Supporting Information

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Metal-free catalytic hydrogenation of enamines, imines and conjugated phosphinoalkenylboranes.

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(Dedicated to Professor Reinhard W. Hoffmann on the occasion of his 75th birthday)

Experimental Section

Materials: All reactions involving air or moisture-sensitive compounds were carried out under an inert gas (argon) using Schlenk-type glassware or a glovebox. Solvents were dried and distilled prior to use. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Bis(pentafluorophenyl)boran¹ and Chlorodimesitylphosphane² were prepared according to literature procedures. Hydrogen (H₂ 5.0; purity ≥ 99.999 %) and deuterium (Aldrich; 99.8 atom% ²H) for hydrogenation experiments was taken directly from the gas bottle. Hydrogenations at 60 bar were carried out in a standard steel autoclave with a special protection ventile, which was filled in the glove box under an argon atmosphere.

Techniques: The following instruments were used for physical characterisation of the compounds: melting points: DSC 2010 TA-instruments; elemental analyses: Foss–Heraeus CHNO-Rapid; NMR: Bruker AV 300 (¹H: 300 MHz; ¹³C: 75 MHz; ³¹P: 122 MHz; ¹⁹F: 282 MHz), Bruker AV 400 (¹H: 400 MHz; ¹³C: 101 MHz), Varian UNITY plus NMR spectrometer (¹H: 600 MHz, ¹³C: 151 MHz; ³¹P: 243 MHz; ¹⁹F: 564 MHz); UV-spectroscopy: Varian Cary 1.3 Bio; IR-spectroscopy: Varian Excalibur 3600 FT-IR; X-Ray Crystal Structure Determinations: Data sets were collected with Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, Methods in Enzymology, 1997, 276, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Cryst. 2003, A59, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, Acta Cryst. 1990, A46, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHARAL (E. Keller, 1997). CCDC 679345 & 679346 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

Dimesitylvinylyphosphane. Chlorodimesitylphosphane (5.13 g, 16.8 mmol) was dissolved in thf (60 ml). 0.7 M vinylmagnesium bromide solution in thf (24.0 ml, 16.8 mmol) was added. The solution was stirred for 1h at room temperature, the solvent was removed on the rotary evaporator and the residue was extracted with pentane (100 ml). The pentane phase was removed in the oil pump vacuum and a brown oil could be obtained (3.93 g, 79%). The crude product was purified via column-chromatography (silica gel; CH$_2$Cl$_2$ : cyclohexane 2 : 8, R$_f$ = 0.49). A colorless oil (2.37 g, 48 %) which solidified after a few days (2.37 g, 48 %) could be obtained.

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{P} \quad \text{C} \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{P} \quad \text{C} \quad \text{CH}_3
\end{align*}
\]

m.p. 59°C; $^1$H-NMR (500 MHz, 298 K, benzene-d$_6$): δ 6.98 (1H, ddd, $^2$J$_{PH}$ = 26.4 Hz, $^3$J$_{HH,\text{trans}}$ = 18.0 Hz, $^3$J$_{HH,\text{cis}}$ = 11.7 Hz, $^6$CH$^+$), 6.69 (4H, dm, $^4$J$_{PH}$ = 2.6 Hz, m-Mes), 5.35 (1H, ddd, $^3$J$_{PH,\text{trans}}$ ≈ 30 Hz, $^3$J$_{HH,\text{cis}}$ = 11.7 Hz, $^3$J$_{HH}$ = 2.2 Hz, =CH$_2$(E)), 5.29 (1H, ddd, $^3$J$_{HH,\text{trans}}$ = 18.0 Hz, $^3$J$_{HH,\text{cis}}$ = 11.9 Hz, $^2$J$_{HH}$ = 2.2 Hz, =CH$_2$(Z)), 2.34 (12H, s, o-CH$_3$Mes), 2.07 (6H, s, p-CH$_3$Mes);

$^{13}$C{$^1$H}-NMR (126 MHz, 298 K, benzene-d$_6$): δ 142.4 (d, $^2$J$_{PC}$ = 14.9 Hz, o-Mes), 137.9 (p-Mes), 137.1 (d, $^1$J$_{PC}$ = 18.2 Hz, $^3$CH$_2$), 131.4 (d, $^1$J$_{PC}$ = 17.2 Hz, i-Mes), 130.3 (d, $^3$J$_{PC}$ = 3.6 Hz, m-Mes), 121.8 (d, $^2$J$_{PC}$ = 17.3 Hz, $^2$CH$_2$), 23.2 (d, $^3$J$_{PC}$ = 14.4 Hz, o-CH$_3$Mes), 20.9 (p-CH$_3$Mes); $^{31}$P{$^1$H}-NMR (202 MHz, 298 K, benzene-d$_6$): δ -22.0 ($\nu_{1/2}$ = 1.1 Hz); IR (ATR): $\nu$ = 2966 (m), 2918 (m), 1604 (m), 1576 (w), 1558 (w), 1454 (s), 1410 (m), 1375 (m), 1290 (w), 1268 (w), 1018 (m), 1001 (m), 905 (s), 860 (vs), 693 (m), 658 (w), 624 (s), 607 (s), 554 (s); Anal. Calcd for C$_{20}$H$_{25}$P: C, 81.05; H, 8.50; Found: C, 80.62; H, 8.50.

Di-tert-butyl(prop-1-ynyl)phosphane (3a).\(^3\) Propynyllithium (360 mg, 7.83 mmol) was dissolved in thf (80 ml) and chloro-di(tert-butyl)phosphane (1.38 g, 7.64 mmol) was added at -78°C. The solution was stirred for 2 h at room temperature. Then the solvent was removed in the oil-pump vacuum, the residue was extracted with pentane, filtered over celite and evaporated to dryness. The yellow residue (1.08 g, 5.86 mmol) was used without further purification.

\[
\begin{align*}
\text{P} & \quad \text{CH}_3 \\
\text{P} & \quad \text{CH}_3
\end{align*}
\]

$^1$H-NMR (300 MHz, 300 K, chloroform-d$_1$): δ 1.96 (3H, m, CH$_3$), 1.15 (18H, d, $^3$J$_{PH}$ = 12.3 Hz, 1Bu); $^{13}$C{$^1$H}-NMR (76 MHz, 300 K, chloroform-d$_1$): δ 102.6 (d, $^2$J$_{PC}$ = 2.9 Hz, $^3$C$^\text{Me}$), 76.3 (d, $^1$J$_{PC}$ = 16.1 Hz, $^6$C$^\text{Me}$), 32.3 (d, $^1$J$_{PC}$ = 15.9 Hz, i-Bu), 29.4 (d, $^2$J$_{PC}$ = 13.9 Hz, 1Bu), 5.1 (d, $^3$J$_{PC}$ = 1.1 Hz, Me); $^{31}$P{$^1$H}-NMR (122 MHz, 300 K, chloroform-d$_1$): δ 12.7 ($\nu_{1/2}$ = 0.8 Hz); IR (ATR): $\nu$ = 2949

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(s), 2895 (s), 2863 (m, C≡C), 1468 (s), 1363 (s), 1176 (s), 1031 (s), 934 (w), 810 (s), 600 (m), 578 (m).

**Dimesityl(prop-1-ynyl)phosphane (3b).** Analogous to the preparation of dimesitylvinylphosphane, reaction of chlorodimesitylphosphane (5.83 g, 19.1 mmol) and 0.5 M propynylmagnesium bromide solution in thf (38.2 ml, 19.1 mmol) yielded a pale yellow crude product (3.76 g, 64%). After chromatography (silica gel; CH₂Cl₂ : cyclohexane 3 : 10, Rf = 0.46) a white solid (2.77 g, 47%) could be obtained.

![Chemical Structure](image)

m.p. 105°C; ¹H-NMR (300 MHz, 298 K, benzene-d₆): δ 6.68 (4H, dm, ⁴Jₚₕ = 3.2 Hz, m-Mes), 2.50 (12H, s, o-CH₃Mes), 2.07 (6H, s, p-CH₃Mes), 1.47 (3H, d, ⁴J₂ₚ = 2.5 Hz, ⁵CH₃);

¹³C{¹H}-NMR (76 MHz, 298 K, benzene-d₆): δ 142.1 (d, ²JPC = 15.5 Hz, o-Mes), 138.1 (p-Mes), 131.2 (d, ¹JPC = 13.1 Hz, i-Mes), 130.3 (d, ³JPC = 3.5 Hz, m-Mes), 104.8 (d, ²JPC = 2.7 Hz, ⁷CMe), 77.2 (d, ¹JPC = 8.3 Hz, ⁶PC), 23.2 (d, ³JPC = 14.4 Hz, o-CH₃Mes), 20.9 (p-CH₃Mes), 5.2 (d, ³JPC = 1.3 Hz, ⁵CH₃); ³¹P{¹H}-NMR (122 MHz, 298 K, benzene-d₆): δ -55.0 (ν₁/₂ = 0.5 Hz); IR (ATR): ν = 2966 (m), 2916 (m), 2176 (m), 1603 (m), 1438 (s), 1376 (m), 1291 (w), 1032 (w), 844 (s), 724 (w), 612 (s), 553 (m); Anal. Calcd for C₂₁H₂₅P: C, 81.79; H, 8.17; Found: C, 81.72; H, 8.14.

