267800	1.38899800
C	4.98507800	-2.09177400	-1.51368800
H	3.53183800	-1.18546100	-2.80931100
C	5.33287100	-2.39539300	-0.20062700
H	4.75861400	-2.22850800	1.86736400
H	5.63089500	-2.39587900	-2.33201200
H	6.25130800	-2.93461800	0.01066200
C	1.81609400	1.65238200	-1.02003300
C	1.33683600	2.58077400	-1.95054000
C	2.54492400	2.12347200	0.07764100
C	1.56637000	3.94482400	-1.78422400
H	0.77941400	2.22553600	-2.81203700
C	2.77777600	3.48474400	0.24412900
H	2.92897500	1.42098200	0.80913700
C	2.28647000	4.40030800	-0.68344700
H	1.19075600	4.65032300	-2.51966900
H	3.34447000	3.83262700	1.10268000
H	2.47057300	5.46223200	-0.55177600
C	-0.62441700	-3.09399000	-1.29903400
H	0.38228300	-3.22634600	-1.70252600
H	-1.10065000	-4.06753500	-1.15812400
H	-1.20926400	-2.49926800	-2.00220300
C	0.49190000	-3.25584700	1.37321800
H	0.59875900	-2.75048900	2.33490200
H	0.01891300	-4.23182100	1.50692200
H	1.48613900	-3.38037300	0.93734700
C	-3.42702200	2.85799600	-0.23927700
H	-3.76824100	3.68405200	0.39027600
H	-3.04960200	3.25529100	-1.18449900
H	-4.26370200	2.18940800	-0.45258200
C	-0.84236100	3.19078700	0.95853400
H	-0.45542800	3.58945700	0.01738700

H	-1.27532100	3.99953400	1.55304500
H	-0.01316500	2.72701900	1.49389000
C	-2.84256300	1.43350800	2.17751600
H	-3.25439000	2.29686400	2.70595500
H	-3.64175600	0.71496300	1.97470500
H	-2.07274900	0.95394200	2.78458800

REACTION 3

Pathway 1 of reaction 3

As shown in Figure S30, pathway 1 involves in an initial dissociation of bromide, followed by a 1,2-proton shift and subsequent association of bromide to the other boron center. Compared to another computed mechanism (vide infra), this pathway was found to have an overall lower barrier.

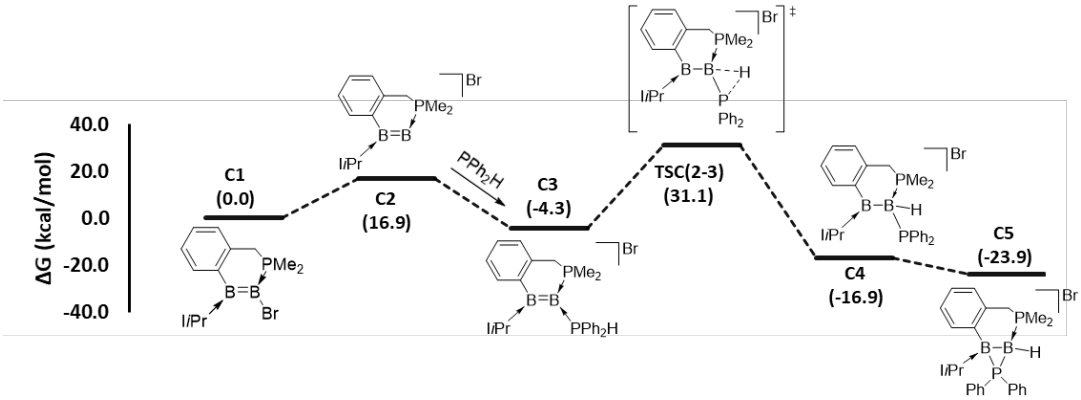
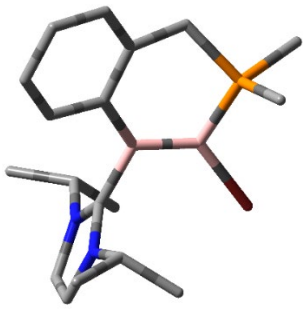


Figure S30. Computed mechanism 1 for 1,1-hydrophosphination of the unsymmetrical diborene **C1**.

41) Diborene **C1**



Note: Hydrogen atoms are omitted for clarity.

Number of imaginary frequencies = 0

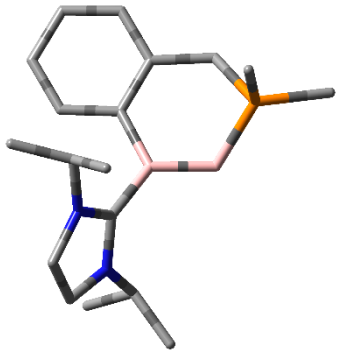
E_{total} = -3774.90368147 a.u

$G_{correction}$ = 0.387920 a.u

Cartesian coordinates:

B	0.18126100	0.27570500	-0.38194800
P	2.30364900	-1.55908600	-0.03520400
N	-2.38863500	0.47789300	-0.92125100
N	-1.82094100	1.24090600	1.00864600
C	3.56320500	2.16470400	-0.91430100
H	4.60903800	1.91901400	-1.08715600
C	2.93684800	-3.14651100	-0.68770900
H	2.41790300	-3.95968400	-0.17328300
C	2.62704100	1.13713300	-0.83027800
C	1.25475200	1.41417600	-0.60009200
C	3.10428200	-0.28039700	-1.06450100
H	4.19146800	-0.35660600	-0.95376100
H	2.85543000	-0.57749500	-2.09264200
C	-3.19690400	1.33044200	0.93393100
H	-3.79853800	1.71791300	1.73922700
C	0.91183200	2.77702300	-0.49804800
H	-0.13258300	3.04122900	-0.34087000
C	3.18877100	3.49979200	-0.78406400
H	3.93455900	4.28602800	-0.84478900
C	-1.22993500	0.32533200	3.19792900
H	-0.53183900	0.41513700	4.03487000
H	-1.06558500	-0.63392800	2.69940500
H	-2.24869200	0.34502800	3.60054600
C	3.06517700	-1.45369200	1.62939100
H	2.90904100	-0.43848100	2.00153500
C	-1.32125600	0.70471000	-0.12756400
C	-2.31012900	-0.14743700	-2.24880000
H	-1.23883700	-0.30818700	-2.40137000
C	1.84742900	3.80221700	-0.58132200
H	1.52874400	4.83681900	-0.48624400
C	-1.27557000	2.84880200	2.79722000
H	-1.11319800	3.62769200	2.04771800
H	-0.59131900	3.02749600	3.63037800
H	-2.29640900	2.93841900	3.18419600
C	-3.55342500	0.85415500	-0.28096700
H	-4.52344800	0.75341400	-0.73862900
C	-1.00691300	1.46874400	2.21108000
H	0.02376100	1.42447100	1.85325400
C	-3.00500600	-1.50513700	-2.22216700
H	-4.08245900	-1.39990700	-2.05268700
H	-2.57522400	-2.12278800	-1.43000300
H	-2.86322800	-2.01071600	-3.18113600
C	-2.85606400	0.79822900	-3.31338300
H	-3.92690300	0.98334000	-3.17540600
H	-2.72053000	0.35403600	-4.30293600
H	-2.33117000	1.75653800	-3.28901400
B	0.47813100	-1.23428500	-0.10749900
H	2.54957300	-2.15131600	2.29406400
H	4.13521100	-1.68057800	1.61393700
H	2.70079400	-3.21402300	-1.75203600
H	4.01545800	-3.25115400	-0.54225800
Br	-0.70515700	-2.64936600	0.65172800

42) Intermediate **C2**



Note: Hydrogen atoms are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -1202.87770276 a.u

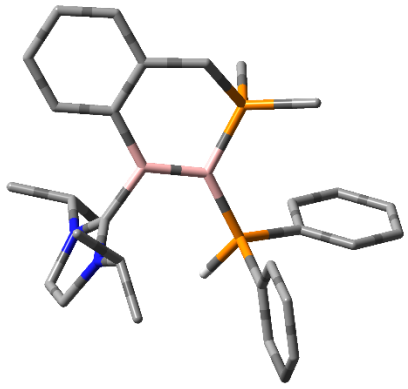
$G_{correction}$ = 0.388712 a.u

Cartesian coordinates:

B	0.04592500	-0.44938700	-0.21314600
P	2.55660700	-1.62292400	0.74799000
N	-2.55282200	-0.79370000	-0.24871300
N	-1.88177300	0.85223100	0.97796500
C	2.99931600	1.64612400	-1.67911500
H	4.08305900	1.60161900	-1.74383000
C	3.65829100	-3.07028000	0.80428700
H	3.37394800	-3.71887200	1.63633400
C	2.29956300	0.58274200	-1.10741000
C	0.88709100	0.63119400	-1.01176500
C	3.10980400	-0.63569900	-0.71548900
H	4.15753600	-0.37242100	-0.53317500
H	3.10211100	-1.35956000	-1.54038700
C	-3.25509600	0.79914000	1.09328200
H	-3.81351700	1.48388300	1.70957100
C	0.24395600	1.75830700	-1.55336800
H	-0.84114200	1.81677400	-1.51353300
C	2.33408100	2.75736400	-2.18404200
H	2.89815400	3.57336200	-2.62256000
C	-0.94871500	1.39070900	3.18581200
H	-0.24758000	2.03928200	3.71651500
H	-0.62083200	0.35431800	3.30247400
H	-1.92905500	1.49937700	3.65938200
C	2.91782100	-0.67491900	2.26640300
H	2.46338300	0.31272300	2.16712900
C	-1.45457300	-0.13042300	0.15950500
C	-2.56727500	-1.90538100	-1.22441100
H	-1.51265900	-2.11677000	-1.41685900
C	0.94573800	2.80878700	-2.13010900
H	0.41404300	3.66419000	-2.53366100
C	-1.43257600	3.22360400	1.48093200
H	-1.47196300	3.45256700	0.41364000

H	-0.71097100	3.89692200	1.94863700
H	-2.41116200	3.42977400	1.92453400
C	-3.67586600	-0.22777000	0.31729700
H	-4.66938200	-0.59613800	0.12236900
C	-0.99892100	1.78098100	1.71191100
H	-0.01259100	1.63976100	1.26480600
C	-3.21352100	-3.13919700	-0.60542600
H	-4.27345000	-2.97598300	-0.38757400
H	-2.70569800	-3.42575900	0.31858800
H	-3.14565600	-3.97228500	-1.30849000
C	-3.24171300	-1.45105700	-2.51493500
H	-4.30115900	-1.22721900	-2.35631700
H	-3.17710100	-2.24673800	-3.26046600
H	-2.75286600	-0.56160800	-2.92008500
B	0.83626400	-1.74652000	0.11532700
H	2.49176600	-1.17901900	3.13677100
H	3.99692300	-0.57237100	2.40898800
H	3.55548900	-3.63129000	-0.12637300
H	4.69806100	-2.76020100	0.93790200

