Supporting information for:

Diverse Ring-Opening Reactions of Rhodium η⁴-Azaborete Complexes

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General considerations

All manipulations were performed under an atmosphere of dry argon using glovebox or standard Schlenk line techniques. Deuterated solvents were dried over 4 Å molecular sieves and degassed by three freeze-pump-thaw cycles. All other solvents were dried by distillation from appropriate drying agents under an argon atmosphere and stored under argon over activated 4 Å molecular sieves. All NMR spectra were obtained from a Bruker Avance III HD 300 NMR spectrometer ($^{13}$C($^1$H, $^{31}$P): 75.5 MHz), from a Bruker Avance I 400 NMR spectrometer ($^1$H: 400.6 MHz, $^{13}$C($^1$H): 100.6 MHz, $^{11}$B: 128.5 MHz, $^{31}$P($^1$H): 162.2 MHz, $^{19}$F: 376.5 MHz) or from a Bruker Avance I 500 NMR spectrometer ($^1$H: 500.1 MHz, $^1$H($^{31}$P): 500.1 MHz, $^{13}$C($^1$H): 125.8 MHz, $^{11}$B: 160.5 MHz, $^{31}$P($^1$H): 202.5 MHz, $^{19}$F: 470.6 MHz) at 298 K unless otherwise stated. Chemical shifts (δ) are provided in ppm and internally referenced to the carbon nuclei ($^{13}$C($^1$H), $^{13}$C($^1$H, $^{31}$P)) or residual protons ($^1$H, $^1$H($^{31}$P)) of the solvent. $^{11}$B, $^{31}$P($^1$H) and $^{19}$F NMR spectra were referenced against external BF$_3$·Et$_2$O, 85% H$_3$PO$_4$ or Cl$_3$CF, respectively. For higher-order spin systems of the P(CH$_3$)$_3$ groups $N(N = |J_{PC} + 3J_{PC}|$ or $|2J_{PH} + 4J_{PH}|$) is given. UV/Vis absorption spectra were measured on a JASCO V-660 UV/Vis spectrometer or on a METTLER TOLEDO UV/Vis-Excellence UV5 spectrophotometer. High-resolution mass spectrometry data were acquired on a Thermo Scientific Exactive Plus Spectrometer in LIFDI or ASAP mode. Photoreactions were performed using a LOT-Quantum Design GmbH mercury-xenon vapor lamp (I = 19 A, U = 26 V).

Chemicals: $\{[(COE)$_2$RhCl]_2\}$, trimethylphosphine, triisopropylphosphine, (tert-butylimino)mesitylborane, N,N-dimethyl-4-[2-[4-trifluoromethyl]phenyl|ethynyl|benzenamine, ethynylferrocene, 1,3-dimethylimidazol-2-ylidene (IME), 1,3-diisopropylimidazol-2-ylidene (I/iPr) and 1b were synthesized according to modified literature procedures. $\{[(P\text{Pr}_3)$_2$RhCl]_2\}$ was prepared in situ according to a modified literature procedure. All other chemicals were purchased from either abcr, Acros, Sigma-Aldrich or TCI Chemical Co. and used without further purification.

The rhodium azaborate complexes 1a, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k and 1l were synthesized according to a standardized procedure adapted from a previously published route. All manipulations (except the washing procedure) during the synthesis of the complexes 1a, 1b, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k and 1l were performed as far as possible with the exclusion of light.
Synthetic procedures

Abbreviations

Aza  azaborote (four-membered ring system)
Aza1 azaborinine (six-membered ring system)
Bpin 4,4,5,5-tetramethyl-1,3,2-dioxaborolanyl
br  broad
COE  cyclooctene
Cp  cyclopentadienyl
d  doublet
Et  ethyl
Fc  ferrocenyl
IiPr 1,3-diisopropylimidazol-2-ylidene
IMe 1,3-dimethylimidazol-2-ylidene
iPr  isopropyl
m  multiplet
Me  methyl
Mes  mesityl = 2,4,6-trimethylphenyl
Ph  phenyl
q  quartet
s  singlet
sept  septet
t  triplet
tBu  tert-butyl
THF  tetrahydrofuran
v  virtual
Synthesis of 1a

\[
\begin{align*}
\text{tBu} & \quad \text{N} \quad \text{Mes} \\
\text{Cl} & \quad \text{Rh} \quad \text{PtPr}_3
\end{align*}
\]

\([(\text{COE})_2\text{RhCl}]_2 \) (1.00 g, 1.39 mmol) was suspended in pentane (15 mL) and triisopropylphosphine (2.00 mL, 10.5 mmol) was added. After stirring the reaction mixture for 15 min, propyne was passed through the suspension for 2 min. All volatiles were removed \textit{in vacuo} and the residue was dissolved in THF (15 mL). A stock solution of (tert-butylimino)mesitylborane in heptane (3.45 mL, 6.97 mmol, 2.02 M) was added and the reaction mixture was stirred for 15 h at room temperature. After removing all volatiles \textit{in vacuo} the residue was washed with pentane (5 x 5 mL) and dried under reduced pressure to yield 1a as a yellow solid (1.27 g, 2.35 mmol, 85%). Crystals of 1a suitable for X-ray diffraction were obtained by evaporation of a saturated pentane solution at \(-30^\circ\text{C}\).