**Dimesityl(phenylethynyl)phosphane (3c).**⁴ Phenylacetylene (2.50 ml, 22.6 mmol) was dissolved in thf (100 ml). At -78°C 1.6 M n-butyllithium solution in hexane (14.1 ml, 22.6 mmol) was added. The dilution is stirred for 2 h at room temperature. Then the reaction mixture was again cooled to -78°C and a solution of chlorodimesitylphosphane (5.00 g, 22.6 mmol) in thf (20 ml), was added. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed on the rotary evaporator and the residue was extracted with pentane (200 ml). The pentane was removed in the oil pump vacuum and the crude product was cleaned via column chromatography (silica gel; CH₂Cl₂ : cyclohexane 3 : 10, Rf = 0.57). A white solid (3.66 g, 44%) could be obtained

m.p. 119°C; ¹H-NMR (300 MHz, 300 K, benzene-d₆): δ 7.25 (2H), 6.87 (3H) (m, Ph), 6.69 (4H, dm, ⁴Jₚₕ = 3.3 Hz, m-Mes), 2.56 (12H, s, o-CH₃Mes), 2.06 (6H, s, p-CH₃Mes);

¹³C{¹H}-NMR (76 MHz, 300 K, benzene-d₆): 142.3 (d, ²JPC = 15.7 Hz, o-Mes), 138.4 (p-Mes), 131.4 (d, ⁴JPC = 2.0 Hz, o-Ph), 130.5 (d, ³JPC = 3.7 Hz, m-Mes), 130.4 (d, ¹JPC = 12.5

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Hz, \(i\)-Mes), 128.5, 128.3 (\(\rho\), \(m\)-Ph) [resonance from DEPT90 and DEPT135 experiments], 124.2 (d, \(^3J_{PC} = 1.5\) Hz, \(i\)-Ph), 107.4 (d, \(^2J_{PC} = 7.5\) Hz, \(\equiv\)C\(^\text{Ph}\)), 88.7 (d, \(^1J_{PC} = 8.3\) Hz, \(p\)C\(^-\)), 23.3 (d, \(^3J_{PC} = 14.5\) Hz, \(\equiv\)CH\(_3\)\(^\text{Mes}\)), 20.9 (\(p\)-CH\(_3\)\(^\text{Mes}\)); \(^{31}\)P\{\(^1\)H\}-NMR (122 MHz, 300 K, benzene-d\(_6\)): \(\delta\) -55.8 (\(v_{1/2} = 0.8\) Hz); IR (ATR): \(\nu\) = 2969 (m), 2923 (m), 1602 (m), 1554 (w), 1486 (m), 1464 (s), 1441 (s), 1405 (m), 1377 (m), 1291 (w), 1222 (w), 1070 (w), 1027 (m), 920 (w), 848 (s), 755 (vs), 691 (vs), 638 (w), 620 (m), 598 (m), 555 (m); Anal. Calcd for C\(_{26}\)H\(_{27}\)P: C, 84.29; H, 7.35; Found: C, 84.14; H, 7.46.

(Z)-\{2-[Bis(pentafluorophenyl)boryl]prop-1-enyl\}di-tert-butylphospane (5a). Di-tert-butyl(prop-1-ynyl)phosphane (3a) (32.0 mg, 0.17 mmol) and bis(pentafluorophenyl)borane (4) (59.0 mg, 0.17 mmol) were dissolved in benzene (5ml) and stirred for 10 minutes at 80°C. Then the mixture was evaporated to dryness and an orange viscous oil could be obtained (90 mg, 100 %).

\[\begin{align*}
\begin{array}{c}
\text{B}(C_6F_5)_2 \\
\text{P}
\end{array}
\begin{array}{c}
\text{CH}_3
\end{array}
\end{align*}\]

\(^1\)H-NMR (400 MHz, 300 K, benzene-d\(_6\)): \(\delta\) 7.31 (1H, dq, \(^3J_{PH} = 4.5\) Hz, \(^4J_{HH} = 1.3\) Hz, \(\equiv\)CH\(^-\)), 2.29 (3H, t, \(^4J_{PH} \approx ^4J_{HH} \approx 1.3\) Hz, CH\(_3\)), 1.06 (18H, d, \(^3J_{PH} = 11.5\) Hz, \(\text{tBu}\)); \(^{13}\)C\{\(^1\)H\}-NMR (101 MHz, 300 K, benzene-d\(_6\)): \(\delta\) 161.7 (broad, \(\equiv\)CB), 158.0 (d, \(^1J_{PC} = 33.7\) Hz, \(\equiv\)C\(^-\)), 147.0 (dm, \(^1J_{FC} = 246\) Hz, C\(_6\)F\(_5\)), 143.3 (dm, \(^1J_{FC} = 259\) Hz, \(\rho\)-C\(_6\)F\(_5\)), 137.7 (dm, \(^1J_{FC} = 252\) Hz, C\(_6\)F\(_5\)), 114.1 (broad, \(i\)-C\(_6\)F\(_5\)), 32.8 (d, \(^1J_{PC} = 20.1\) Hz, \(i\)-Bu), 29.5 (d, \(^2J_{PC} = 14.4\) Hz, \(\text{tBu}\)), 20.1 (d, \(^1J_{PC} = 23.4\) Hz, CH\(_3\)); \(^{19}\)F-NMR (282 MHz, 300 K, benzene-d\(_6\)): \(\delta\) -129.8 (4F, \(\equiv\)C\(_6\)F\(_5\)), -147.1 (2F, \(\rho\)-C\(_6\)F\(_5\)), -160.6 (4F, \(m\)-C\(_6\)F\(_5\)); \(^{31}\)P\{\(^1\)H\}-NMR (122 MHz, 300 K, benzene-d\(_6\)): \(\delta\) 3.2 (\(v_{1/2} = 4\) Hz), \(^{11}\)B\{\(^1\)H\}-NMR (96 MHz, 300 K, benzene-d\(_6\)): \(\delta\) 62 (\(v_{1/2} = 930\) Hz); IR (KBr): \(\nu\) = 3539 (m), 2971 (s), 2866 (s), 2374 (w), 2212 (w), 1645 (s), 1518 (s), 1460 (s), 1378 (s), 1323 (m), 1279 (s), 1181 (w), 1134 (s), 1083 (s), 1027 (m), 971 (s), 897 (m), 811 (s), 753 (s), 717 (m), 692 (m), 673 (m); UV/Vis (pentane): \(\lambda_{\text{max}}(\varepsilon) = 397\) nm (1500).

(Z)-\{2-[Bis(pentafluorophenyl)boryl]prop-1-enyl\}dimesitylphospane (5b). Dimesityl(prop-1-ynyl)phosphane (3b) (344 mg, 1.12 mmol) and bis(pentafluorophenyl)borane (4) (386 mg, 1.12 mmol) were dissolved in pentane (15 ml). The mixture was stirred for 10 minutes at ambient temperature. The resulting red solution was evaporated to dryness. A red solid (591 mg 82 %) could be obtained.

\[\begin{align*}
\begin{array}{c}
\text{H}_3\text{C}
\end{array}
\begin{array}{c}
\text{CH}_3
\end{array}
\begin{array}{c}
\text{B}(C_6F_5)_2
\end{array}
\begin{array}{c}
\text{CH}_3
\end{array}
\end{align*}\]

m.p. 119°C; \(^1\)H-NMR (600 MHz, 298 K, benzene-d\(_6\)): \(\delta\) 8.17
(1H, d, $^2J_{\text{PH}} = 8.0$ Hz, $^6\text{CH}_3^+$), 6.66 (4H, d, $^4J_{\text{PH}} = 3.3$ Hz, $m$-Mes), 2.33 (12H, s, $o$-CH$_3^{\text{Mes}}$), 1.97 (6H, s, $p$-CH$_3^{\text{Mes}}$), 1.78 (3H, d, $^1J_{\text{PH}} = 3.2$ Hz, $^6\text{CH}_3^+$); $^{13}$C{$^1$H}-NMR (101 MHz, 300 K, benzene-$d_6$): $\delta$ 171.4 (d, $^1J_{\text{PC}} = 22.8$ Hz, $^6\text{CH}_3^+$), 151.8 (broad, $^6\text{C}^B$), 146.2 (dm, $^1J_{\text{PC}} = 248$ Hz, C$_6$F$_5$), 143.2 (d, $^2J_{\text{PC}} = 14.9$ Hz, $o$-Mes), 142.4 (dm, $^1J_{\text{PC}} = 268$ Hz, $p$-C$_6$F$_5$), 139.6 (p-Mes), 137.5 (dm, $^1J_{\text{PC}} = 253$ Hz, C$_6$F$_5$), 130.4 (d, $^3J_{\text{PC}} = 4.7$ Hz, $m$-Mes), 128.9 (d, $^2J_{\text{PC}} = 8.0$ Hz, i-Mes), 114.5 (broad, $i$-C$_6$F$_5$), 23.7 (d, $^3J_{\text{PC}} = 14.7$ Hz, $o$-CH$_3^{\text{Mes}}$), 20.8 ($p$-CH$_3^{\text{Mes}}$), 18.9 (d, $^3J_{\text{PC}} = 14.0$ Hz, $^6\text{CH}_3^+$); $^{31}$P{$^1$H}-NMR (122 MHz, 300 K, benzene-$d_6$): $\delta$ -27.1 (v$_{1/2}$ = 7 Hz); $^{19}$F-NMR (282 MHz, 300 K, benzene-$d_6$): $\delta$ -130.8 (4F, $o$-C$_6$F$_5$), -149.2 (2F, $p$-C$_6$F$_5$), -160.9 (4F, $m$-C$_6$F$_5$); $^{11}$B{$^1$H}-NMR (96 MHz, 300 K, benzene-$d_6$): $\delta$ -22.0 (v$_{1/2}$ = 9 Hz); IR (KBr): $\nu = 3484$ (br. m), 2964 (m), 2923 (m), 1644 (m), 1605 (m), 1515 (s), 1459 (vs), 1384 (w), 1274 (m), 1082 (s), 1031 (w), 966 (s), 851 (w), 802 (m), 702 (m), 648 (w); UV/Vis (pentane): $\lambda_{\text{max}}$(ε) = 432 nm (10500); Anal. Calcd for C$_{33}$H$_{26}$BF$_{10}$P: C, 60.57; H, 4.01; Found: C, 60.13; H, 4.04.