43) Intermediate **C3**



Note: Selected hydrogen atoms are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -2008.08552408 a.u

$G_{correction}$ = 0.572409 a.u

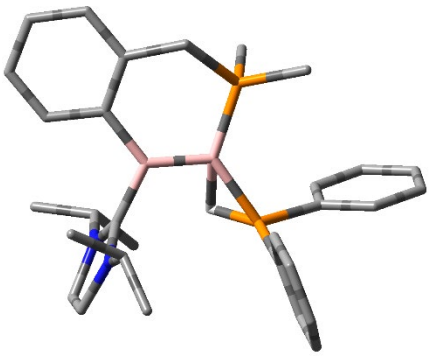
Cartesian coordinates:

B	0.10622200	-0.68768000	-0.31323500
B	-1.37687800	-0.15935300	-0.17477300
P	0.18958400	-2.29860500	-1.23066700
C	-2.65257600	-0.85847800	-0.78820600
C	-3.94438200	-0.51126400	-0.35827200
H	-4.06028700	0.29054300	0.36822300
C	-5.08794800	-1.15183300	-0.82256800
H	-6.06678700	-0.85457100	-0.45998400
C	-4.96502500	-2.17414500	-1.75471200
H	-5.84430600	-2.68866400	-2.12767900
C	-3.70161700	-2.53086400	-2.21788500

H	-3.61092300	-3.31937900	-2.96040400
C	-1.22753500	-2.27612100	-2.38019500
H	-0.95699700	-1.53802300	-3.14671600
H	-1.30212200	-3.24906800	-2.87646900
C	-2.55507400	-1.88881400	-1.75448900
P	1.57377500	0.11269300	0.46514900
H	1.27979700	0.73064700	1.70056800
C	-1.63231200	1.10526800	0.76038200
N	-1.48554300	2.40396000	0.43583500
N	-1.95972600	1.07694000	2.06663400
C	-1.24108600	2.87113000	-0.94373500
C	-1.72962200	3.19686800	1.54031200
C	-2.01919800	2.36310100	2.56704400
C	-2.18453400	-0.15993900	2.83737200
H	-0.71583900	2.03757800	-1.41958900
C	-2.57606000	3.09421800	-1.64925100
C	-0.33984700	4.09818700	-0.95297800
H	-1.67328000	4.27175700	1.50730100
H	-2.25591900	2.57501000	3.59647300
C	-3.55615300	-0.13224000	3.50235200
C	-1.04385600	-0.37569100	3.82638300
H	-2.16180700	-0.95704100	2.09019400
H	-3.14591000	3.89230000	-1.16324000
H	-3.17400800	2.17872100	-1.64207600
H	-2.40247400	3.38315500	-2.68875100
H	-0.84409400	4.97967200	-0.54490100
H	-0.06879800	4.32800900	-1.98554900
H	0.58337400	3.92026300	-0.39521200
H	-3.73880400	-1.08954700	3.99558700
H	-4.34558400	0.02765700	2.76455600
H	-3.62154600	0.65079400	4.26390700
H	-0.08453700	-0.42057800	3.30401300
H	-1.19012500	-1.31902400	4.35788500
H	-1.00120800	0.42651000	4.56935600
C	2.94059600	-1.02732200	0.85093100
C	4.18381800	-0.92953200	0.22434500
C	2.69059700	-2.07885900	1.74081900
C	5.16691000	-1.88283800	0.48073900
H	4.38687600	-0.11587300	-0.46459100
C	3.67837900	-3.02078200	2.00126500
H	1.72008400	-2.16363700	2.22346200
C	4.91614400	-2.92498000	1.36713700
H	6.13092000	-1.80535400	-0.01032400
H	3.48502500	-3.82780900	2.70003600
H	5.68499200	-3.66351000	1.56755700
C	2.31521400	1.52038700	-0.42427200
C	3.08837400	2.46446200	0.25905000
C	2.10025000	1.65935400	-1.79555500
C	3.64275400	3.53768800	-0.42896500
H	3.25977500	2.36084500	1.32735300
C	2.66302700	2.73051200	-2.48375700
H	1.47144800	0.93603400	-2.30911300
C	3.43051600	3.66946000	-1.80054500

H	4.23986200	4.27085600	0.10264200
H	2.49653800	2.83732100	-3.55049200
H	3.86351100	4.50847900	-2.33489300
C	-0.01532500	-3.81123700	-0.22629700
H	0.81469400	-3.89225100	0.47940300
H	-0.95142000	-3.72807800	0.33031100
H	-0.04378400	-4.70545900	-0.85503700
C	1.65380500	-2.65192200	-2.26147800
H	1.78948500	-1.85319000	-2.99401900
H	2.54006600	-2.69339400	-1.62216500
H	1.54448100	-3.60680400	-2.78193600

44) **TSC(3-4)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*1180.4)

E_{total} = -2008.02609942 a.u

$G_{correction}$ = 0.567465 a.u

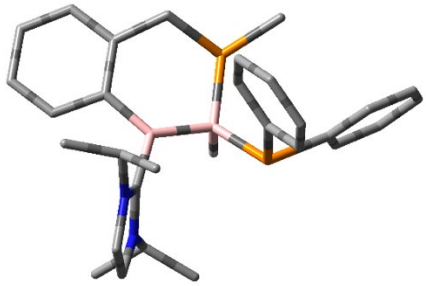
Cartesian coordinates:

B	0.15682500	-0.69458400	-0.35744800
B	-1.34395500	-0.17895800	-0.16471100
P	0.25149500	-2.27842900	-1.36340500
C	-2.60929300	-0.86840000	-0.81270900
C	-3.90207400	-0.53155500	-0.37411600
H	-4.01753400	0.26091600	0.36171000
C	-5.04662000	-1.16797700	-0.83992900
H	-6.02402700	-0.87728400	-0.46874600
C	-4.92479800	-2.17799500	-1.78510900
H	-5.80378400	-2.69118100	-2.16046900
C	-3.66313900	-2.52195600	-2.26150200
H	-3.57607300	-3.29834900	-3.01688800
C	-1.20049400	-2.25935000	-2.46722600
H	-0.96113200	-1.51669500	-3.23992500
H	-1.28823600	-3.22775700	-2.97018500
C	-2.51411300	-1.88221600	-1.79957400
P	1.60795000	0.16638000	0.48249700
H	0.43436700	-0.31698000	1.28291200
C	-1.63810700	1.06148100	0.80005000

N	-1.56157300	2.36786000	0.48680100
N	-1.99089900	1.00352100	2.09912200
C	-1.28918500	2.86850900	-0.87527400
C	-1.87560300	3.13615400	1.58935900
C	-2.13723900	2.27939100	2.60452600
C	-2.14836400	-0.24428400	2.87021500
H	-0.74367100	2.05226800	-1.35795500
C	-2.60814700	3.09969900	-1.60744300
C	-0.39486500	4.10039500	-0.83207100
H	-1.88067200	4.21278000	1.56490700
H	-2.40364000	2.46975400	3.63091500
C	-3.55589200	-0.34529600	3.44738400
C	-1.06017900	-0.34117500	3.93580200
H	-2.00205500	-1.04056000	2.13526000
H	-3.19465200	3.88329500	-1.11784700
H	-3.20138400	2.18155700	-1.63551200
H	-2.41156100	3.41445000	-2.63522600
H	-0.91409600	4.96806900	-0.41349700
H	-0.09879800	4.35757400	-1.85115400
H	0.51462600	3.91086100	-0.25611900
H	-3.67135000	-1.30560000	3.95503900
H	-4.31003500	-0.28398600	2.65999300
H	-3.74759100	0.44313000	4.18155600
H	-0.06557600	-0.23624500	3.49366500
H	-1.12087100	-1.31058400	4.43593400
H	-1.17912000	0.43586000	4.69723700
C	2.92674700	-1.01218600	0.89430800
C	4.15689700	-0.97985200	0.23231700
C	2.68903500	-2.00992600	1.84794300
C	5.12953300	-1.93623900	0.51504300
H	4.35938400	-0.20788700	-0.50381800
C	3.65856400	-2.96788200	2.11875800
H	1.74001100	-2.03863700	2.37782300
C	4.88236800	-2.93327900	1.45248000
H	6.08326600	-1.89875700	-0.00083100
H	3.46499700	-3.73427500	2.86219100
H	5.64121600	-3.67676500	1.67098300
C	2.34215900	1.57867600	-0.41295700
C	3.17307900	2.49488000	0.23893000
C	2.03268000	1.75427600	-1.76203100
C	3.69910100	3.57245200	-0.46532500
H	3.41022900	2.36116300	1.29032600
C	2.56798900	2.82854700	-2.46535500
H	1.35993500	1.05055500	-2.24918500
C	3.39735500	3.73975900	-1.81584800
H	4.34505600	4.28305900	0.03937500
H	2.33699200	2.95884200	-3.51772900
H	3.80773800	4.58353400	-2.36036300
C	0.13365100	-3.79489200	-0.36094900
H	0.97798000	-3.83040500	0.33204200
H	-0.79682200	-3.76000400	0.21014400
H	0.14018600	-4.68739300	-0.99204400
C	1.71844400	-2.50692200	-2.41650600

H	1.80428700	-1.67100400	-3.11417100
H	2.60749000	-2.52221200	-1.77986600
H	1.65926900	-3.44335700	-2.97665900

45) Intermediate **C4**



Note: Selected hydrogens are omitted for clarity

Number of imaginary frequencies = 0

E_{total} = -2008.10793463 a.u

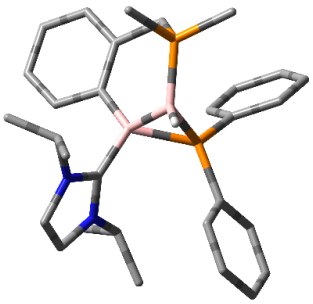
$G_{correction}$ = 0.572850 a.u

Cartesian coordinates:

B	0.40045100	-0.86740400	0.36927400
B	-1.22139000	-0.54741100	0.05759900
P	1.03864300	-2.05900200	-1.02060700
C	-2.12284200	-1.29655300	-0.96377800
C	-3.51312800	-1.35571600	-0.74233500
H	-3.94053500	-0.78943800	0.08182000
C	-4.35788900	-2.12973900	-1.52594000
H	-5.42275500	-2.16210600	-1.32264900
C	-3.81935800	-2.86374700	-2.57666200
H	-4.46207300	-3.47440600	-3.20223200
C	-2.45163300	-2.81806500	-2.83237300
H	-2.04777100	-3.38851400	-3.66367300
C	-0.13261900	-2.00142700	-2.43339500
H	0.08075600	-1.07346500	-2.97780900
H	0.10788400	-2.81842000	-3.12085400
C	-1.59683500	-2.04866200	-2.04619800
P	1.48672700	0.64354100	0.98198100
H	0.33526600	-1.58862700	1.35104900
C	-1.94721100	0.51585700	1.00805500
N	-2.34404600	1.74991200	0.65321900
N	-2.21412900	0.38305900	2.31803100
C	-2.26342700	2.31459300	-0.71132300
C	-2.85699400	2.40581200	1.75274200
C	-2.77778300	1.54740900	2.79623700
C	-1.93424500	-0.81699600	3.13405000
H	-1.62124600	1.62742100	-1.26869600
C	-3.64869000	2.34057700	-1.34801600
C	-1.58915100	3.68056100	-0.68054600
H	-3.22835400	3.41554600	1.70234600

H	-3.06779500	1.66906000	3.82647000
C	-3.21662100	-1.31593300	3.79128800
C	-0.81320800	-0.51981100	4.12318100
H	-1.58861400	-1.56937000	2.42220900
H	-4.32988700	2.97906500	-0.77743800
H	-4.07498700	1.33639100	-1.40878900
H	-3.57628300	2.74658600	-2.35965900
H	-2.22431300	4.43215700	-0.20204100
H	-1.40062300	4.00733200	-1.70494700
H	-0.62946500	3.63450100	-0.16152200
H	-3.01475000	-2.25520700	4.31080300
H	-3.99745700	-1.49512300	3.04778700
H	-3.59412800	-0.60462500	4.53180900
H	0.06859600	-0.13691000	3.60282400
H	-0.54331600	-1.43511600	4.65536200
H	-1.12896400	0.21940900	4.86566600
C	3.18311500	-0.08839300	0.97913000
C	4.26998600	0.45241100	0.28699900
C	3.38617200	-1.26283400	1.71896400
C	5.51206500	-0.17795100	0.30785800
H	4.14959100	1.36291400	-0.29095200
C	4.62370600	-1.89662400	1.73312700
H	2.56229800	-1.69369200	2.28250800
C	5.69313800	-1.35910500	1.01946500
H	6.34115300	0.25674300	-0.24150800
H	4.75598500	-2.80889400	2.30660100
H	6.66005900	-1.85071100	1.02919700
C	1.57003700	1.84459800	-0.41304300
C	2.15869500	3.09466600	-0.16950400
C	1.03624200	1.61621500	-1.68530200
C	2.23131500	4.06300800	-1.16588700
H	2.56789900	3.30701100	0.81448800
C	1.08948300	2.58731000	-2.68269100
H	0.55494300	0.66773100	-1.90044400
C	1.69409400	3.81351000	-2.42669400
H	2.70139600	5.01817200	-0.95584900
H	0.66360700	2.38348500	-3.66053600
H	1.74500000	4.57060800	-3.20192500
C	1.03127400	-3.79022700	-0.46229700
H	1.74600700	-3.89108600	0.35801000
H	0.03410000	-4.04353700	-0.09513800
H	1.30680300	-4.47144800	-1.27082000
C	2.66888800	-1.78835900	-1.78036700
H	2.76628000	-0.74289000	-2.08050800
H	3.45179700	-2.00659300	-1.05077400
H	2.78581100	-2.43708100	-2.65237500

46) Product **C5**



Note: Hydrogen atoms are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -2008.12061120 a.u

$G_{correction}$ = 0.574453 a.u

Cartesian coordinates:

B	-0.01461500	-0.71085700	-0.02744500
P	2.22952500	-0.86497500	-1.94924600
P	0.22673300	1.17314700	-0.51589100
N	-2.44777800	-0.55000900	1.09542600
N	-2.17612200	-2.13224600	-0.34429700
C	3.22526800	-2.27621100	1.61928500
H	4.29893600	-2.30296800	1.45209900
C	1.93806100	1.99078000	1.50699000
H	1.41389900	1.26124100	2.11679200
C	3.23169800	0.09429400	-3.12706800
H	4.22961900	-0.33741300	-3.23789300
C	2.42184700	-1.52286000	0.75960000
C	1.01986800	-1.46754100	0.94571500
C	-1.23088600	2.19981200	-0.84026100
C	3.12931000	-0.79114700	-0.36416100
H	4.12902200	-1.20831900	-0.52239000
H	3.26509200	0.27088400	-0.13170900
C	-3.46039700	-2.24899100	0.13823700
H	-4.13900200	-3.01700100	-0.19360000
C	3.00303800	2.71336900	2.03644100
H	3.29697300	2.56143500	3.06939400
C	0.50900000	-2.22445800	2.01572200
H	-0.56454200	-2.25065900	2.18091000
C	2.25342700	3.09982900	-0.62363700
H	1.95761500	3.25212700	-1.65787100
C	2.68513200	-2.99377200	2.67816400
H	3.32908500	-3.57244700	3.33147900
C	-2.37132800	-3.18421600	-2.56331500
H	-1.84427400	-3.81885400	-3.27973600
H	-2.51339400	-2.19966900	-3.01589200
H	-3.35235100	-3.63571700	-2.38689200
C	2.30512700	-2.60213900	-2.48590100
H	1.87152400	-3.22403100	-1.69870100
C	-1.54793400	-1.08834000	0.23962600

C	-2.22477700	0.57693200	2.02694300
H	-1.30283500	1.04688600	1.68552200
C	1.31010500	-2.97232800	2.87076400
H	0.85899100	-3.53767500	3.68004500
C	-1.32028700	-4.42059000	-0.59248700
H	-0.72496500	-4.28886900	0.31473300
H	-0.78213200	-5.09364500	-1.26472300
H	-2.26680300	-4.90109500	-0.32571200
C	-3.63204900	-1.25396900	1.03800800
H	-4.49121200	-0.98921000	1.63091600
C	-1.35874000	3.45968600	-0.24723000
H	-0.56593400	3.85001000	0.38365300
C	-1.55000900	-3.08038500	-1.28390600
H	-0.58812800	-2.62509600	-1.52008900
C	3.31168600	3.82381200	-0.08702500
H	3.84518900	4.53962300	-0.70333000
C	-2.26121400	1.71017300	-1.64991300
H	-2.16598200	0.73913900	-2.12455200
C	3.68872800	3.62652700	1.24067700
H	4.52009700	4.18716100	1.65472400
C	-3.52642700	3.73041000	-1.27406600
H	-4.41622800	4.32629800	-1.44646900
C	-3.40441500	2.47291900	-1.86059800
H	-4.19662700	2.08888300	-2.49468100
C	-2.50144100	4.22144200	-0.47064800
H	-2.59054200	5.20094400	-0.01293100
C	-3.36792300	1.58187200	1.92542000
H	-4.28278000	1.19960100	2.38916800
H	-3.57667300	1.84129400	0.88599900
H	-3.09012500	2.49460200	2.45672400
C	-2.02552700	0.06136500	3.44977800
H	-2.90281900	-0.49459000	3.79487600
H	-1.88130000	0.90929700	4.12401400
H	-1.14817000	-0.58419200	3.52098800
B	0.44557100	-0.33123000	-1.67902400
H	-0.26226300	-0.39294600	-2.64638700
C	1.56321400	2.17694100	0.17245100
H	1.73285200	-2.73358500	-3.40680200
H	3.33944100	-2.91084200	-2.65530800
H	2.73543700	0.11511200	-4.09959500
H	3.32101700	1.11863400	-2.75692200

Pathway 2 of reaction 3

Figure S31 shows the computed free energy profile for the conceived mechanism 2 for 1,1-hydrophosphination of diborene **C1**. This mechanism involves (i) dissociation of the chelating phosphine, (ii) 1,3-proton shift, and (iii) subsequent rearrangements. The overall barrier of this mechanism was found to be 4.5 kcal/mol higher in energy than that of mechanism 1.

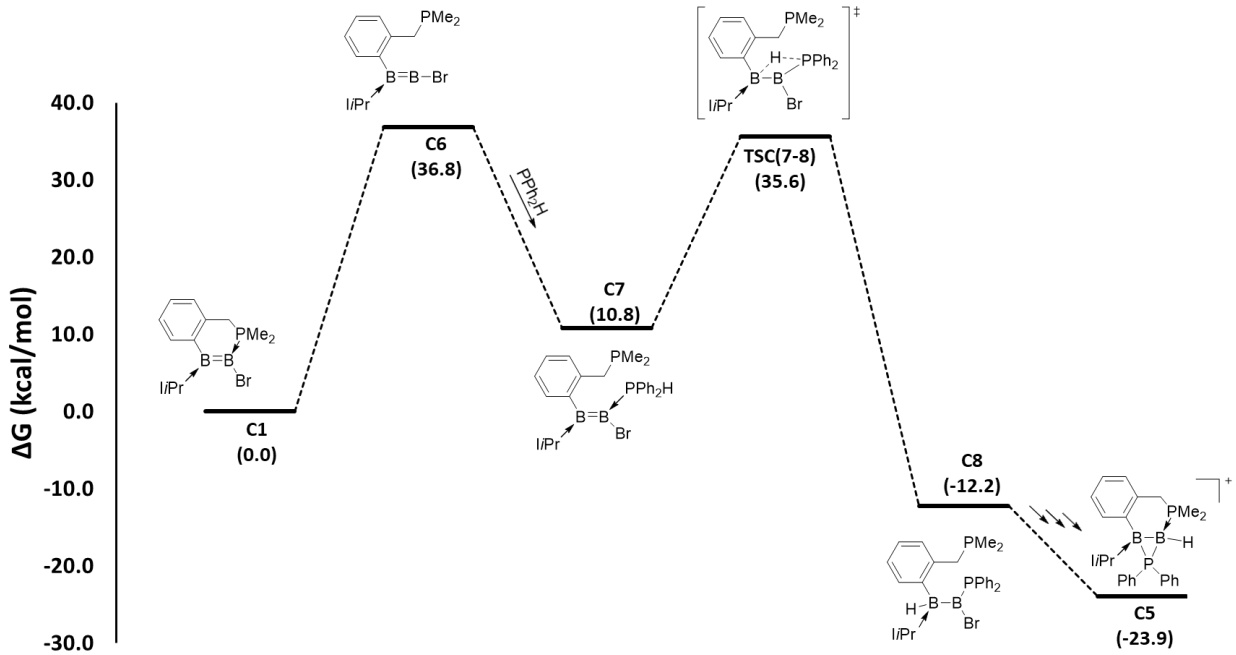
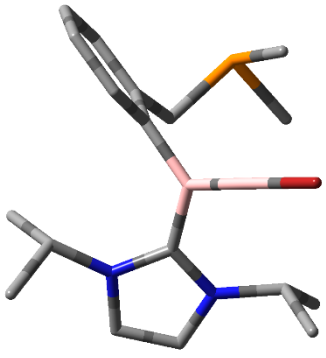


Figure S31. Computed mechanism 2 for a net 1,1-hydrophosphination of the unsymmetrical diborene **C1**.