\( ^1\text{H} \text{NMR} \) (500.1 MHz, C\(_6\)D\(_6\), 298 K): \( \delta = 6.83 \) (s, 2H, Mes-CH), 3.39 (s, 3H, Mes-CH\(_3\)), 2.78 (s, 1H, Aza-CH), 2.54 (s, 3H, Mes-CH\(_3\)), 2.18-2.08 (m, 3H, iPr-CH) overlapping with 2.14 (s, 3H, Mes-CH\(_3\)), 1.53 (s, 3H, Aza-CH\(_3\)), 1.34 (s, 9H, tBu-CH\(_3\)), 1.12 (dd, \(^3J_{\text{PH}} = 14.0\) Hz, \(^3J_{\text{HH}} = 7.3\) Hz, 9H, iPr-CH\(_3\)), 1.07 (dd, \(^3J_{\text{PH}} = 13.3\) Hz, \(^3J_{\text{HH}} = 7.2\) Hz, 9H, iPr-CH\(_3\)) ppm.

\( ^1\text{H}[{}^{31}\text{P}] \text{NMR} \) (500.1 MHz, C\(_6\)D\(_6\), 298 K): \( \delta = 6.83-6.82 \) (m, 2H, Mes-CH), 3.38 (s, 3H, Mes-CH\(_3\)), 2.78 (s, 1H, Aza-CH), 2.54 (s, 3H, Mes-CH\(_3\)), 2.17-2.09 (m, 3H, iPr-CH) overlapping with 2.14 (s, 3H, Mes-CH\(_3\)), 1.53 (s, 3H, Aza-CH\(_3\)), 1.34 (s, 9H, tBu-CH\(_3\)), 1.12 (d, \(^3J_{\text{HH}} = 7.2\) Hz, 9H, iPr-CH\(_3\)), 1.07 (d, \(^3J_{\text{HH}} = 7.2\) Hz, 9H, iPr-CH\(_3\)) ppm.

\( ^{13}\text{C}[^1\text{H}] \text{NMR} \) (125.8 MHz, C\(_6\)D\(_6\), 298 K): \( \delta = 141.5 \) (s, Mes-C\(_q\)), 140.4 (s, Mes-C\(_q\)), 138.1 (s, Mes-C\(_q\)), 131.1 (bs, Mes-C\(_q\)), 128.5 (s, Mes-CH), 127.5 (s, Mes-CH), 103.8-103.7 (m, Aza-C\(_q\)), 56.0 (d, \(^4J_{\text{PC}} = 1.5\) Hz, tBu-C\(_q\)), 49.0 (bs, Aza-CH), 29.0 (d, \(^4J_{\text{PC}} = 2.9\) Hz, tBu-CH\(_3\)), 26.9 (d, \(^4J_{\text{RHC}} = 0.5\) Hz, Mes-CH\(_3\)), 25.2 (dd, \(^1J_{\text{PC}} = 21.0\) Hz, \(^2J_{\text{RHC}} = 1.3\) Hz, iPr-CH), 23.7 (s, Mes-CH\(_3\)), 21.3 (s, Mes-CH\(_3\)), 20.3 (dd, \(^2J_{\text{PC}} = 1.9\) Hz, \(^3J_{\text{RHC}} = 0.5\) Hz, iPr-CH\(_3\)), 19.6 (s, iPr-CH\(_3\)), 19.6 (d, \(^2J_{\text{RHC}} = 1.3\) Hz, Aza-CH\(_3\)) ppm.

\( ^{13}\text{C}[{}^1\text{H}, {}^{31}\text{P}] \text{NMR} \) (75.5 MHz, C\(_6\)D\(_6\), 298 K): \( \delta = 141.5 \) (s, Mes-C\(_q\)), 140.4 (s, Mes-C\(_q\)), 138.1 (s, Mes-C\(_q\)), 128.5 (s, Mes-CH), 127.5 (s, Mes-CH), 103.9-103.7 (m, Aza-C\(_q\)), 56.0 (s, tBu-C\(_q\)), 49.0 (bs, Aza-CH), 29.1 (s, tBu-CH\(_3\)), 26.9 (d, \(^4J_{\text{RHC}} = 0.6\) Hz, Mes-CH\(_3\)), 25.2 (d,
$J_{\text{RhC}} = 1.5$ Hz, iPr-CH), 23.7 (s, Mes-CH$_3$), 21.3 (s, Mes-CH$_3$), 20.3 (d, $J_{\text{RhC}} = 0.7$ Hz, iPr-CH$_3$), 19.6 (d, $J_{\text{RhC}} = 0.6$ Hz, iPr-CH$_3$), 19.6 (d, $J_{\text{RhC}} = 1.4$ Hz, Aza-CH$_3$) ppm.