(Z)-{2-[Bis(pentafluorophenyl)boryl]-2-phenylvinyl}dimesitylphosphane (5c). Dimesitylphenylethynyl)phosphane (3c) (200 mg, 0.54 mmol) and bis(pentafluorophenyl)borane (4) (187 mg, 0.54 mmol) were dissolved in pentane (15 ml). The mixture was stirred for 10 minutes at ambient temperature. The resulting red solution was evaporated to dryness. A red solid (356 mg, 93%) could be obtained.

\[ \text{CH}_3 \quad \text{B(C}_6\text{F})_2 \]

m.p. 138°C; $^1$H-NMR (600 MHz, 298 K, benzene-$d_6$): $\delta$ 8.37 (1H, d, $^2J_{\text{PH}} = 10.2$ Hz, $^6\text{CH}_3^+$), 6.94 (2H, m, o-Ph), 6.76 (2H, m, m-Ph), 6.72 (1H, m, p-Ph), 6.53 (4H, d, $^4J_{\text{PH}} = 3.3$ Hz, m-Mes), 2.20 (12H, s, $o$-CH$_3^{\text{Mes}}$), 1.95 (6H, s, $p$-CH$_3^{\text{Mes}}$); $^{13}$C{$^1$H}-NMR (101 MHz, 300 K, benzene-$d_6$): $\delta$ 170.3 (1H, d, $^2J_{\text{PC}} = 12.0$ Hz, $^6\text{CH}_3^+$), 156.0 (broad, $^6\text{C}^B$), 145.9 (dm, $^1J_{\text{FC}} = 244$ Hz, C$_6$F$_5$), 142.9 (d, $^2J_{\text{PC}} = 14.8$ Hz, o-Mes), 142.2 (dm, $^1J_{\text{FC}} = 257$ Hz, p-C$_6$F$_5$), 140.8 (d, $^3J_{\text{PC}} = 2.7$ Hz, i-Ph), 139.5 (p-Mes), 137.5 (dm, $^1J_{\text{FC}} = 257$ Hz, C$_6$F$_5$), 130.2 (d, $^3J_{\text{PC}} = 4.6$ Hz, m-Mes), 129.4 (d, $^1J_{\text{PC}} = 6.0$ Hz, i-Mes), 127.9 (d, $^4J_{\text{PC}} = 3.4$ Hz, o-Ph), 127.7 (m-Ph), 126.7 (p-Ph), 114.8 (broad, $i$-C$_6$F$_5$), 23.6 (d, $^3J_{\text{PC}} = 14.1$ Hz, $o$-CH$_3^{\text{Mes}}$), 20.8 ($p$-CH$_3^{\text{Mes}}$); $^{31}$P{$^1$H}-NMR (122 MHz, 300 K, benzene-$d_6$): $\delta$ -22.0 (v$_{1/2} = 9$ Hz); $^{19}$F-NMR (282 MHz, 300 K, benzene-$d_6$): $\delta$ -130.7 (4F, $o$-C$_6$F$_5$), -149.7 (2F, $p$-C$_6$F$_5$), -161.1 (4F, m-C$_6$F$_5$); $^{11}$B{$^1$H}-NMR (96 MHz, 300 K, benzene-$d_6$): $\delta$ 59 (v$_{1/2} = 700$ Hz); IR (KBr): $\nu = 3484$ (br. m), 2964 (m), 2923 (m), 1644 (m), 1605 (m), 1515 (s), 1459 (vs), 1384 (w), 1274 (m), 1082 (s), 1031 (w), 966 (s), 851 (w), 802 (m), 702 (m), 648 (w); UV/Vis...
(pentane): \( \lambda_{\text{max}}(\varepsilon) = 434 \text{ nm} \) (10700); Anal. Calcd for C\(_{38}\)H\(_{28}\)BF\(_{10}\)P: C, 63.71; H, 3.94; Found: C, 62.74; H, 4.22.

[2-(Dimesitylphosphino)ethyl]bis(pentafluorophenyl)borane (1).\(^5\) Dimesitylvinylphosphate (200 mg, 0.67 mmol) and bis(pentafluorophenyl)borane (4) (233 mg, 0.67 mmol) were dissolved in pentane (10 ml) and stirred for 1 h at ambient temperature. The resulting solution was filtered and the clear filtrate was evaporated to dryness (in vacuo) to yield 1 (322 mg, 75%) as a yellow solid.

\[ \text{H_3C-} \begin{array}{c} \text{P} \\ \text{B(C_6F_5)_2} \end{array} \]

\[ \text{m.p. 81°C; }^{1}\text{H-NMR (500 MHz, 298 K, THF-d}_8\text{): } \delta \ 7.87 \ (1\text{H}, \text{ dt, }^{1}\text{J}_{PH} = 487 \text{ Hz, }^{3}\text{J}_{HH} = 7.3 \text{ Hz, P-H}), \ 7.11 \ (4\text{H, }^{4}\text{J}_{PH} = 4.2 \text{ Hz, } m\text{-Mes}), \ 2.91 \ (1\text{H, broad, B-H}), \ 2.80 \ (2\text{H, m, }^{p}\text{CH}_2), \ 2.45 \ (12\text{H, s, o-CH}_3\text{Mes}), \ 2.32 \ (6\text{H, s, p-CH}_3\text{Mes}), \ 1.25 \ (2\text{H, broad m, CH}_2\text{B}); \]

\[ ^{13}\text{C}\{^{1}\text{H}\}\text{-NMR (126 MHz, 298 K, THF-d}_8\text{): } \delta \ 149.0 \ (\text{dm, }^{1}\text{J}_{FC} = 237 \text{ Hz, C}_6\text{F}_5), \ 145.8 \ (\text{d, }^{4}\text{J}_{PC} = 2.7 \text{ Hz, } p\text{-Mes}), \ 144.2 \ (\text{d, }^{2}\text{J}_{PC} = 9.5 \text{ Hz, o-Mes}), \ 138.3 \ (\text{dm, }^{1}\text{J}_{FC} = 243 \text{ Hz, o-CH}_3\text{Mes}); \]

\[ ^{19}\text{F-NMR (282 MHz, 300 K, benzene-d}_6\text{): } \delta \ -128.9 \ (4\text{F, o-C}_6\text{F}_5), \ -157.0 \ (2\text{F, p-C}_6\text{F}_5), \ -163.6 \ (4\text{F, m-C}_6\text{F}_5); \]

\[ ^{11}\text{B}\{^{1}\text{H}\}\text{-NMR (96 MHz, 300 K, benzene-d}_6\text{): } \delta \ 8.8 \ (\nu_{1/2} = 510 \text{ Hz}). \]

[2-(Dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2). Dimesitylvinylphosphate (200 mg, 0.70 mmol) and bis(pentafluorophenyl)borane (4) (233 mg, 0.70 mmol) were dissolved in pentane (10 ml). Under vigorous stirring, dihydrogen gas (2.5 bar) was pressed on the solution for 15 min at room temperature. The product precipitated during this time as a white solid. It was collected by filtration, washed with pentane (5 ml) and dried in vacuo to yield the product as a white solid (247 mg, 55%).

\[ \text{m.p. 81°C; }^{1}\text{H-NMR (500 MHz, 298 K, THF-d}_8\text{): } \delta \ 7.87 \ (1\text{H, dt, }^{1}\text{J}_{PH} = 487 \text{ Hz, }^{3}\text{J}_{HH} = 7.3 \text{ Hz, P-H}), \ 7.11 \ (4\text{H, }^{4}\text{J}_{PH} = 4.2 \text{ Hz, } m\text{-Mes}), \ 2.91 \ (1\text{H, broad, B-H}), \ 2.80 \ (2\text{H, m, }^{p}\text{CH}_2), \ 2.45 \ (12\text{H, s, o-CH}_3\text{Mes}), \ 2.32 \ (6\text{H, s, p-CH}_3\text{Mes}), \ 1.25 \ (2\text{H, broad m, CH}_2\text{B}); \]

\[ ^{13}\text{C}\{^{1}\text{H}\}\text{-NMR (126 MHz, 298 K, THF-d}_8\text{): } \delta \ 149.0 \ (\text{dm, }^{1}\text{J}_{FC} = 237 \text{ Hz, C}_6\text{F}_5), \ 145.8 \ (\text{d, }^{4}\text{J}_{PC} = 2.7 \text{ Hz, } p\text{-Mes}), \ 144.2 \ (\text{d, }^{2}\text{J}_{PC} = 9.5 \text{ Hz, o-Mes}), \ 138.3 \ (\text{dm, }^{1}\text{J}_{FC} = 243 \text{ Hz, o-CH}_3\text{Mes}); \]

\[ ^{19}\text{F-NMR (282 MHz, 300 K, benzene-d}_6\text{): } \delta \ -128.9 \ (4\text{F, o-C}_6\text{F}_5), \ -157.0 \ (2\text{F, p-C}_6\text{F}_5), \ -163.6 \ (4\text{F, m-C}_6\text{F}_5); \]

\[ ^{11}\text{B}\{^{1}\text{H}\}\text{-NMR (96 MHz, 300 K, benzene-d}_6\text{): } \delta \ 8.8 \ (\nu_{1/2} = 510 \text{ Hz}). \]

HZ, C₆F₅), 137.1 (dm, ¹JPC = 247 Hz, C₆F₅), 132.2 (d, ³JPC = 10.8 Hz, m-Mes), 128.1 (broad, i-C₆F₅), 114.8 (d, ¹JPC = 76.2 Hz, i-Mes), 26.9 (d, ¹JPC = 34.4 Hz, ⁹CH₂), 21.9 (d, ³JPC = 6.8 Hz, o-CH₃Mes), 21.0 (d, ⁵JPC = 1.3 Hz, p-CH₃Mes), 17.8 (broad m, CH₂B); ³¹P{¹H}-NMR (202 MHz, 298 K, THF-d₈): δ -6.5 (dm, ¹JPH = 487 Hz); ¹⁹F-NMR (470 MHz, 298K, THF-d₈): δ -133.4 (4F, o-C₆F₅), -165.8 (2F, p-C₆F₅), -168.0 (4F, m-C₆F₅); ¹¹B{¹H}-NMR (160 MHz, 298 K, THF-d₈): δ -20.1 (ν₁/₂ = 67 Hz); ¹¹B-NMR (160 MHz, 298 K, THF-d₈): δ -19.8 (ν₁/₂ = 85 Hz); ¹H-NMR (300 MHz, 300 K, benzene-d₆): δ 7.09 (dt, 1H, ¹JPH = 481 Hz, ³JHH = 7.3 Hz, PH), 6.31 (4H, ⁴JPH = 4.0 Hz, m-Mes), 3.60 (1H, broad, B-H), 2.57 (2H, m, ⁹CH₂), 1.86 (12H, s, o-CH₃Mes), 1.54 (6H, s, p-CH₃Mes), 1.52 (2H, broad m, CH₂B); ¹⁹F-NMR (282 MHz, 300 K, benzene-d₆): δ -132.7 (4F, o-C₆F₅), -162.6 (2F, p-C₆F₅), -165.5 (4F, m-C₆F₅); ³¹P{¹H}-NMR (122 MHz, 300 K, benzene-d₆): δ -8.3 (dm, ¹JPH = 481 Hz); ¹¹B{¹H}-NMR (96 MHz, 298 K, benzene-d₆): δ -19.8 (ν₁/₂ = 85 Hz); ¹¹B-NMR (96 MHz, 298 K, benzene-d₆): δ -19.8 (ν₁/₂ = 85 Hz); IR (KBr): ν% = 2972 (s), 2927 (s), 2324 (vs, νPH or νBH [no clear assignment]), 1630 (s), 1605 (vs), 1558 (m), 1509 (vs), 1458 (vs), 1273 (s), 1181 (s), 1081 (vs), 971 (vs), 856 (s), 807 (w), 747 (m), 703 (m), 642 (s), 555 (m) cm⁻¹; Anal. Calcd for C₃₂H₂₈BF₁₀P: C, 59.95; H, 4.38; Found: C, 59.30; H, 4.31.