Note: Details of species **C1**, **C5** are provided above in Pathway-1 of reaction-3.

47) Intermediate **C6**



Note: Hydrogens are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -3774.83868448 a.u

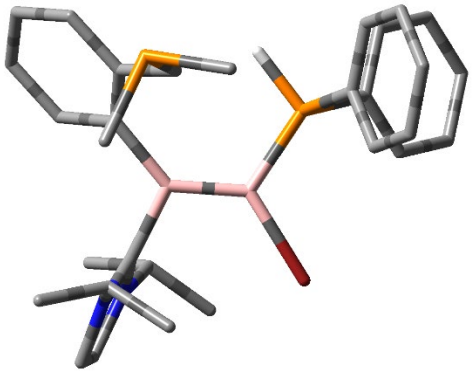
$G_{correction}$ = 0.381510 a.u

Cartesian coordinates:

C	-2.19316100	0.78019100	-0.10391600
C	-3.49534600	1.22345000	0.15128400
C	-1.31950800	0.48754900	0.97005400
C	-3.95565100	1.41104600	1.44920900
H	-4.15238700	1.44006100	-0.68814100
C	-1.81150100	0.69937300	2.26982200
C	-3.10127200	1.15750500	2.51672600
H	-3.43955200	1.30763400	3.53794900
B	0.16243300	-0.06590500	0.74896500
B	1.35995900	0.68488900	1.32468200
C	-1.73906300	0.68907100	-1.54222500
H	-0.77571700	0.17816500	-1.61306400
H	-2.46032000	0.12661400	-2.14734100
C	0.39618600	-1.38828000	-0.04106400
N	-0.39609900	-2.49781900	-0.03377500
N	1.39815100	-1.68028100	-0.92220400
C	-1.56048300	-2.71056100	0.83880900
C	0.10451000	-3.45575100	-0.89306700
C	1.22953400	-2.95022000	-1.44073600
C	2.48103900	-0.76654800	-1.29555600
H	-1.58767200	-1.84244200	1.49622900
H	-0.37338400	-4.41055000	-1.03535600
H	1.91557300	-3.38019100	-2.15072400
H	2.11775700	0.21759000	-0.97486800
Br	2.82373700	1.57789800	2.03106100
C	-2.84529700	-2.74311300	0.01797600
H	-2.97479700	-1.80292700	-0.52163700
H	-2.83937300	-3.57080700	-0.69952000
H	-3.70348300	-2.87390600	0.68213700
C	-1.36238800	-3.96231800	1.69058300
H	-2.16997600	-4.03271600	2.42355200
H	-1.38079100	-4.87694200	1.08865500
H	-0.41202100	-3.91734700	2.22814300
C	2.69285700	-0.75662800	-2.80690700
H	3.37935500	0.05254300	-3.06794500
H	3.13697600	-1.69001100	-3.16867700
H	1.74954000	-0.59055500	-3.33375200
C	3.75674900	-1.10354300	-0.52717600
H	4.52943600	-0.36050400	-0.74202700
H	3.57826900	-1.10318300	0.55066200
H	4.13703200	-2.08942300	-0.81591200
H	-4.96974900	1.75820500	1.62246900
H	-1.15511000	0.47737400	3.10725300
P	-1.57750200	2.38568000	-2.32673800
C	-0.41828000	3.18352400	-1.12418100
H	0.41079300	2.52241600	-0.85190400
H	-0.02868000	4.10740100	-1.56158600
H	-0.96263700	3.43866600	-0.21172900
C	-0.36105700	1.94927000	-3.66074300

H	-0.81749900	1.24732700	-4.36510500
H	-0.08014700	2.84757400	-4.21760000
H	0.54676000	1.49599500	-3.24595500

48) Intermediate **C7**



Note: Selected hydrogens are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -4579.99480255 a.u

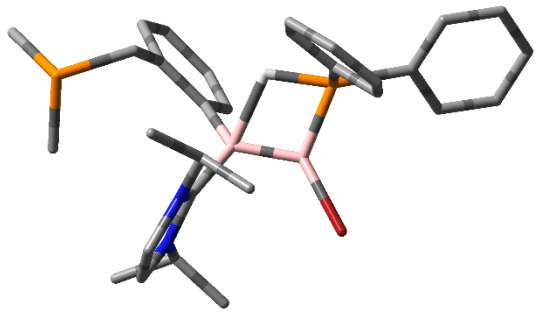
$G_{correction}$ = 0.568984 a.u

Cartesian coordinates:

B	1.16566700	-0.29272000	0.44007800
B	-0.13605900	-0.73989900	-0.30322100
P	0.16713000	4.33688300	0.61416400
C	1.42345900	0.62858000	1.71638100
C	2.34168400	0.16518300	2.68078800
H	2.83401900	-0.79051100	2.51059600
C	2.64062800	0.85816600	3.84430200
H	3.34875300	0.44903300	4.55953600
C	2.02297900	2.08199500	4.08430200
H	2.23645600	2.64175200	4.99003200
C	1.13437800	2.58657300	3.14583200
H	0.66563400	3.55155100	3.32155200
C	0.82920700	1.89260100	1.96629200
C	-0.13583900	2.53500000	0.99085200
H	-1.16038600	2.50290500	1.38475500
H	-0.14347200	1.96776600	0.05413000
C	1.65205300	4.17427400	-0.48348400
H	1.95350400	5.15599400	-0.85889800
H	2.48043000	3.76417200	0.10207200
H	1.45339100	3.51439900	-1.33566700
C	-1.14927200	4.53530200	-0.67698900
H	-1.04345600	5.50610600	-1.16946800
H	-1.11338100	3.74363200	-1.43351500
H	-2.13362100	4.50243400	-0.20184000
P	-1.80347100	-0.36258000	0.43295200
H	-1.61857000	0.21930200	1.69543900
C	-2.86279500	0.86676300	-0.42096300

C	-3.75127500	1.68374500	0.28145100
C	-2.72906100	1.01641500	-1.80373800
C	-4.49799400	2.64586500	-0.39036400
H	-3.85670200	1.57681700	1.35802600
C	-3.48370700	1.97475400	-2.47348800
H	-2.03583600	0.37800000	-2.34426200
C	-4.36282800	2.79226200	-1.76869300
H	-5.17931400	3.28484300	0.16241600
H	-3.37715400	2.08809400	-3.54745600
H	-4.94160900	3.54628500	-2.29267000
C	-2.94149000	-1.74240800	0.80182200
C	-3.80293700	-1.67970800	1.90071500
C	-2.96149300	-2.86692300	-0.02850500
C	-4.68148800	-2.72505800	2.16308000
H	-3.78493500	-0.81687600	2.56135000
C	-3.84598500	-3.90757700	0.23542100
H	-2.27704400	-2.92139500	-0.86909100
C	-4.70632900	-3.83857400	1.32737700
H	-5.34511100	-2.67185800	3.02028600
H	-3.85889900	-4.77665600	-0.41459600
H	-5.39454100	-4.65297100	1.53078600
C	2.48970800	-0.90029200	-0.20995000
N	3.31506300	-0.27889900	-1.07630300
N	2.97393900	-2.15406000	-0.08181100
C	3.05397700	1.07209100	-1.58850400
C	4.29790300	-1.14326000	-1.51311400
C	4.08591100	-2.32220500	-0.88363400
C	2.34359800	-3.20958900	0.72625500
H	2.33003900	1.48640800	-0.88375700
C	2.40042000	0.97776800	-2.96427800
C	4.31763500	1.92098700	-1.56749100
H	5.05395500	-0.85250000	-2.22311800
H	4.62429200	-3.25374100	-0.93809800
H	1.52028100	-2.69882900	1.23440000
C	1.75403900	-4.27674700	-0.19095800
C	3.33062300	-3.76706600	1.74586800
H	2.06160400	1.96689700	-3.28587800
H	3.11085200	0.60260200	-3.70932600
H	1.54332000	0.30083500	-2.92286200
H	5.06366900	1.55925500	-2.28318100
H	4.06544000	2.94767400	-1.84477700
H	4.76390900	1.93412800	-0.56990600
H	2.53926200	-4.82478200	-0.72377600
H	1.18004600	-4.99520400	0.40022900
H	1.08982300	-3.80344700	-0.91687900
H	2.82040500	-4.48942500	2.38795400
H	4.16408500	-4.28546900	1.25946100
H	3.73912900	-2.97424300	2.37792200
Br	-0.20681300	-1.71363500	-2.06587600

49) **TSC(7-8)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*991.3)

E_{total} = -4579.95267941 a.u

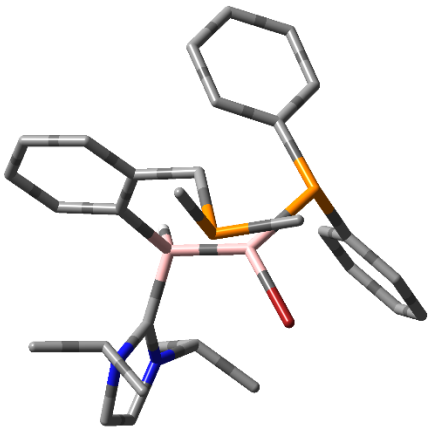
$G_{correction}$ = 0.566407 a.u

Cartesian coordinates:

B	0.60902800	0.55092000	0.20098600
B	-0.90581300	0.61877800	0.78268400
P	3.99679400	-1.00745000	-2.07015400
C	1.24278500	1.53759800	-0.88806200
C	0.98717500	2.91291100	-0.74580600
C	1.43565800	3.85850000	-1.66381100
H	1.21376500	4.91073200	-1.51331400
C	2.14313500	3.44120400	-2.78237700
H	2.47931600	4.15882500	-3.52452100
C	2.39827700	2.08507300	-2.95951300
H	2.90424600	1.75562900	-3.86271100
C	1.98289900	1.13126200	-2.02616600
C	2.26337700	-0.32468700	-2.30798900
H	2.02440900	-0.55817000	-3.35329800
H	1.60389300	-0.95711100	-1.70649800
P	-1.95834200	0.41610500	-0.73199900
H	-0.50672100	0.20216100	-1.23958400
H	0.40504000	3.23846200	0.11133500
C	-3.65103100	1.17116400	-0.72375600
C	-4.63861600	0.85297200	-1.66058500
C	-3.90961500	2.15553800	0.23232900
C	-5.86711400	1.50439900	-1.63475500
H	-4.44993300	0.08351000	-2.40463000
C	-5.14341300	2.79733200	0.26696800
H	-3.14497900	2.40337800	0.96506200
C	-6.12222200	2.47627900	-0.66946800
H	-6.62863700	1.25102700	-2.36607800
H	-5.34101900	3.54975400	1.02434000
H	-7.08277000	2.98169100	-0.64794700
C	-2.37305200	-1.35601500	-1.00156800
C	-1.67287400	-2.11793300	-1.94136300
C	-3.34762400	-1.98425200	-0.21827600

C	-1.93329400	-3.47656200	-2.09512100
H	-0.90964600	-1.64143500	-2.55251900
C	-3.61507700	-3.34034700	-0.37576800
H	-3.88987100	-1.40589900	0.52395700
C	-2.90777000	-4.09116400	-1.31238100
H	-1.38332200	-4.05198600	-2.83383700
H	-4.37109700	-3.81486500	0.24210600
H	-3.11619000	-5.14951800	-1.43410800
Br	-1.54716700	0.20642100	2.59834800
C	1.59151400	-0.31305900	1.12046200
N	2.42213800	0.16957700	2.06910800
N	1.64042200	-1.65595300	1.23613400
C	2.98008200	-0.86822200	2.78681000
C	2.49341800	-2.01522200	2.25838900
H	3.67251000	-0.70834800	3.59591800
H	2.67974800	-3.04407400	2.51704500
C	0.79488100	-2.59531200	0.47794200
H	0.28492400	-1.96954700	-0.25549400
C	2.59042000	1.60084400	2.37267400
H	2.21489700	2.12057600	1.48930600
C	-0.25962900	-3.19942000	1.39869200
H	0.19582500	-3.86433500	2.14127500
H	-0.80582600	-2.40769000	1.91586000
H	-0.96786500	-3.77958100	0.80191000
C	1.63996400	-3.64005900	-0.23855600
H	2.13640500	-4.31254600	0.46957200
H	0.98455800	-4.24716600	-0.86861600
H	2.40326100	-3.17963500	-0.87294500
C	1.73706900	1.97263100	3.58277300
H	2.12511600	1.49657900	4.48992100
H	1.75763000	3.05543200	3.73212200
H	0.70272400	1.65160400	3.43875100
C	4.06364300	1.94742000	2.55743000
H	4.16545700	3.02984600	2.66571500
H	4.47847800	1.48913100	3.46118200
H	4.65785500	1.62887800	1.69818100
C	4.98083700	0.01713700	-3.25960900
H	4.63915800	-0.16209500	-4.28310700
H	4.91744800	1.08774900	-3.04480500
H	6.02774200	-0.29343900	-3.19808600
C	4.53993800	-0.18484900	-0.50413400
H	4.16801500	0.84327600	-0.44272300
H	4.19932800	-0.75038300	0.36528900
H	5.63373100	-0.16977700	-0.48137900

50) Intermediate **C8**



Note: Selected hydrogens are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -4580.03289392 a.u

$G_{correction}$ = 0.570456 a.u

Cartesian coordinates:

B	-0.41646400	0.09062000	-0.55710300
H	-0.40242500	0.18352700	1.76995100
B	0.43005300	-0.09896000	0.91622800
C	-3.20931500	3.32049800	0.21093900
H	-4.00832900	3.06022400	-0.47827900
C	-2.39125400	4.69272000	2.01746600
H	-2.54408500	5.49179600	2.73625900
C	-3.40786200	4.34177300	1.13177100
H	-4.35704500	4.86856700	1.15353300
C	-1.17909400	4.01438500	1.96978700
H	-0.37623800	4.27862200	2.65103900
C	-0.98358300	2.98287200	1.05473700
H	-0.03174000	2.46745200	1.04680200
C	-3.22008100	0.24758200	-0.94247000
C	-3.92966300	0.15222000	0.26077800
H	-3.62302900	0.74975500	1.11369300
C	-5.03666200	-0.68510400	0.36706200
H	-5.58295600	-0.73481500	1.30443000
C	-5.43597800	-1.46131000	-0.71795200
H	-6.29894800	-2.11467300	-0.63524600
C	-4.72063900	-1.39327900	-1.91029300
H	-5.02381500	-1.99466900	-2.76172300
C	-3.62909400	-0.53864200	-2.02548100
H	-3.08640200	-0.48065900	-2.96362100
C	1.74239400	0.81108500	1.26939100
C	2.22167000	0.70470700	2.58713500
H	1.69497500	0.04209200	3.27075600
C	3.32505800	1.40635300	3.05563800
H	3.65364300	1.28456600	4.08383200

C	3.99113800	2.27815500	2.20034700
H	4.84871700	2.84755400	2.54541300
C	3.53005100	2.42745800	0.90040400
H	4.02903300	3.12854600	0.23524200
C	2.03580300	1.93518000	-1.02106200
H	0.96902000	1.75334800	-1.17522000
C	2.42639000	1.70842100	0.41926500
P	-1.75636300	1.36371600	-1.15853800
C	-1.99912900	2.61237800	0.17010600
H	2.19948500	2.98272500	-1.30230600
P	2.93981500	0.83419700	-2.23499400
Br	-0.19967000	-1.27716900	-1.95490600
C	0.71465400	-1.68373300	1.13270700
N	-0.20671300	-2.58060600	1.56072600
N	1.85531500	-2.39218500	0.98020700
C	-1.65381300	-2.33749200	1.67842300
C	0.36036200	-3.83208600	1.69094400
C	1.65516300	-3.71268200	1.33049100
C	3.09566200	-1.91609700	0.34345200
H	-1.78938000	-1.27604900	1.47446800
C	-2.13679100	-2.62276600	3.09508300
C	-2.38630300	-3.14004600	0.60698700
H	-0.20034600	-4.68981700	2.02275000
H	2.44262200	-4.44618100	1.28778200
H	2.91094100	-0.87513100	0.08918700
C	4.26604500	-1.99007600	1.31526100
C	3.32244600	-2.68313900	-0.95444000
H	-3.19963700	-2.37918700	3.17174000
H	-2.01591100	-3.67880700	3.35861800
H	-1.58760500	-2.01636100	3.81955200
H	-2.29639500	-4.21738900	0.78302500
H	-3.44542200	-2.87594700	0.60440100
H	-1.97186600	-2.90699200	-0.37631700
H	4.48951800	-3.02397300	1.60099200
H	5.15682700	-1.57320700	0.83870400
H	4.05492200	-1.40747000	2.21477400
H	4.15781500	-2.23586300	-1.49706500
H	3.54984600	-3.73904800	-0.77132000
H	2.42986300	-2.60613300	-1.57915200
C	1.99925100	1.28226100	-3.76483400
H	1.01969400	0.79827100	-3.71796900
H	1.86240500	2.36310200	-3.87465500
H	2.52383300	0.89979600	-4.64489800
C	4.47727100	1.83880000	-2.48294500
H	5.07982700	1.80449900	-1.57088000
H	5.06955600	1.40330600	-3.29272100
H	4.26295600	2.88570600	-2.72518600

REACTION 4

Pathway 1 of reaction 4

As shown in Figure S32, the mechanistic pathway for this reaction can be described in straightforward terms. This pathway involves coordination of PPh_2H to the boryl boron atom, followed by a 1,3-proton shift.

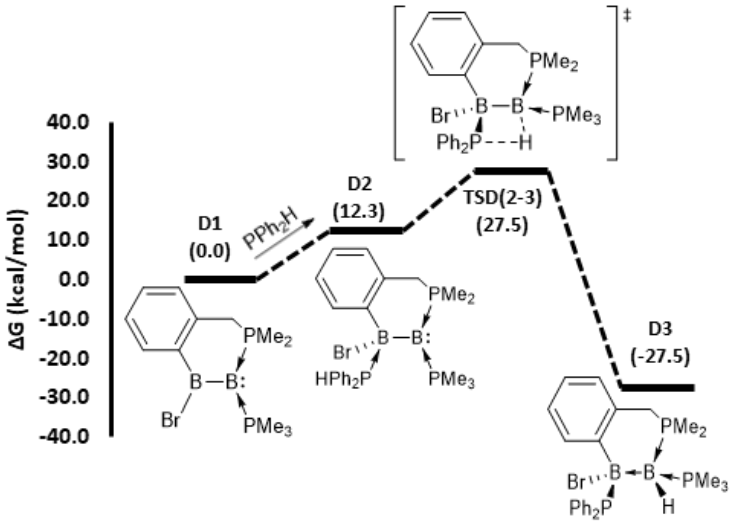
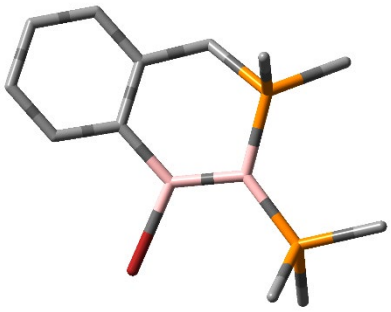


Figure 32. Computed mechanism 1 for a net 1,2-hydrophosphination of the borylborylene **D1**. The transition state computed for phosphine association step (**D1** to **D2**) is not included in the free energy profile as the barrier for this step has an energy just above that of the higher energy intermediate ($\Delta G^{\ddagger}$ = 14.3 kcal/mol).