(Z)-[1-(Di-tert-butylphosphonio)prop-1-en-2-yl]bis(pentafluorophenyl)hydridoborate (6a). Di-tert-butyl(prop-1-ynyl)phosphane (3a) (111 mg, 0.60 mmol) and bis(pentafluorophenyl)borane (4) (208 mg, 0.60 mmol) were dissolved in toluene and stirred for 10 minutes at 80°C. Then the reaction mixture was stirred at room temperature, for 3 h, in a steel autoclave under a hydrogen atmosphere of 60 bar. The solvent was removed and the residue was suspended in pentane (15 ml). The overlaying liquid was removed via filter cannula and the resulting solid was dried in the oil-pump vacuum. A white powder (200 mg, 0.38 mmol, 63 %) could be obtained.

m.p. 163°C; ¹H-NMR (600 MHz, 298 K, benzene-d₆): δ 5.11 (1H, dd, ²JPH = 31.5 Hz, ³JHH = 12.9 Hz, ⁹CH₂), 4.57 (1H, dd, ¹JPH = 435 Hz, ³JHH = 12.9 Hz, P-H), 4.04 (1H, broad 1:1:1:1 q [partial relaxed ¹JBH coupling constant], ¹JBH = 93 Hz, B-H), 1.99 (3H, s, CH₃), 0.51 (18H, d, ³JPH = 16.4 Hz, ¹Bu); ¹³C{¹H}-NMR (151 MHz, 298 K, benzene-d₆): δ 202.0 (broad, ¹⁶C), 148.8 (dm, ¹JPC = 230 Hz, C₆F₅), 139.0 (dm, ¹JPC = 224 Hz, p-C₆F₅), 137.4 (dm, ¹JPC = 241 Hz, C₆F₅), 124.8 (broad, i-C₆F₅), 90.2 (d, ¹JPC = 65 Hz, ³C═), 32.6 (d, ¹JPC = 41.4...
(Z)-[1-(Dimesitylphosphonio)prop-1-en-2-yl]bis(pentafluorophenyl)hydridoborate (6b).

Procedure A: Dimesityl(prop-1-ynyl)phosphane (3b) (200 mg, 0.65 mmol), dimesitylvinylnaphosphane (19.2 mg, 0.07 mmol) and bis(pentafluorophenyl)borane (4) (247 mg, 0.72 mmol) were dissolved in toluene. The mixture was stirred for 5 minutes at ambient temperature. The resulting red solution was degassed and set under vacuum. Under vigorous stirring, dihydrogen gas (2.5 bar, \( p_{\text{H}_2} \approx 2.5 \) bar) was pressed on the Schlenk flask, for 4 h at room temperature. The yellow solution was evaporated to dryness and the residue was suspended in pentane (20 ml). After the overlaying liquid was removed via filter capillary the solid was dried in the oil-pump vacuum. A white powder (358, mg, 84 %) could be obtained.

Procedure B: Dimesityl(prop-1-ynyl)phosphane (3b) (200 mg, 0.65 mmol), [2-(Dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) (42.0 mg, 0.07 mmol) and bis(pentafluorophenyl)borane (4) (224 mg, 0.65 mmol) were dissolved in toluene. Then the reaction mixture was degassed, set under hydrogen pressure and worked up analogously as described in procedure A. A white solid (298 mg, 70 %) was obtained.

Procedure C: Dimesityl(prop-1-ynyl)phosphane (3b) (100 mg, 0.32 mmol) and bis(pentafluorophenyl)borane (4) (112 mg, 0.32 mmol) were dissolved in toluene (10 ml) and stirred at ambient temperature for 5 minutes. Tri(tert-butyl)phosphane (10.0 mg, 0.05 mmol, 15 %) was added. Hydrogenation can be carried out in two different ways: a) reaction mixture was degassed, and stirred for 3 days under hydrogen pressure (2.5 bar, \( p_{\text{H}_2} \approx 2.5 \) bar); b) reaction mixture was stirred in a steel autoclave under a hydrogen atmosphere of 60 bars for 3 hours at ambient temperature. The yellow solution was evaporated to dryness and the residue was suspended in pentane (15 ml). After the overlaying liquid was removed via filter capillary, the solid was dried in the oil-pump vacuum. A white powder (a: 135 mg, 64 %; b: 142 mg, 68 %) could be obtained.
m.p. 153°C; $^1$H-NMR (600 MHz, 298 K, benzene-d$_6$): δ 7.58 (1H, dd, $^1$J$_{PH}$ = 469 Hz, $^3$J$_{HH}$ = 7.8 Hz, P-H), 6.36 (4H, d, $^4$J$_{PH}$ = 4.3 Hz, m-Mes), 5.47 (1H, dd, $^2$J$_{PH}$ = 38.4 Hz, $^3$J$_{HH}$ = 7.8 Hz, $^5$CHF), 4.11 (1H, broad 1:1:1:1 q [partial relaxed $^1$J$_{BH}$ coupling constant], $^1$J$_{BH}$ = 95 Hz, B-H), 2.12 (3H, s, =CH$_3$), 1.93 (12H, s, o-CH$_3^{Mes}$), 1.83 (6H, s, p-CH$_3^{Mes}$); $^{13}$C{$^1$H}-NMR (151 MHz, 298 K, benzene-d$_6$): δ 201.2 (broad, =CB), 148.8 (dm, $^1$J$_{FC}$ = 238 Hz, C$_6$F$_5$), 145.0 (d, $^4$J$_{PC}$ = 2.7 Hz, p-Mes), 143.1 (d, $^2$J$_{PC}$ = 10.0 Hz, o-Mes), 138.9 (dm, $^1$J$_{FC}$ = 219 Hz, p-C$_6$F$_5$), 137.5 (dm, $^1$J$_{FC}$ = 237 Hz, C$_6$F$_5$), 131.6 (d, $^3$J$_{PC}$ = 10.6 Hz, m-Mes), 124.4 (broad, i-C$_6$F$_5$), 113.7 (d, $^1$J$_{PC}$ = 82.0 Hz, i-Mes), 96.8 (d, $^1$J$_{PC}$ = 68.3 Hz, $^5$CH$_3$), 23.7 (d, $^3$J$_{PC}$ = 21.9 Hz, $^3$CH$_3$), 21.3 (d, $^3$J$_{PC}$ = 8.4 Hz, o-CH$_3^{Mes}$), 20.8 (p-CH$_3^{Mes}$); $^{31}$P{$^1$H}-NMR (122 MHz, 300 K, benzene-d$_6$): δ -36.2 ($\nu_{1/2}$ = 25 Hz), [(experiment with catalytic amount of (Mes$_2$(H)P$_7$(CH$_2$)$_2$B-(H)(C$_6$F$_5$)$_2$ ($^2$) (< 10 %): δ -7.9)]; $^{31}$P-NMR (122 MHz, 300 K, benzene-d$_6$): δ -36.2 (dd, $^1$J$_{PH}$ = 469 Hz, $^2$J$_{PH}$ = 38 Hz). [2: δ -7.9 (d, $^1$J$_{PH}$ = 485 Hz)]; $^{19}$F-NMR (282 MHz, 300 K, benzene-d$_6$): δ -161.6 (2F, p-C$_6$F$_5$), -165.3 (4F, m-C$_6$F$_5$), [experiment with catalytic amount of (Mes$_2$(H)P$_7$(CH$_2$)$_2$B-(H)(C$_6$F$_5$)$_2$ ($^2$) (< 10 %): δ -132.5 (4F, o-C$_6$F$_5$), -163.0 (4F, p-C$_6$F$_5$), -165.7 (4F, m-C$_6$F$_5$)]; $^{11}$B{$^1$H}-NMR (96 MHz, 300 K, benzene-d$_6$): δ -18.0 ($\nu_{1/2}$ = 90 Hz), [(experiment with catalytic amount of (Mes$_2$(H)P$_7$(CH$_2$)$_2$B-(H)(C$_6$F$_5$)$_2$ ($^2$) (< 10 %): δ -19.6]; $^{11}$B-NMR (96 MHz, 300 K, benzene-d$_6$): δ -18.0 (d, $^1$J$_{BH}$ = 95 Hz); IR (KBr): $\bar{\nu}$ = 3406 (br. m), 2975 (s), 2932 (s, $v_{PH}$ or $v_{BH}$ [no clear assignment]), 1641 (s), 1606 (s), 1544 (s), 1510 (vs), 1460 (vs), 1274 (s), 1096 (vs), 1031 (m), 957 (s), 852 (m), 802 (m), 760 (w), 650 (m), 614 (w), 553 (w); Anal. Calcd for C$_{33}$H$_{28}$BF$_{10}$P: C, 60.39; H, 4.30; Found: C, 59.87; H, 4.18.

Crystals suitable for X-ray crystal structure analysis were obtained by diffusion of pentane into a concentrated solution of 6b in THF at room temperature.

X-ray crystal structure analysis for 6b: formula C$_{33}$H$_{28}$BF$_{10}$P, $M = 656.33$, colorless crystal 0.35 x 0.20 x 0.20 mm, $a = 13.0699(4), b = 16.1472(5), c = 15.1163(5)$ Å, $\beta = 100.271(1)^\circ$, $V = 3139.06(17)$ Å$^3$, $\rho_{calc} = 1.389$ g cm$^{-3}$, $\mu = 1.515$ mm$^{-1}$, empirical absorption correction (0.619 ≤ $T$ ≤ 0.752), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), $\lambda = 1.54178$ Å, $T = 223$ K, $\omega$ and $\phi$ scans, 32792 reflections collected (±h, ±k, ±l), [(sin0)/$\lambda$] = 0.60 Å$^{-1}$, 5640 independent ($R_{int}$ = 0.048) and 5080 observed reflections [$I \geq 2 \sigma(I)$], 421 refined parameters, $R = 0.042, wR^2 = 0.111, \text{max. (min.)residual electron density 0.25 (-0.27) e Å}^{-3}$, hydrogen atoms at P and B.
from difference fourier calculations and refined free, others calculated and refined as riding atoms.

(Z)-[1-(Dimesitylphosphonio)prop-1-en-2-yl]bis(pentafluorophenyl)hydridoborate-D2 (6b-D2). Dimesityl(prop-1-ynyl)phosphane (3b) (100 mg, 0.32 mmol), dimesitylvinylnaphosphate (11 mg, 0.04 mmol) and bis(pentafluorophenyl)borane (4) (124 mg, 0.36 mmol) were dissolved in benzene-d6 (4 ml). The mixture was stirred for 5 minutes at ambient temperature. The resulting red solution was degassed and set under vacuum. Under vigorous stirring, dideuterium gas (2.5 bar, \( p_{D2} \approx 2.5 \) bar) was pressed on the Schlenk flask for 4 h at room temperature. The yellow solution was evaporated to dryness. A white powder (260 mg, 73 %) could be obtained. According to the \(^1\)H-NMR spectrum a mixture of 5% (6b-D1(P-H)), 81 % (6b-D2), and 14% (dimesitylvinylnaphosphane) was obtained.

[C\(_{32}\)H\(_{23}\)D\(_2\)BF\(_{10}\)P, \( M = 643.32 \) g/mol]

\(^1\)H-NMR (500 MHz, 298 K, benzene-d\(_6\)): \( \delta \) 6.36 (4H, d, \( ^4\)J\(_{PH} = 4.4 \) Hz, m-Mes), 5.47 (1H, d, \( ^1\)J\(_{PH} = 38.0 \) Hz, \( ^8\)CH\(_2\)), 2.12 (3H, s, =CH\(_3\)), 1.93 (12H, s, o-CH\(_3\)Mes), 1.83 (6H, s, p-CH\(_3\)Mes); \(^2\)H-NMR (77 MHz, 298 K, benzene-h\(_6\)): \( \delta \) 7.55 (d, 1D, \( ^1\)J\(_{PD} \approx 70 \) Hz, P-D), 4.08 (broad s, 1D, B-D); \(^{13}\)C\({[1^1\)H]}\)-NMR (126 MHz, 298 K, benzene-d\(_6\)): \( \delta \) 201.5 (broad, \( ^8\)C\(_B\)), 148.8 (d, \( ^1\)J\(_{FC} = 232 \) Hz, C\(_6\)F\(_5\)), 144.9 (d, \( ^4\)J\(_{PC} = 2.7 \) Hz, p-Mes), 143.1 (d, \( ^2\)J\(_{PC} = 10.0 \) Hz, o-Mes), 138.9 (dm, \( ^1\)J\(_{FC} = 251 \) Hz, \( p\)-C\(_6\)F\(_5\)), 137.4 (dm, \( ^1\)J\(_{FC} = 248 \) Hz, C\(_6\)F\(_5\)), 131.6 (d, \( ^3\)J\(_{PC} = 11.0 \) Hz, m-Mes), 124.4 (broad, \( i\)-C\(_6\)F\(_5\)), 113.8 (d, \( ^1\)J\(_{PC} = 81.0 \) Hz, \( i\)-Mes), 96.6 (d, \( ^1\)J\(_{PC} = 69.2 \) Hz, \( ^8\)CH\(_2\)), 23.7 (d, \( ^3\)J\(_{PC} = 21.8 \) Hz, \( ^8\)CH\(_3\)), 21.3 (d, \( ^3\)J\(_{PC} = 8.5 \) Hz, o-CH\(_3\)Mes), 20.8 (d, \( ^5\)J\(_{PC} = 1.4 \) Hz, p-CH\(_3\)Mes); \(^{31}\)P\({[2^2\)H, \(^1\)H]}\)-NMR (202 MHz, 298 K, benzene-d\(_6\)): 10
\[ \delta -36.4 \ (20 \%, \ P^1 H), -36.8 \ (80 \%, \ P^3 H); \ 3^1 P-NMR \ (202 \text{ MHz}, \ 298 \text{ K}, \ \text{benzene-}d_6): \ \delta -36.8 \ (1:1:1 \ \text{t}, \ ^1 J_{PH} \approx 70 \text{ Hz}); \ 1^9 F-NMR \ (470 \text{ MHz}, \ 298 \text{K}, \ \text{benzene-}d_6): \ \delta -131.5 \ (4F, \ -C_6F_5), -161.7 \ (2F, \ p-C_6F_5), -165.4 \ (4F, \ m-C_6F_5); \ 1^1 B\{^1 H\}-NMR \ (160 \text{ MHz}, \ 298 \text{ K}, \ \text{benzene-}d_6): \ \delta -18.3 \ (\nu_{1/2} = 81 \text{ Hz}); \ 1^1 B-NMR \ (160 \text{ MHz}, \ 298 \text{ K}, \ \text{benzene-}d_6): \ \delta -18.3 \ (\nu_{1/2} = 87 \text{ Hz}); \ IR \ (\text{KBr}): \ \nu \approx 2965 \ (m), 2925 \ (m), 2375 \ (w), 1638 \ (m), 1605 \ (m), 1559 \ (m), 1509 \ (s), 1462 \ (vs), 1381 \ (m), 1084 \ (s), 972 \ (s), 853 \ (m), 826 \ (m), 799 \ (m).

(Z)-[1-(Dimesitylphosphonio)-2-phenylethenyl]bis(pentafluorophenyl)hyridoborate (6c). Conversion of dimesityl(phenylethynyl)phosphane (3c) (241 mg, 0.65 mmol), bis(pentafluorophenyl)borane (4) (225 mg, 0.65 mmol) and [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hyridoborate (2) (42.0 mg, 0.07 mmol) as described for compound (6c) in procedure B yielded a white solid (373 mg, 80%).

\[ \begin{array}{cccc}
\text{H}_3\text{C} & \text{CH}_3 & \text{H} & \text{B(C}_6\text{F}_5)_2 \\
\end{array} \]

m.p. 169°C; \(^1 H\)-NMR (600 MHz, 298 K, benzene-\(d_6\)): \( \delta \ 7.44 \ (2H, \ m, \ o-\text{Ph}), 6.98 \ (1H, \ dd, \ ^1 J_{PH} = 487 \text{ Hz}, \ ^3 J_{HH} = 10.1 \text{ Hz, P-H}), 6.88 \ (2H, \ m, \ m-\text{Ph}), 6.86 \ (1H, \ m, \ p-\text{Ph}), 6.34 \ (4H, \ d, \ ^4 J_{PH} = 4.3 \text{ Hz, m-Mes}), 5.79 \ (1H, \ dd, \ ^2 J_{PH} = 36.2 \text{ Hz, } ^3 J_{HH} = 10.1 \text{ Hz, PCH=}), 4.62 \ (1H, \ broad 1:1:1:1 \ q \ [\text{partial relaxed } ^1 J_{BH} \ \text{coupling constant}], \ ^1 J_{BH} = 96 \text{ Hz, B-H}), 4.85 \ (6H, \ s, \ o-\text{CH}_3\text{Mes}), 1.83 \ (6H, \ s, \ p-\text{CH}_3\text{Mes}); \ ^13 C\{^1 H\}-NMR (151 MHz, 298 K, benzene-\(d_6\)): \( \delta 200.9 \ (\text{broad, } ^a \text{C}^B), 148.8 \ (\text{dm, } ^1 J_{FC} = 236 \text{ Hz, } C_6\text{F}_5), 145.6 \ (\text{d, } ^3 J_{PC} = 17.6 \text{ Hz, i-Ph}), 144.9 \ (\text{d, } ^3 J_{PC} = 2.7 \text{ Hz, p-Mes}), 142.6 \ (\text{d, } ^3 J_{PC} = 10.0 \text{ Hz, o-Mes}), 138.9 \ (\text{dm, } ^1 J_{FC} = 240 \text{ Hz, p-C}_6\text{F}_5), 137.4 \ (\text{dm, } ^1 J_{FC} = 252 \text{ Hz, C}_6\text{F}_5), 131.5 \ (\text{d, } ^3 J_{PC} = 11.0 \text{ Hz, m-Mes}), 128.16 \ (m), 128.15 \ (p) \ (\text{Ph}) \ [\text{resonance from DEPT90 and DEPT135 experiments}], 127.1 \ (o-\text{Ph}), 123.7 \ (i-C_6\text{F}_5), 115.7 \ (\text{d, } ^1 J_{PC} = 83.6 \text{ Hz, i-Mes}), 100.2 \ (\text{d, } ^1 J_{PC} = 72.8 \text{ Hz, } ^9 \text{CH}^+), 21.4 \ (\text{d}, \ ^3 J_{PC} = 8.3 \text{ Hz, } o-\text{CH}_3\text{Mes}), 20.9 \ (\text{p-CH}_3\text{Mes}); \ ^31 P\{^1 H\}-NMR (122 MHz, 300 K, benzene-\(d_6\)): \( \delta -28.0 \ (\nu_{1/2} = 16 \text{ Hz}); \ ^31 P-NMR (122 MHz, 298 K, benzene-\(d_6\)): \( \delta -28.0 \ (\text{dd, } ^1 J_{PH} = 487 \text{ Hz, } ^2 J_{PH} = 36 \text{ Hz}); \ ^19 F-NMR (282 MHz, 300 K, benzene-\(d_6\)): \( \delta -130.9 \ (4F, \ -C_6\text{F}_5), -161.3 \ (2F, \ p-C_6\text{F}_5), -165.3 \ (4F, \ m-C_6\text{F}_5); \ 1^1 B\{^1 H\}-NMR (96 MHz, 298 K, benzene-\(d_6\)): \( \delta -18.1 \ (\nu_{1/2} = 90 \text{ Hz}); \ 1^1 B-NMR (96 MHz, 298 K, benzene-\(d_6\)): \( \delta -18.1 \ (\text{d, } ^1 J_{BH} = 96 \text{ Hz}); \ IR \ (\text{KBr}): \ \nu = 3433 \ (\text{br. m}), 2979 \ (m), 2925 \ (m), 2365 \ (m, \ \nu_{PH} \ or \ \nu_{BH} \ [\text{no clear assignment}]), 1640 \ (s), 1605 \ (s), 1510 \ (vs), 1461 \ (vs), 1379 \ (m), 1274 \ (s), 1182 \ (w), 1096 \ (vs), 1031 \ (m), 967 \ (vs), 903 \ (m), 854 \ (s), 780 \ (s), 703 \ (s), 647 \ (s), 551 \ (m); \ Anal. Calcd for C\text{\_38}H\text{\_30}BF\text{\_10}P: \ C, 63.53; \ H, 4.21; \ Found: \ C, 62.58; \ H, 4.16.
Crystals suitable for X-ray crystal structure analysis were obtained by diffusion of pentane into a concentrated solution of 6c in THF at room temperature. X-ray crystal structure analysis for 6c: formula C_{38}H_{30}BF_{10}P \times \frac{1}{2} C_4H_8O, \ M = 754.45, colorless crystal 0.45 x 0.35 x 0.20 mm, a = 12.7455(4), b = 13.9604(4), c = 21.8082(7) Å, α = 83.068(1), β = 88.124(1), γ = 73.459(1), V = 3692.6(2) Å^3, \rho_{\text{calc}} = 1.357 \text{ g cm}^{-3}, \mu = 1.373 \text{ mm}^{-1}, \text{empirical absorption correction (0.577 } \leq T \leq 0.771), Z = 4, \text{triclinic, space group P1bar (No. 2), } \lambda = 1.54178 \text{ Å, } T = 223 \text{ K, } \omega \text{ and } \phi \text{ scans, 56835 reflections collected (} \pm h, \pm k, \pm l\text{), }[(\sin \theta)/\lambda] = 0.60 \text{ Å}^{-1}, 13071 \text{ independent } (R_{\text{int}} = 0.048) \text{ and 11338 observed reflections } [I \geq 2 \sigma(I)], 974 \text{ refined parameters, } R = 0.049, wR^2 = 0.132, \text{max. (min.) residual electron density 0.37 \ (-0.40) e Å}^{-3}, \text{two almost identical molecules in the asymmetric unit, hydrogen atoms at P and B from difference fourier calculations and refined free, others calculated and refined as riding atoms.}