51) Diborene **D1**



Note: Hydrogens are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -3773.97767586 a.u

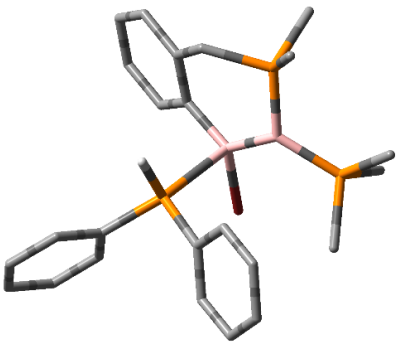
$G_{correction}$ = 0.266486 a.u

Cartesian coordinates:

Br	0.21442800	-2.62542200	-0.15424700
C	-1.87864800	-0.43614300	-0.10538400
P	0.08249900	2.09884800	-0.03588400
B	-0.31622600	-0.68851400	-0.16962800

B	0.82039000	0.42426300	-0.13548300
P	2.60551000	0.01377200	0.08587000
C	-2.78493200	-1.43875000	0.27205800
H	-2.40099500	-2.43605100	0.46207200
C	-4.65298300	0.07266800	0.17715700
H	-5.71314400	0.27697300	0.29154300
C	-4.14647500	-1.19847300	0.41750700
H	-4.81012000	-2.00339900	0.71911200
C	-2.41844300	0.84790800	-0.35727800
C	-3.78435200	1.08665500	-0.21322700
H	-4.17733300	2.08116900	-0.41191400
C	-1.55035500	1.98987800	-0.84576500
H	-2.07051800	2.94770000	-0.73629200
H	-1.32555400	1.85294800	-1.91109900
C	-0.27516400	2.81699200	1.61889400
H	-0.77450700	3.78828300	1.54867500
C	0.89512500	3.50274000	-0.89334200
H	1.85056100	3.72733400	-0.41228100
C	3.73294000	1.45219200	0.19214000
H	3.44076200	2.09336800	1.02801200
H	3.67757100	2.02909300	-0.73395100
H	4.76360600	1.12213100	0.34473900
C	3.30305000	-0.99252000	-1.27160300
H	4.32299700	-1.31994100	-1.05114200
H	3.28951600	-0.40516300	-2.19227500
H	2.64946800	-1.85841100	-1.40091200
C	3.00310200	-0.96370900	1.58262600
H	2.33923900	-1.83162800	1.58645800
H	2.79160900	-0.36026400	2.46837000
H	4.04739800	-1.28933200	1.59407900
H	1.08324900	3.22765300	-1.93327700
H	0.26920300	4.39923200	-0.85995100
H	0.65930900	2.92951300	2.17517300
H	-0.91543200	2.11389000	2.15657200

52) **TSD(1-2)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*149.9)

E_{total} = -4579.06905149 a.u

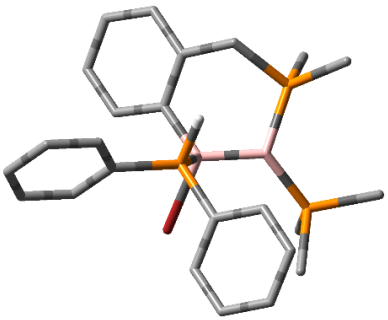
$G_{correction}$ = 0.446618 a.u

Cartesian coordinates:

Br	0.25128100	0.14574100	2.36384600
P	1.31165700	-0.16118000	-0.73798200
C	-0.24727500	2.29379900	0.23122600
B	-0.51174500	0.74928800	0.55002100
P	-2.73072300	0.89270600	-1.24190200
C	0.46141900	3.13256700	1.10184100
H	0.86528400	2.70519500	2.01363600
B	-1.81069700	-0.07832400	-0.00506400
C	0.65021300	4.48574800	0.84381100
H	1.20802600	5.09820000	1.54607300
P	-2.59495900	-1.44724400	0.94040500
C	0.12131700	5.04970800	-0.31047900
H	0.25579700	6.10600900	-0.52244700
C	-0.77358900	2.88471500	-0.94124400
C	-0.58955400	4.24461500	-1.19349500
H	-1.00745100	4.67981100	-2.09848500
C	-1.52790700	2.06840400	-1.96862500
H	-0.83665300	1.44747100	-2.55219200
H	-2.04970800	2.72351800	-2.67441300
C	1.13517600	-1.96639700	-0.92467500
C	0.22186100	-2.49340300	-1.84355900
H	-0.33301900	-1.82517000	-2.49359000
C	0.02127500	-3.86832000	-1.92982400
H	-0.68085300	-4.26547500	-2.65670600
C	0.72031000	-4.73040900	-1.08939000
H	0.56663000	-5.80264800	-1.15947500
C	1.62009800	-4.21136700	-0.16147200
H	2.16859300	-4.87748000	0.49686300
C	1.82615000	-2.83829800	-0.07857000
H	2.53440300	-2.44205300	0.64329600
C	3.12157100	0.07131300	-0.55196100
C	4.00508400	0.05214800	-1.63647600
H	3.62542200	-0.12277100	-2.63918900
C	5.36610900	0.25155600	-1.43815100
H	6.04478800	0.23791000	-2.28539500
C	5.85957100	0.46510300	-0.15256500
H	6.92292800	0.61943000	0.00176300
C	4.98804400	0.48604400	0.93122500
H	5.36873600	0.65781900	1.93306800
C	3.62254000	0.29846600	0.73424100
H	2.93332100	0.33018800	1.57370500
C	-3.28304200	-0.99705900	2.58468500
H	-2.47505700	-0.52856700	3.15194800
H	-3.67195900	-1.86367700	3.12850700
H	-4.07686400	-0.25874100	2.44529400
C	-1.49687200	-2.85163700	1.34221200
H	-1.24049800	-3.38481000	0.42506100
H	-1.97476500	-3.53275900	2.05201500
H	-0.58203900	-2.44336200	1.77559500
C	-4.02383700	-2.23433100	0.10428900
H	-3.69670800	-2.65253600	-0.85026200
H	-4.80507500	-1.49176200	-0.08073000
H	-4.44097900	-3.03218800	0.72420000

C	-4.13763300	1.97629200	-0.73527700
H	-4.91938400	1.36504900	-0.27487200
C	-3.44861100	0.05948200	-2.71750900
H	-3.86916700	0.78298900	-3.42268100
H	-4.56545100	2.52961600	-1.57764700
H	-3.76391600	2.67870600	0.01346300
H	-2.66701300	-0.52253700	-3.21077100
H	-4.24033500	-0.62649500	-2.40495000
H	1.15622500	0.21868600	-2.08943700

53) Intermediate **D2**



Note: Selected hydrogens are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -4579.07244061 a.u

$G_{correction}$ = 0.447562 a.u

Cartesian coordinates:

Br	0.29176200	-0.21656400	2.27923500
P	1.11929500	-0.32546700	-0.75079100
C	0.08178200	2.17366500	0.33305400
B	-0.24857200	0.59641100	0.42221400
P	-2.53421900	1.24409100	-1.25197500
C	0.80056100	2.84959700	1.32859800
H	1.14132500	2.28617800	2.19095900
B	-1.72640500	0.01761200	-0.18072600
C	1.06391700	4.21331800	1.26360800
H	1.62158200	4.69465900	2.06176000
P	-2.76107900	-1.19291500	0.72434100
C	0.60478800	4.95608900	0.18299900
H	0.79810000	6.02256600	0.11882600
C	-0.38223600	2.94725400	-0.75646100
C	-0.12022500	4.31753700	-0.81607100
H	-0.49250800	4.89298800	-1.66061100
C	-1.19062300	2.32990100	-1.87730600
H	-0.56955000	1.69714400	-2.52187500
H	-1.62344800	3.10858600	-2.51399800
C	0.93268300	-2.12890100	-0.83235000
C	0.15767800	-2.71635200	-1.83439000
H	-0.31994900	-2.09103200	-2.58123400
C	-0.02050900	-4.09627200	-1.85991100
H	-0.61720400	-4.54881000	-2.64559000

C	0.55956400	-4.89191300	-0.87568900
H	0.41690200	-5.96783200	-0.89377900
C	1.32195000	-4.30706000	0.13205800
H	1.77079900	-4.92454900	0.90322100
C	1.51298800	-2.92984200	0.15348800
H	2.10231700	-2.47555000	0.94352800
C	2.92422000	-0.05211600	-0.61268500
C	3.73044700	-0.00720900	-1.75440000
H	3.28927800	-0.15333500	-2.73681000
C	5.09673700	0.22129200	-1.64086600
H	5.71536600	0.25416700	-2.53217700
C	5.66834100	0.40817500	-0.38474600
H	6.73515500	0.58704500	-0.29482400
C	4.87061400	0.37041500	0.75456700
H	5.31300400	0.52210700	1.73386100
C	3.50161300	0.14682800	0.64504700
H	2.87385700	0.12433600	1.53074400
C	-3.36415300	-0.70434300	2.39804500
H	-2.49150400	-0.40070200	2.98105000
H	-3.89414400	-1.51414200	2.91059700
H	-4.02441600	0.16084300	2.29410400
C	-1.98057900	-2.81052500	1.07527800
H	-1.77112800	-3.32547500	0.13603300
H	-2.62222400	-3.42934000	1.70920400
H	-1.03373200	-2.61920200	1.58396200
C	-4.32594800	-1.64244700	-0.12241400
H	-4.10291300	-2.08493800	-1.09539100
H	-4.93861000	-0.74883800	-0.27125500
H	-4.89615200	-2.35533600	0.47910800
C	-3.75564800	2.47546300	-0.59936500
H	-4.62840200	1.94835700	-0.20226800
C	-3.39926300	0.70543600	-2.78695400
H	-3.72050900	1.56194800	-3.38808300
H	-4.08723400	3.19007900	-1.36033100
H	-3.27550600	3.01239200	0.22229200
H	-2.72473000	0.07501600	-3.36996300
H	-4.27993300	0.11311200	-2.52435700
H	0.90716500	0.04360700	-2.08981500

54) **TSD(2-3)**

(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*1119.9)

E_{total} = -4579.04735622 a.u

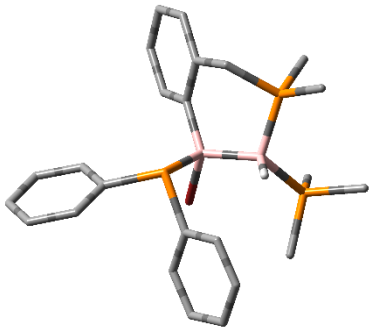
$G_{correction}$ = 0.445249 a.u

Cartesian coordinates:

Br	-0.11968600	-2.42220600	1.45914700
P	1.07144700	-0.37376200	-0.81148900
C	-0.17261000	0.61809900	1.79959500
B	-0.32265400	-0.49778600	0.64498400
P	-2.55151700	1.14826900	-0.33829300
C	0.56328600	0.34685400	2.96523400
H	0.99314300	-0.64265000	3.08200100
B	-1.55581100	-0.38746000	-0.55972900
C	0.75228100	1.28322600	3.97340300
H	1.33626800	1.02251900	4.85132200
P	-2.47671900	-1.89905700	-1.10643900
C	0.18130600	2.54555700	3.85850400
H	0.30759200	3.28760100	4.64108900
C	-0.73811200	1.91015200	1.69995500
C	-0.56318600	2.84414300	2.72635600
H	-1.01496800	3.82859700	2.62685700
C	-1.50020200	2.39351000	0.48220800
H	-0.80445600	2.74463200	-0.28683300
H	-2.13485900	3.24682900	0.74621100
C	2.86671100	-0.83586100	-0.71480100
C	3.86150600	-0.21295700	-1.47902100
H	3.60904500	0.63493100	-2.10919400
C	5.17579800	-0.66326200	-1.42570600
H	5.93968700	-0.17056900	-2.01982400
C	5.51428600	-1.73781800	-0.60601100
H	6.54210200	-2.08481900	-0.56058200
C	4.53133000	-2.36507500	0.15375300
H	4.79014600	-3.20167700	0.79559300
C	3.21278800	-1.92485100	0.09408300

H	2.44081800	-2.41895400	0.67643300
C	1.20455700	1.40355700	-1.22301300
C	0.66863400	1.91622900	-2.40785100
H	0.17589900	1.24323200	-3.10328300
C	0.73897800	3.27860100	-2.68514900
H	0.31757100	3.66634100	-3.60775900
C	1.35120400	4.14248700	-1.77959100
H	1.40350600	5.20589000	-1.99144200
C	1.90211700	3.63793300	-0.60429700
H	2.37857000	4.30646800	0.10539700
C	1.83126300	2.27634800	-0.32797000
H	2.24423200	1.89086700	0.59916500
H	-0.11276200	-0.65564300	-1.74253800
C	-3.47991600	-2.79814300	0.14526300
H	-2.82042900	-3.02664600	0.98543800
H	-4.27933000	-2.14118200	0.49828200
H	-3.91418400	-3.71847400	-0.25748800
C	-3.69467100	-1.60173300	-2.44411200
H	-3.19868300	-1.11929300	-3.28884200
H	-4.14340300	-2.54285100	-2.77288300
H	-4.49128800	-0.94614000	-2.08148300
C	-1.38876400	-3.20523300	-1.77684200
H	-1.96574000	-4.09846000	-2.03042500
H	-0.87468900	-2.83110700	-2.66499300
H	-0.64922700	-3.44625900	-1.01017100
C	-3.14295100	2.03475600	-1.83089800
H	-3.81901300	1.39798500	-2.40624500
H	-3.66354400	2.95891000	-1.56351800
H	-2.27471600	2.27221100	-2.44968000
C	-4.06010000	1.08610800	0.71839700
H	-4.51988000	2.07214200	0.83830400
H	-4.79339400	0.40162700	0.28227800
H	-3.76404000	0.69987400	1.69675400

55) Product **D3**



Note: Selected hydrogens are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -4579.13418990 a.u

$G_{correction}$ = 0.449264 a.u

Cartesian coordinates:

Br	-0.54706200	-0.03685900	-2.03845400
P	-1.21157800	0.07884100	1.25002400
C	0.63259900	2.01392000	-0.13047200
B	0.19718400	0.43957600	-0.12834200
P	2.80649800	0.37000200	1.29788600
C	0.37613100	2.88981200	-1.19832200
H	-0.11300100	2.49213300	-2.08116800
B	1.50866000	-0.67655900	0.36407500
H	1.19733200	-1.47595500	1.22345100
C	0.72265900	4.23633000	-1.17254800
H	0.48542700	4.86733600	-2.02427900
P	2.22802400	-1.84007400	-0.97145100
C	1.36863400	4.77088000	-0.06450200
H	1.63707300	5.82202100	-0.02780400
C	1.32705500	2.57842700	0.96673300
C	1.68379500	3.92806000	0.99302900
H	2.21512400	4.32115800	1.85702800
C	1.81970200	1.69022100	2.08599900
H	0.99774000	1.19112900	2.61341000
H	2.42987000	2.24284300	2.80689300
C	-1.57684000	-1.71458400	0.98165600
C	-1.06663200	-2.65799800	1.87978900
H	-0.52171000	-2.31196900	2.75390600
C	-1.24857800	-4.02463800	1.67546700
H	-0.84638800	-4.73773800	2.38971000
C	-1.96572600	-4.47187800	0.56966800
H	-2.11920900	-5.53506200	0.40994600
C	-2.50177100	-3.54384600	-0.32107000
H	-3.07100800	-3.88339000	-1.18152100
C	-2.31097200	-2.18155400	-0.11703000
H	-2.71693700	-1.46729600	-0.82435700
C	-2.81407300	0.81092800	0.70746100
C	-4.00236800	0.33705900	1.28272000
H	-3.96090300	-0.48035600	1.99777200
C	-5.23353600	0.88697500	0.94813000
H	-6.13893800	0.49651200	1.40371800
C	-5.30567200	1.93674000	0.03512000
H	-6.26580300	2.37207000	-0.22494900
C	-4.13538900	2.42326300	-0.53566400
H	-4.17681200	3.23978500	-1.25067500
C	-2.90295600	1.86269400	-0.20865400
H	-2.00655800	2.25985200	-0.66622900
C	2.77626400	-1.04519500	-2.51516600
H	1.93513400	-0.45763900	-2.89046400
H	3.08038800	-1.78973900	-3.25484500
H	3.61677500	-0.37893100	-2.30360500
C	1.00422100	-3.11190300	-1.39524000
H	0.71579300	-3.63960000	-0.48181900
H	1.40840200	-3.81399200	-2.12877400
H	0.12069500	-2.60578400	-1.78788200
C	3.68851600	-2.78736900	-0.40367300

H	3.44447600	-3.29787800	0.53111600
H	4.53050700	-2.11192100	-0.22800500
H	3.98510400	-3.52935900	-1.14958400
C	4.07969800	1.22339500	0.30877000
H	4.79074600	0.49561100	-0.09178900
C	3.71136600	-0.48744200	2.63073500
H	4.32043300	0.21357800	3.20734800
H	4.61896100	1.95476300	0.91597300
H	3.58501600	1.74226400	-0.51517800
H	2.98237300	-0.96099100	3.29218400
H	4.35694900	-1.26379600	2.21317400

Opposite 1,2-hydrophosphination path using borylborylene D1

While the 1,2-hydrophosphinated product obtained experimentally complies with the computed partial charges argument and places the phosphinyl unit on the boryl boron atom and the hydride substituent on the borylene boron atom, we wanted to compare this to the inverse situation, with the phosphinyl unit ultimately bound to the borylene boron atom and the hydride substituent on the boryl boron atom. The computed free energy profile, as shown in Figure S33, shows a free energy barrier of 47.9 kcal/mol, which in comparison to the computed feasible pathway is 20.4 kcal/mol higher in energy. This strongly suggests that hydrophosphination outcomes are dictated by the partial charge distribution.

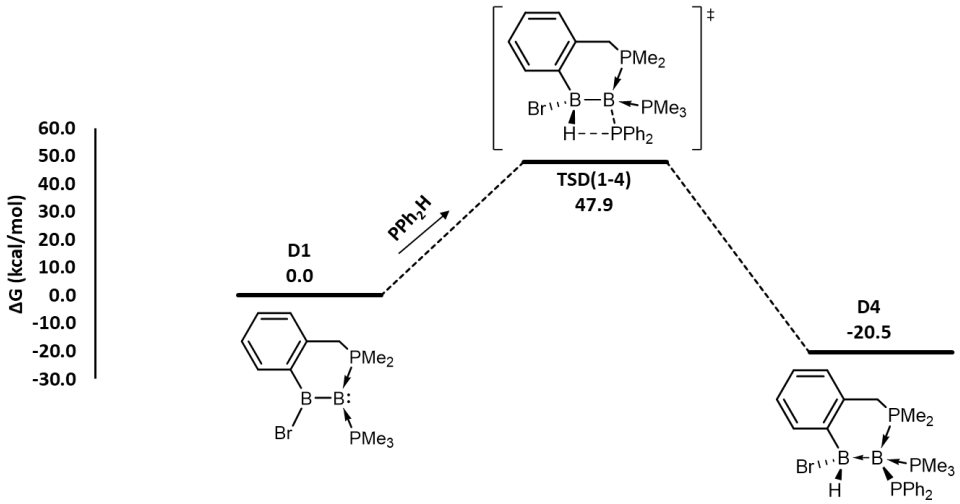
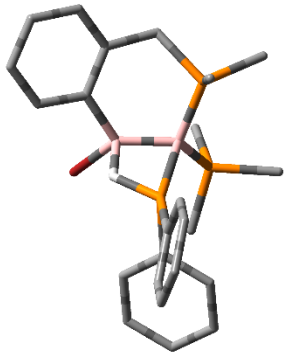


Figure S33. Computed pathway for the contrasting 1,2-hydrophosphination of borylborylene **D1**.

Note: Details of species **C1** are provided above in Pathway 1 of reaction 4.

56) **TSD(1-4)**



(Selected hydrogens are omitted for clarity)

Number of imaginary frequencies = 1 (*i*1119.9)

E_{total} = -4579.00598522 a.u

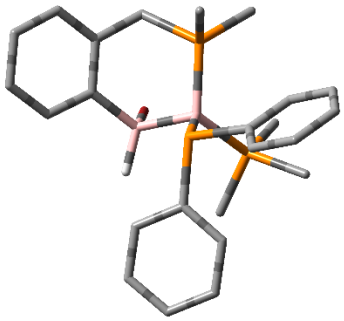
$G_{correction}$ = 0.443134 a.u

Cartesian coordinates:

B	0.99666300	-0.49517700	0.79799300
P	1.71820800	0.77148200	1.98885400
B	1.27576300	0.02202300	-0.74272700
P	-1.37292000	0.67532200	0.13629400
C	2.84885000	2.08291600	-0.15811900
C	1.99312400	1.42468800	-1.06453400
C	3.40502700	3.32619500	-0.47176500
H	4.06046200	3.81638600	0.24463400
C	1.75154800	2.07004300	-2.28655200
H	1.10357600	1.57781300	-3.00693900
C	2.30830700	3.30166300	-2.60454700
H	2.09244400	3.76643400	-3.56191700
C	3.14187700	3.93829200	-1.68989100
H	3.58268300	4.90331600	-1.92025300
C	3.20467600	1.46481900	1.18110300
H	3.67812800	2.20217100	1.83899300
H	3.90387400	0.62909200	1.05297500
H	-0.07492800	0.41943200	-0.98975700
C	-3.07559200	1.48759500	0.21517700
C	-3.10817400	2.71249700	0.89746800
C	-4.25587700	1.05906100	-0.41047300
C	-4.27168300	3.47077200	0.97781000
H	-2.19919900	3.07796900	1.37219700
C	-5.41885800	1.81961600	-0.34660400
H	-4.26659100	0.11845100	-0.95284700
C	-5.43286800	3.02383100	0.35369600
H	-4.27287300	4.41146500	1.52083000
H	-6.32028600	1.46952700	-0.84124500
H	-6.34393200	3.61215700	0.40831300
C	-2.02440700	-0.99308700	-0.33532300
C	-1.84829100	-1.54322300	-1.60824400