**Hydrogenation of Imines**

**Hydrogenation of N-benzylidene-t-butylamine (7a) catalysed by [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (4)**

a) **Stoichiometric reaction of [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) and N-benzylidene-t-butylamine (7a):**

[2-(Dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) (44.0 mg, 0.07 mmol) was dissolved in benzene-d_6 (0.8 ml), N-benzylidene-t-butylamine (7a) (14.0 mg, 0.08 mmol) was added. The yellow solution was analysed by NMR-spectroscopy. The sample is a mixture of non reduced imine (7a) (4%), N-benzyl-t-butylamine (8a) (48%) and the catalyst without hydrogen 1 [an interaction of 1 with 7a or 8a could not be ruled out]
(48%). The chemical shifts are slightly shifted compared to the resonances of the pure compounds.

(8a) $^1$H-NMR (300 MHz, 300 K, benzene-d$_6$): $\delta$ 7.32, 7.16 (5H, m, Ph), 3.64 (2H, broad s, CH$_2$), 0.95 (9H, broad s, t-Bu), n.o. (NH).

(1) $^1$H-NMR (300 MHz, 300 K, benzene-d$_6$): $\delta$ 6.47 (4H, d, $^4$J$_{Ph} = 2.9$ Hz, m-Mes), 2.74 (2H, broad, $^p$CH$_2$), 2.26 (2H, broad, CH$_2^B$), 2.06 (12H, s, $o$-CH$_3^{Mes}$), 1.95 (6H, s, $p$-CH$_3^{Mes}$); $^{19}$F-NMR (282 MHz, 300 K, benzene-d$_6$): $\delta$ -128.8 (broad, 4F, $o$-C$_6$F$_5$), -157.0 (broad, 2F, $p$-C$_6$F$_5$), 163.5 (broad, 4F, $m$-C$_6$F$_5$); $^{31}$P($^1$H)-NMR (122 MHz, 300 K, benzene-d$_6$): $\delta$ 20.2 ($\nu_{1/2} = 600$ Hz); $^{11}$B($^1$H)-NMR (96 MHz, 300 K, benzene-d$_6$): $\delta$ 7.6 ($\nu_{1/2} = 550$ Hz), [0.6 (approx. 10%, $\nu_{1/2} = 160$ Hz, not identified compound)].

(7a) $^1$H-NMR (300 MHz, 300 K, benzene-d$_6$): $\delta$ 8.13 (s, 1H, $^{Ph}$CH$^+$), 7.81 (m, 2H, Ph), 7.32, 7.16 (m, 3H, Ph), 1.24 (s, 9H, t-Bu).

b) Catalytic hydrogenation

[2-(Dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) (200 mg, 0.31 mmol, 0.2 eq) was dissolved in toluene (5ml), N-benzylidene-t-butylamine (7a) (250 mg, 1.55 mmol) was added and the yellow solution was stirred 45 minutes under a hydrogen atmosphere of 1.5 bar. During this time the reaction mixture turned colorless. Then 1 M aqueous HCl (20 ml) was added, the aqueous layer was separated, neutralized with 1M aqueous sodium hydroxide-solution (23 ml) and extracted with diethylether (3 $\times$ 15 ml). The combined organic layers were dried over magnesium sulfate. After evaporation a colorless oil (220 mg, 1.34 mmol, 87 %) could be obtained.

$^1$H-NMR (400 MHz, 300 K, benzene-d$_6$): $\delta$ 7.37 (m, 2H, Ph), 7.21 (m, 2H, Ph), 7.12 (m, 1H, $p$-Ph), 3.57 (s, 2H, CH$_2$), 1.00 (s, 9H, t-Bu), n.o. (NH); $^{13}$C($^1$H)-NMR (101 MHz, 300 K, benzene-d$_6$): $\delta$ 142.1 ($i$-Ph), 128.6, 128.5 ($o$,$m$-Ph), 126.9 ($p$-Ph), 50.4 ($i$-$^1$Bu), 47.3 (CH$_3$), 29.1 ($^1$Bu); IR (ATR): $\tilde{\nu}$ = 2991 (s), 1650 (m), 1480 (s), 1461 (s), 1400 (s), 1378 (s), 1250 (s), 1248 (s), 1100 (m), 1073 (m), 1047 (s), 911 (m), 704 (s), 600 (m) cm$^{-1}$; HRMS: (calc: 164.1439) found: 164.1450 [C$_{11}$H$_{17}$N + H$^+$].
Hydrogenation of N-(1-phenylethylidene)-t-butylamine (7b) catalysed by [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2)

a) Stoichiometric reaction of [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) and N-(1-phenylethylidene)-t-butylamine (7b):

[2-(Dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) (38 mg, 0.06 mmol) was dissolved in benzene-d6 (0.8 ml), N-(1-phenylethylidene)-t-butylamine (7b) (10 mg, 0.06 mmol) was added. The yellow solution was analysed by NMR-spectroscopy. A mixture of three compounds was obtained: 47% (8b), 47% (1) (an interaction of 1 with 8b could not be ruled out), 6% (unidentified compound, detected by 31P, 11B, and 19F).

(8b) 1H-NMR (600 MHz, 298 K, benzene-d6): δ 7.38 (2H, m, Ph), 7.20 (2H, m, Ph), 7.08 (1H, m, Ph), 3.82 (1H, dq, 3JHH = 6.7 Hz, 3JH(NH) = 1.7 Hz, NCH), 1.17 (3H, d, 3JHH = 6.7 Hz, CH3), 0.93 (9H, s, tBu), n.o. (NH); 13C{1H}-NMR (151 MHz, 298 K, benzene-d6): δ 149.9 (i-Ph), 128.4, 126.7, 126.5 (Ph), 52.7 (NCHMe), 51.1 (i- tBu), 30.2 (tBu), 27.7 (Me);

(1): 1H-NMR (600 MHz, 298 K, benzene-d6): δ 6.44 (4H, d, 4JPh = 2.8 Hz, m-Mes), 2.85 (2H, q, 3JHH = 2JPh = 8 Hz, pCH2), 2.27 (2H, dt, 3JPh = 41 Hz, CH2B), 2.03 (12H, s, o-CH3Mes), 1.90 (6H, s, p-CH3Mes); 13C{1H}-NMR (151 MHz, 298 K, benzene-d6): δ 148.2 (dm, 1JFC = 246 Hz, C6F5), 142.0 (d, 2JPC = 8.0 Hz, o-Mes), 140.8 (d, 4JPC = 2.6 Hz, p-Mes), 140.2 (dm, 1JFC = 256 Hz, p-C6F5), 137.4 (dm, 1JFC = 249 Hz, C6F5), 130.8 (d, 3JPC = 7 Hz, m-Mes), 126.8 (d, 1JPC = 20 Hz, i-Mes), 119.3 (i-C6F5), 29.3 (d, 1JPC = 35 Hz, pCH2), 22.5 (d, 3JPC = 6.5 Hz, o-CH3Mes), 20.5 (p-CH3Mes), 18.2 (broad, CH2B); 31P{1H}-NMR (122 MHz, 300 K, benzene-d6): δ 19.7 (v1/2 = 140 Hz); 31P-NMR (122 MHz, 300 K, benzene-d6): δ 19.7 (d, 1JPH = 480 Hz); 11B{1H}-NMR (96 MHz, 300 K, benzene-d6): δ 8.7 (v1/2 = 600 Hz).

(unidentified compound): 19F-NMR (282 MHz, 300 K, benzene-d6): δ -131.6 (2F) -133.1 (2F), -161.3 (1F), -162.2 (1F), -165.4 (4F); 31P{1H}-NMR (122 MHz, 300 K, benzene-d6): δ -4.9 (v1/2 = 20 Hz); 31P-NMR (122 MHz, 300 K, benzene-d6): δ -4.9 (d, 1JPH = 480 Hz); 11B{1H}-NMR (96 MHz, 300 K, benzene-d6): δ 0.2 (v1/2 = 120 Hz).

b) Catalytic hydrogenation

Hydrogenation of N-(1-phenylethylidene)-tert-butyl-amine (7b) catalysed by [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) was carried out under similar conditions (RT, pH2 = 2.5 bar) and similar workup as described above for the hydrogenation of N-benzylidene-tert-butylamine (8a).
<table>
<thead>
<tr>
<th>molar amount</th>
<th>amount of imine (7b)</th>
<th>amount of catalyst</th>
<th>reaction time</th>
<th>yield amine (8b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 %</td>
<td>133 mg (0.76 mmol)</td>
<td>98.0 mg (0.15 mmol)</td>
<td>45 min</td>
<td>100 mg (0.56 mmol, 74 %)</td>
</tr>
<tr>
<td>10 %</td>
<td>137 mg (0.78 mmol)</td>
<td>50.0 mg (0.08 mmol)</td>
<td>90 min</td>
<td>90.0 mg (0.51 mmol, 65 %)</td>
</tr>
<tr>
<td>5%</td>
<td>100 mg (0.57 mmol)</td>
<td>19.0 mg (0.03 mmol)</td>
<td>180 min</td>
<td>71.0 mg (0.39 mmol, 70 %)</td>
</tr>
</tbody>
</table>

N-(1-Phenylethyl)-t-butylamine (8b) was identified as the product of the hydrogenation procedure: [C\textsubscript{12}H\textsubscript{19}N, M = 177.29 g/mol]

\[
\begin{align*}
\text{HN} & \text{CH}_3 \\
\text{Ph} & \text{CH}_3 \\
\end{align*}
\]

\[^1\text{H}-\text{NMR} \ (400 \text{ MHz, } 300 \text{ K, benzene-d}_6): \delta \ 7.38 \ (2 \text{H, m, Ph}), \ 7.20 \ (2 \text{H, m, Ph}), \ 7.08 \ (1 \text{H, m, p-Ph}), \ 3.82 \ (1 \text{H, q, } ^3\text{J}_{HH} = 6.7 \text{ Hz, } ^1\text{CH}^{\text{Me}}), \ 1.17 \ (3 \text{H, d, } ^3\text{J}_{HH} = 6.7 \text{ Hz, Me}), \ 0.93 \ (9 \text{H, s, } ^1\text{Bu}), \ n.o. \ (\text{NH}); \ ^{13}\text{C}\{^1\text{H}\}-\text{NMR} \ (101 \text{ MHz, } 300 \text{ K, benzene-d}_6): \delta \ 149.9 \ (i-\text{Ph}), \ 128.4, \ 126.8 \ (o,m-\text{Ph}), \ 126.5 \ (p-\text{Ph}), \ 52.7 \ (^1\text{CH}^{\text{Me}}), \ 51.2 \ (i-\text{Bu}), \ 30.1 \ (i-\text{Bu}), \ 27.7 \ (\text{Me}); \ IR \ (\text{ATR}): \nu = 2960 \ (\text{m}), \ 1457 \ (\text{w}), \ 1364 \ (\text{w}), \ 1261 \ (\text{w}), \ 1229 \ (\text{w}), \ 1089 \ (\text{m}), \ 1024 \ (\text{m}), \ 803 \ (\text{m}), \ 761 \ (\text{m}), \ 700 \ (\text{s}), \ 513 \ (\text{m}) \ \text{cm}^{-1}; \ \text{Anal. Calcd for } \text{C}_{11}\text{H}_{19}\text{N}: \text{C}, \ 81.30; \ H, \ 10.80; \ N, \ 7.90; \ Found: \text{C}, \ 80.41; \ H, \ 10.57; \ N, \ 7.73.

**Hydrogenation of Enamines**

**Hydrogenation of 1-(1-phenylethen-1-yl)piperidine (9) catalysed by [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2)**

a) Stoichiometric reaction of [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) and 1-(1-phenylethen-1-yl)piperidine (9):

[2-(Dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) (30.0 mg, 0.05 mmol) was dissolved in benzene-d\textsubscript{6} (0.8 ml), 1-(1-phenylethen-1-yl)piperidine (9) (9.35 mg, 0.05 mmol) was added. The yellow solution was analysed by NMR-spectroscopy.

The sample is a mixture of 1-(1-phenylethyl)piperidine (10) and 1. The chemical shifts are slightly shifted compared to the resonances of the pure compounds.

(10): \[^1\text{H}-\text{NMR} \ (300 \text{ MHz, } 300 \text{ K, benzene-d}_6): \delta \ 7.17-7.34 \ (m, 5 \text{H, Ph}), \ 3.36 \ (q, 1 \text{H, } ^3\text{J}(\text{H,H}) = 6.8 \text{ Hz, CH}), \ 2.40 \ (m, 4 \text{H, CH}_2\text{-N}), \ 1.58 \ (m, 4 \text{H, CH}_2), \ 1.38 \ (m, 2 \text{H, CH}_2), \ 1.35 \ (d, 3 \text{H}, ^3\text{J}(\text{H,H}) = 6.8 \text{ Hz, CH}_3); ^{13}\text{C}\{^1\text{H}\}-\text{NMR} \ (75.5 \text{ MHz, } 297 \text{ K, benzene-d}_6): \delta \ 145.4 \ (i-\text{Ph}), \ 128.4, \ 127.8, \ 126.9 \ (\text{Ph}), \ 65.3 \ (\text{CH}), \ 51.8, \ 26.8, \ 25.1 \ (\text{CH}_2), \ 19.5 \ (\text{CH}_3); \]

15
(1) $^1$H-NMR (300 MHz, 300 K, benzene-$d_6$): $\delta$ 6.56 (br s, 4H, $m$-Mes), 2.65 (broad, 2H, $^p$CH$_2$), 2.24 (br, 12H, $o$-CH$_3$Mes), 1.95 (s, 6H, $p$-CH$_3$Mes), n.o. (CH$_2^B$), $^{10}$F-NMR (282 MHz, 300 K, benzene-$d_6$): $\delta$ -128.9 (broad, 4F, $o$-C$_6$F$_5$), -157.0 (broad, 2F, $p$-C$_6$F$_5$), -163.7 (broad, 4F, $m$-C$_6$F$_5$); $^{31}$P{$^1$H}-NMR (122 MHz, 300 K, benzene-$d_6$): $\delta$ 20.5 ($\nu_{1/2}$ = 170 Hz); $^{31}$P-NMR (122 MHz, 300 K, benzene-$d_6$): $\delta$ 20.5 ($\nu_{1/2}$ = 140 Hz); $^{11}$B{$^1$H}-NMR (96 MHz, 300 K, benzene-$d_6$): $\delta$ 8.1 ($\nu_{1/2}$ = 500 Hz); $^{11}$B-NMR (96 MHz, 300 K, benzene-$d_6$): $\delta$ 8.1 ($\nu_{1/2}$ = 500 Hz).

b) Catalytic hydrogenation

[2-(Dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) (128 mg, 0.2 mmol, 0.2 eq) was dissolved in toluene, (5ml) 1-(1-phenylethen-1-yl)piperidine (9) (200 mg, 1.07 mmol) was added and the yellow solution was stirred 20 hours under a hydrogen atmosphere of 2.5 bar. During this time the reaction mixture turned colorless. Then 1 M HCl (20 ml) was added, the aqueous layer was separated, neutralized with 1M sodiumhydroxide-solution (23 ml) and extracted with diethylether (3 $\times$ 20 ml). The combined organic layers were dried over magnesium sulfate. After evaporation a yellow oil (180 mg, 0.95 mmol, 89 %) could be obtained.

<table>
<thead>
<tr>
<th>molar amount of catalyst (2)</th>
<th>amount of enamine (9)</th>
<th>amount of catalyst (2)</th>
<th>reaction time</th>
<th>yield of amine (10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 %</td>
<td>200 mg (1.07 mmol)</td>
<td>128 mg (0.2 mmol)</td>
<td>20 hours</td>
<td>180 mg (0.95 mmol, 89 %)</td>
</tr>
<tr>
<td>15 %</td>
<td>200 mg (1.07 mmol)</td>
<td>103 mg (0.16 mmol)</td>
<td>20 hours</td>
<td>150 mg (0.80 mmol, 80 %)</td>
</tr>
<tr>
<td>10%</td>
<td>200 mg (1.07 mmol)</td>
<td>68.9 mg (0.11 mmol)</td>
<td>20 hours</td>
<td>200 mg (1.06 mmol, 99 %)</td>
</tr>
</tbody>
</table>

The obtained oil was identified as 1-(1-phenylethyl)piperidine (10), the product of the hydrogenation procedure: [C$_{13}$H$_{19}$N, M = 189.33 g/mol]

![Chemical structure](image)

(10) $^1$H-NMR (200 MHz, 300 K, chloroform-$d_1$): $\delta$ 7.17-7.27 (m, 5H, Ph), 3.30 (q, 1H, $^3$J(H,H) = 6.8 Hz, CH), 2.26-2.37 (m, 4H, CH$_2$-N), 1.48-1.57 (m, 4H, CH$_2$), 1.31 (d, 3H, $^3$J(H,H) = 6.8 Hz, CH$_3$), 1.30-1.39 (m, 2H, CH$_2$); $^{13}$C{$^1$H}-NMR (101 MHz, 294 K, chloroform-$d_1$): $\delta$ 144.0
Hydrogenation of 1-(cyclohex-1-en-1-yl)piperidine (11a) catalysed by [2-(dimesitylphosphinio)ethyl]bis(pentafluorophenyl)hydridoborate (2)

a) Stoichiometric reaction of [2-(dimesitylphosphinio)ethyl]bis(pentafluorophenyl)hydridoborate (2) and 1-(cyclohex-1-en-1-yl)piperidine (11a):

[2-(Dimesitylphosphinio)ethyl]bis(pentafluorophenyl)hydridoborate (2) (30 mg, 0.05 mmol) was dissolved in benzene-d$_6$ (0.8 ml), 1-(cyclohex-1-en-1-yl)piperidine (11a) (8.25 mg, 0.05 mmol) was added. The yellow solution was analysed by NMR-spectroscopy.

(12a) $^1$H-NMR (300 MHz, 300 K, benzene-d$_6$): δ 2.44 (pt, 4H, CH$_2$-N), 2.34 (m, 1H, CH-N), 0.96-1.86 (m, 16H, CH$_2$); $^{13}$C{$^1$H}-NMR (75.5 MHz, 300 K, benzene-d$_6$): δ 64.6 (CH), 50.5 (CH$_2$-N), 27.3, 27.0, 26.5, 25.7, 24.5 (CH$_2$); $^3$P{$^1$H}-NMR (122 MHz, 300 K, benzene-d$_6$): δ 20.3 (v$_{1/2}$ = 70 Hz); $^3$P-NMR (122 MHz, 300 K, benzene-d$_6$): δ 20.3 (v$_{1/2}$ = 130 Hz); $^{19}$F-NMR (282 MHz, 300 K, benzene-d$_6$): δ -128.9 (4F, o-C$_6$F$_5$), -157.0 (2F, p-C$_6$F$_5$), -163.6 (4F, m-C$_6$F$_5$); $^{11}$B{$^1$H}-NMR (96 MHz, 300 K, benzene-d$_6$): δ 8.8 (v$_{1/2}$ = 500 Hz); $^{11}$B-NMR (96 MHz, 300 K, benzene-d$_6$): δ 8.5 (v$_{1/2}$ = 150 Hz).