C	-2.81056700	-1.70007500	0.58714300
C	-2.42860100	-2.76594200	-1.94324600
H	-1.22400000	-1.03312500	-2.33371900
C	-3.40246400	-2.91230000	0.25093600
H	-2.97794500	-1.27907300	1.57525500
C	-3.21030200	-3.45220400	-1.02071000
H	-2.26913700	-3.17902900	-2.93454700
H	-4.01440600	-3.43675100	0.97898500
H	-3.67008800	-4.39869800	-1.28740700
P	1.17145500	-2.31832100	1.22196400
Br	1.68450900	-1.34187400	-2.21538300
C	0.23278600	-3.48288800	0.19185600
H	-0.83021800	-3.40782500	0.42117200
H	0.39542500	-3.23597200	-0.85707900
H	0.58725900	-4.49598500	0.40148800
C	2.90629900	-2.86797700	1.01626900
H	3.02304400	-3.93594700	1.22200300
H	3.17503200	-2.65497900	-0.02252700
H	3.56352100	-2.29518300	1.67542600
C	0.71349200	-2.82574800	2.92022900
H	0.81177300	-3.90956500	3.02479400
H	1.35003200	-2.34472600	3.66390700
H	-0.32544000	-2.54013800	3.10095300
C	0.72360400	2.24849000	2.38449300
H	0.45712100	2.74775100	1.45166400
H	-0.19410000	1.95057300	2.89395200
H	1.30965600	2.92676200	3.01127900
C	2.31089500	0.21422000	3.63076000
H	1.46692400	-0.11055600	4.24348100
H	3.01599100	-0.61342800	3.52072700
H	2.81829300	1.03828900	4.13901600

57) D4 (oppositely hydrophosphinated product)



Note: Selected hydrogens are omitted for clarity.

Number of imaginary frequencies = 0

E_{total} = -4579.12623618 a.u

$G_{correction}$ = 0.451955 a.u

Cartesian coordinates:

B	0.20139100	0.24114000	0.39977000
P	1.02872700	2.00338500	0.19138800
B	1.58929200	-0.86177700	0.09764900
P	-1.06675100	0.01068700	-1.10976400
C	2.94815000	0.84601400	-1.38986200
C	2.43142800	-0.45169600	-1.20290000
C	3.59219500	1.20788800	-2.57230000
H	3.97820300	2.21824700	-2.69011400
C	2.62908300	-1.36343800	-2.24675000
H	2.26863200	-2.38143700	-2.12103300
C	3.27766700	-1.01347500	-3.42741900
H	3.40919500	-1.75030900	-4.21458900
C	3.75889200	0.28033300	-3.59566700
H	4.26441100	0.56596500	-4.51304700
C	2.79518900	1.84894200	-0.27377100
H	3.15773700	2.84276500	-0.55676100
H	3.33129400	1.50850700	0.61717500
H	1.25796900	-2.02063400	0.08107600
C	-2.57313000	1.05251100	-0.86179900
C	-2.66950500	2.10228900	0.05681400
C	-3.64746700	0.87220800	-1.74761100
C	-3.78737500	2.93292600	0.10380100
H	-1.85895100	2.27571300	0.75932100
C	-4.77298000	1.68460400	-1.69507000
H	-3.59803400	0.07764100	-2.48711400
C	-4.84820800	2.72328100	-0.76905700
H	-3.82927900	3.73854300	0.83096500
H	-5.59007100	1.51460500	-2.38942300
H	-5.72295000	3.36460200	-0.73349300
C	-1.74641300	-1.69272700	-0.90155300
C	-0.94584200	-2.75319500	-1.34666000
C	-2.98985300	-2.00150700	-0.33713800
C	-1.34420600	-4.07397900	-1.17400900
H	0.00308500	-2.53649300	-1.82424900
C	-3.39698600	-3.32328100	-0.17652900
H	-3.66231500	-1.20446600	-0.03547700
C	-2.56890100	-4.36591100	-0.57949500
H	-0.69647700	-4.87655100	-1.51243600
H	-4.36468400	-3.53498400	0.26830100
H	-2.88119600	-5.39679900	-0.44597400
P	-0.51515000	-0.24386400	2.16308100
Br	2.92669600	-0.78227300	1.77702100
C	-0.36517000	-2.04518100	2.38703900
H	-0.84563000	-2.55905200	1.55242800
H	0.69596500	-2.29883100	2.40266500
H	-0.84137100	-2.33341600	3.32784700
C	0.27431900	0.47518400	3.64909000
H	-0.06757000	-0.07412300	4.53062900
H	1.35615300	0.37550400	3.55153900
H	-0.00796900	1.52430900	3.75842500
C	-2.28256400	0.06942200	2.52200400
H	-2.53934700	-0.43280900	3.45891800
H	-2.47647300	1.13739700	2.62829700
H	-2.91121900	-0.32010600	1.72335100
C	0.37819300	3.01579000	-1.18219700
H	0.52704300	2.45820900	-2.10985100
H	-0.68421000	3.22917300	-1.06559100

H	0.94054400	3.95222600	-1.23212200
C	1.04266100	3.11424300	1.64078700
H	0.02667700	3.32195400	1.98579800
H	1.60810800	2.63880600	2.44453500
H	1.52751100	4.05800900	1.37812500

Crystallographic Details

The crystal data of **Compound 5** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[15] refined with the SHELXL program[16] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except H1 were assigned to idealised positions. The coordinates of H1 were refined freely.

The crystal data of **Compound 6** were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[15] refined with the SHELXL program[16] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except H1 were assigned to idealised positions. The coordinates of H1 were refined freely.

The crystal data of **Compound 7** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[15] refined with the SHELXL program[16] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except H1 were assigned to idealised positions. The coordinates of H1 were refined freely. The structure was refined using the TWIN keyword (matrix: TWIN). The BASF parameter was refined to 3%.

The crystal data of **Compound 8** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[15] refined with the SHELXL program[16] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except H1 were assigned to idealised positions. The coordinates of H1 were refined freely.

The crystal data of **Compound 10** were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated $Mo_{K\alpha}$ radiation. The structure was solved using the intrinsic phasing method,[15] refined with the SHELXL program[16] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms except H1 were assigned to idealised positions. The coordinates of H1 were refined freely.

The unit cell contains one hexane molecule that was treated as a diffuse contribution to the overall scattering without specific atom positions by SQUEEZE/PLATON.[17]

Data	**5**	**6**	**7**	**8**	**10**
Empirical formula	$C_{50}H_{67}B_2P_3$	$C_{34}H_{48}B_2BrP_3$	$C_{40}H_{55}B_2BrN_2P_2$	$C_{34}H_{48}B_2BrP_3$	$C_{58}H_{71}B_2N_4P$
Formula weight ($g \cdot mol^{-1}$)	782.56	651.16	727.33	651.16	876.77
Temperature (K)	100(2)	100(2)	100(2)	100(2)	107(2)
Radiation, λ (Å)	$Mo_{K\alpha}$ 0.71073	$Mo_{K\alpha}$ 0.71073	$Mo_{K\alpha}$ 0.71073	$Mo_{K\alpha}$ 0.71073	$Mo_{K\alpha}$ 0.71073
Crystal system	Triclinic	Orthorhombic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$	*Pbca*	*Fdd*2	$P2_1/n$	$P\bar{1}$
Unit cell dimensions					
a (Å)	10.6022(5)	10.5062(8)	28.3736(16)	11.8091(5)	11.3635(4)
b (Å)	10.6218(5)	17.5469(13)	57.198(3)	16.5734(7)	13.0900(5)
c (Å)	20.1023(10)	36.649(3)	10.0055(5)	17.4767(8)	19.2394(6)
α (°)	94.418(2)	90	90	90	89.9680(10)
β (°)	99.288(2)	90	90	107.828(2)	76.3530(10)
γ (°)	100.371(2)	90	90	90	70.1810(10)
Volume ($Å^3$)	2184.47(18)	6756.3(9)	16237.9(16)	3256.2(2)	2606.41(16)
Z	2	8	16	4	2
Calculated density ($Mg \cdot m^{-3}$)	1.190	1.280	1.190	1.328	1.117
Absorbtion coefficient (mm^{-1})	0.170	1.381	1.120	1.433	0.093
F(000)	844	2736	6144	1368	944
Theta range for collection	2.314 to 26.022°	2.223 to 26.022°	2.408 to 27.205°	2.448 to 26.022°	2.187 to 26.021°
Reflections collected	57183	108270	24574	28879	74317
Independent reflections	8565	6644	8889	6411	10258
Minimum/maximum transmission	0.7003/0.7455	0.6110/0.7455	0.6841/0.7455	0.6566/0.7455	0.7154/0.7454
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	Full-matrix least-squares on F^2
Data / parameters / restrains	8565 / 500 / 0	6644 / 368 / 0	8889 / 434 / 1	6411 / 368 / 0	10258 / 598 / 0
Goodness-of-fit on F^2	1.058	1.057	0.974	0.900	1.031
Final R indices [I>2σ(I)]	$R_1 = 0.0349$, $wR^2 = 0.0842$	$R_1 = 0.0294$, $wR^2 = 0.0698$	$R_1 = 0.0368$, $wR^2 = 0.0701$	$R_1 = 0.0391$, $wR^2 = 0.1118$	$R_1 = 0.0521$, $wR^2 = 0.1174$
R indices (all data)	$R_1 = 0.0385$, $wR^2 = 0.0866$	$R_1 = 0.0353$, $wR^2 = 0.0727$	$R_1 = 0.0483$, $wR^2 = 0.0752$	$R_1 = 0.0572$, $wR^2 = 0.1289$	$R_1 = 0.0660$, $wR^2 = 0.1270$
Maximum/minimum residual electron density ($e \cdot Å^{-3}$)	0.377 / –0.296	0.635 / –0.325	0.329 / –0.513	0.372 / –0.620	0.670 / –0.430
CCDC Number	1954176	1954177	1954178	1954179	1954180

References

1. T. E. Stennett, J. D. Mattock, L. Pentecost, A. Vargas and H. Braunschweig, *Angew. Chem. Int. Ed.*, 2018, **57**, 15276-15281.
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