(unidentified compound): $^3$P{$^1$H}-NMR (122 MHz, 300 K, benzene-d$_6$): δ -16.3 (v$_{1/2}$ = 480 Hz); $^3$P-NMR (122 MHz, 300 K, benzene-d$_6$): δ -16.3 (v$_{1/2}$ = 50 Hz); $^{11}$B{$^1$H}-NMR (96 MHz, 300 K, benzene-d$_6$): δ -6.5; $^{11}$B-NMR (96 MHz, 300 K, benzene-d$_6$): δ -6.5.

b) Catalytic hydrogenation

Hydrogenation of 1-(cyclohex-1-en-1-yl)piperidine (11a) catalysed by [2-(dimesitylphosphinio)ethyl]bis(pentafluorophenyl)hydridoborate (2) was carried out under similar conditions (except 5 mol % catalyst – see footnote) (RT, P$_{H2}$ = 2.5 bar) and similar workup as described above for the hydrogenation of 1-(1-phenylethen-1-yl)piperidine (9).
<table>
<thead>
<tr>
<th>molar amount of catalyst (2)</th>
<th>amount of enamine (11a)</th>
<th>amount of catalyst (2)</th>
<th>reaction time</th>
<th>yield of amine (12a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 %</td>
<td>150 mg (0.9 mmol)</td>
<td>87 mg (0.135 mmol)</td>
<td>20 hours</td>
<td>131 mg (0.78 mmol, 87 %)</td>
</tr>
<tr>
<td>10 %</td>
<td>150 mg (0.9 mmol)</td>
<td>59 mg (0.09 mmol)</td>
<td>20 hours</td>
<td>124 mg (0.74 mmol, 83 %)</td>
</tr>
<tr>
<td>5 %⁶</td>
<td>150 mg (0.9 mmol)</td>
<td>29 mg (0.045 mmol)</td>
<td>20 hours</td>
<td>132 mg (0.79 mmol, 88 %)</td>
</tr>
</tbody>
</table>

1-Cyclohexylpiperidine was identified as the product of the hydrogenation procedure: [C\textsubscript{11}H\textsubscript{21}N, M = 167.33 g/mol]

\[
\text{1C11H21N, M = 167.33 g/mol}
\]

\[
\text{12a} \quad \delta 2.50 (pt, 4H, CH\textsubscript{2}-N), 2.17-2.25 (m, 1H, CH), 1.13-1.84 (m, 16H, CH\textsubscript{2}); 13C\{\textsuperscript{1}H\}-NMR (101 MHz, 275 K, chloroform-d\textsubscript{1}): \delta 64.5 (CH), 50.1 (CH\textsubscript{2}-N), 28.8, 28.4, 26.5, 26.2, 25.0 (CH\textsubscript{2}); IR (ATR): \nu = 2926 (s), 2852 (m), 2790 (w), 1450 (m), 1379 (w), 1258 (w), 1159 (m), 970 (w), 890 (w), 860 (w), 802 (w); HRMS: (calc: 168.1752) found: 168.1765 [C\textsubscript{11}H\textsubscript{21}N + H\textsuperscript{+}].

**Hydrogenation of 4-cyclohex-1-enyl-morpholine (11b) catalysed by [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2)**

a) Stoichiometric reaction of [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) and 4-cyclohex-1-enyl-morpholine (11b):

[2-(Dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) (30 mg, 0.05 mmol) was dissolved in benzene-d\textsubscript{6} (0.8 ml), 4-cyclohex-1-enyl-morpholine (8.35 mg, 0.05 mmol) was added. The yellow solution was analysed by NMR-spectroscopy. A mixture of the amine 4-cyclohexyl-morpholine (12b) and 1 was obtained.

\[
\text{12b} \quad \delta 3.64 (m, 4H, CH\textsubscript{2}-O), 2.34 (m, 4H, CH\textsubscript{2}-N), 2.16 (m, 1H, CH-N), 1.73 (m, 4H, CH\textsubscript{2}), 1.15 (m, 6H, CH\textsubscript{2}); 13C\{\textsuperscript{1}H\}-NMR (75.5 MHz, 297 K, benzene-d\textsubscript{6}): \delta 67.8 (CH\textsubscript{2}-O), 63.3 (CH), 48.7 (CH\textsubscript{2}-N), 27.2, 25.8, 24.7 (CH\textsubscript{2});
\]

(1): \[\delta 6.63 (d, 4H, J\textsubscript{PH} = 2.6 Hz, m-Mes), 2.74 (m, 2H, CH\textsubscript{2}), 2.28 (s, 12H, o-CH\textsubscript{3}\textsubscript{Mes}), 2.06 (s, 6H, p-CH\textsubscript{3}\textsubscript{Mes}), 31P\{\textsuperscript{1}H\}-NMR (122 MHz, 300 K, benzene-d\textsubscript{6}): \delta 5.1 (v\textsubscript{1/2} = 80 Hz); \]

\[
\text{19F-NMR (282 MHz, 297 K, benzene-d\textsubscript{6}): \delta -129.9 (4F, o-C\textsubscript{6}F\textsubscript{5}), -156.5}
\]

⁶ Different procedure: 1-(Cyclohex-1-en-1-yl)piperidine (11a) was dissolved in 3 mL toluene and stirred under hydrogen-atmosphere. Then the catalyst (2) – dissolved in 2 mL toluene – was added. The mixture was stirred further 20 hours under the same conditions as shown above and worked up similarly.
(2F, p-C₆F₅), -163.2 (4F, m-C₆F₅); $^{11}$B{$^1$H}-NMR (96 MHz, 300 K, benzene-d₆); δ 11.0 ($\nu_{1/2} = 800$ Hz); $^{11}$B-NMR (96 MHz, 300 K, benzene-d₆); δ 10.1 ($\nu_{1/2} = 800$ Hz).

(unidentified compound): $^{31}$P{$^1$H}-NMR (122 MHz, 300 K, benzene-d₆): δ -4.9, -13.2, -16.8, -22.1; $^{31}$P-NMR (122 MHz, 300 K, benzene-d₆): δ -4.9, -16.9, -22.1.

### b) Catalytic hydrogenation

Hydrogenation of 4-cyclohex-1-enyl-morpholine (11b) catalysed by [2-(dimesitylphosphonio)ethyl]bis(pentafluorophenyl)hydridoborate (2) was carried out under similar conditions (except for 3 mol % catalyst – see footnote) (RT, $p_{H_2} = 2.5$ bar) and similar workup as described above for the hydrogenation of 1-(1-phenylethen-1-yl)piperidine (9).

<table>
<thead>
<tr>
<th>molar amount of catalyst (2)</th>
<th>amount of enamine (11b)</th>
<th>amount of catalyst (2)</th>
<th>reaction time</th>
<th>yield of amine (12b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 %</td>
<td>150 mg (0.9 mmol)</td>
<td>115.9 mg (0.18 mmol)</td>
<td>20 hours</td>
<td>112 mg (0.66 mmol, 74 %)</td>
</tr>
<tr>
<td>15 %</td>
<td>200 mg (1.19 mmol)</td>
<td>115 mg (0.18 mmol)</td>
<td>20 hours</td>
<td>183 mg (1.09 mmol, 92 %)</td>
</tr>
<tr>
<td>10%</td>
<td>200 mg (1.19 mmol)</td>
<td>77.9 mg (0.12 mmol)</td>
<td>20 hours</td>
<td>178 mg (1.05 mmol, 89 %)</td>
</tr>
<tr>
<td>5%</td>
<td>200 mg (1.19 mmol)</td>
<td>38.6 mg (0.03 mmol)</td>
<td>20 hours</td>
<td>143.3 mg (0.85 mmol, 71 %)</td>
</tr>
<tr>
<td>3%</td>
<td>200 mg (1.19 mmol)</td>
<td>25.8 mg (0.03 mmol)</td>
<td>20 hours</td>
<td>152.7 mg (0.91 mmol, 78 %)</td>
</tr>
</tbody>
</table>

The colourless oil was identified as 4-cyclohexyl-morpholine (12b), the product of the hydrogenation procedure: [C$_{10}$H$_{19}$NO, M = 169.30 g/mol]

(12b) $^1$H-NMR (200 MHz, 300 K, chloroform-d$_1$): δ 3.63-3.68 (m, 4H, CH$_2$-O), 2.45-2.55 (m, 4H, CH$_2$-N), 2.02-2.20 (m, 1H, CH-N), 1.71-1.89 (m, 4H, CH$_2$), 1.01-1.29 (m, 6H, CH$_2$); $^{13}$C{$^1$H}-NMR (101 MHz, 298 K, chloroform-d$_1$): δ 66.4 (CH$_2$-O), 62.8 (CH), 48.7 (CH$_2$-N), 27.9, 25.3, 24.7 (CH$_2$); IR (ATR): $\tilde{\nu} = 2926$ (s), 2852 (s), 2806 (m), 1718 (w), 1450 (s), 1360 (w), 1116 (s), 783 (w); HRMS: (calc: 170.1545) found: 170.1551 [C$_{10}$H$_{19}$NO + H$^+$].

7 Different procedure: 4-Cyclohex-1-enyl-morpholine (11b) was dissolved in 3 mL toluene and stirred under hydrogen-atmosphere. Then the catalyst (2) – dissolved in 2 mL toluene – was added. The mixture was stirred further 20 hours under the same conditions as shown above and worked up similarly.
**Autoclave Ventile**

Pressure control valve: When the pressure is released from the autoclave, pressure can go out of the vial and a rest pressure of 1 bar will stay in the vial. So the compound inside the vial does not get in contact with air and moisture.

Non return valve: H₂ can get into the vial
$^1$H-NMR (600 MHz, 298 K, benzene-d$_6$)

![NMR Spectrum]

Chemical shifts:
- 1.17 ppm
- 2.28 ppm
- 3.69 ppm
- 4.22 ppm
- 12.00 ppm
- 6.83 ppm
$^1$H-NMR (600 MHz, 298 K, benzene-d$_6$)
^1H-NMR (500 MHz, 298 K, benzene-d_6)

* residue of dimesitylvinyliophosphine
$^3$H-NMR (77 MHz, 298 K, benzene)
$^1$H-NMR (600 MHz, 298 K, benzene-d$_6$)
$^1$H-NMR (600 MHz, 298 K, benzene-d$_6$)
$^1$H-NMR (400 MHz, 298 K, benzene-d$_6$)
H-NMR (300 MHz, 298 K, benzene-d$_6$)
$^1$H-NMR (200.1 MHz, 300K, Chloroform-d$_1$)
$^1$H-NMR (200.1 MHz, 300K, Chloroform-d.)