Comment: The broad singlet corresponding to the Mes-C$_n$ nucleus bound to the boron atom could not be observed in the $^{13}$C {$^1$H, $^{31}$P} NMR spectrum.

$^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K): $\delta = 20.9$ (br s) ppm.

$^{31}$P {$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K): $\delta = 61.0$ (d, $J_{\text{RhP}} = 197$ Hz) ppm.

UV-vis (hexane): $\lambda_{\text{abs}} = 240, 296$ (shoulder), 383 nm.

### Synthesis of 1c

[[(COE)$_2$RhCl]$_2$] (400 mg, 557 $\mu$mol) was suspended in pentane (12 mL) and treated with triisopropylphosphine (0.80 mL, 4.19 mmol). After stirring the suspension for 10 min, ethynylferrocene (233 mg, 1.11 mmol) was added. The reaction mixture was stirred for 10 min and all volatiles were removed in vacuo. The residue was dissolved in THF (10 mL) and treated with a stock solution of (tert-butylimino)mesitylborane in heptane (1.45 mL, 2.79 mmol, 1.93 M). The reaction mixture was stirred for 15 h at ambient temperature and all volatiles were removed in vacuo. The residue was washed with pentane (6 x 4 mL) and dried under reduced pressure to yield 1c as a red solid (582 mg, 820 $\mu$mol, 74%). Crystals of 1c suitable for X-ray diffraction were obtained by evaporation of a saturated hexane/benzene (5:1) solution.

$^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K): $\delta = 6.88$ (s, 2H, Mes-CH), 4.440-4.435 (m, 1H, C$_5$H$_4$-CH), 4.35-4.34 (m, 1H, C$_5$H$_4$-CH), 4.09 (s, 5H, Cp-CH), 4.06-4.05 (m, 1H, C$_5$H$_4$-CH), 4.04-4.03 (m, 1H, C$_5$H$_4$-CH), 3.45 (s, 3H, Mes-CH$_3$), 3.17 (s, 1H, Aza-CH), 2.72 (s, 3H, Mes-CH$_3$), 2.24-2.16 (m, 3H, iPr-CH) overlapping with 2.18 (s, 3H, Mes-CH$_3$), 1.56 (s, 9H, tBu-CH$_3$), 1.15 (dd, $J_{\text{PH}} = 13.5$ Hz, $J_{\text{HH}} = 7.2$ Hz, 9H, iPr-CH$_3$), 1.11 (dd, $J_{\text{PH}} = 13.5$ Hz, $J_{\text{HH}} = 7.2$ Hz, 9H, iPr-CH$_3$) ppm.

Comment: The spectrum contains residual hexane from the crystallization process, corresponding to signals at 1.25 (m) and 0.89 (t) ppm.
**Synthesis of 1d**

[(COE)₂RhCl]₂ (440 mg, 613 μmol) was suspended in pentane (10 mL) and treated with triisopropylphosphine (0.88 mL, 4.61 mmol). After stirring the suspension for 10 min, 2-butyne (0.1 mL, 1.28 mmol) was added. The reaction mixture was stirred for 10 min and all volatiles were removed *in vacuo*. The residue was dissolved in THF (12 mL) and treated with a stock solution of (tert-butylimino)mesitylborane in heptane (1.22 mL, 2.46 mmol, 2.02 M). The reaction mixture was stirred for 15 h at room temperature and then all volatiles were removed *in vacuo*. The residue was washed with pentane (4 x 4 mL) and dried under reduced pressure to yield 1d as a yellow solid (602 mg, 1.09 mmol, 89%). Crystals of 1d suitable for X-ray diffraction were obtained by evaporation of a saturated hexane solution.

**1H NMR** (500.1 MHz, C₆D₆, 298 K): δ = 6.84 (s, 1H, Mes-CH), 6.80 (s, 1H, Mes-CH), 3.45 (s, 3H, Mes-CH₃), 2.42 (s, 3H, Mes-CH₃), 2.38-2.27 (m, 3H, iPr-CH), 2.14 (s, 3H, Mes-CH₃), 1.47 (s, 3H, Aza-CH₃), 1.39 (s, 9H, tBu-CH₃), 1.21-1.17 (m, 12H, iPr-CH₃ overlapping with Aza-CH₃), 1.12 (dd, 3Jₕ = 12.9 Hz, 3Jₜt = 7.3 Hz, 9H, iPr-CH₃) ppm.


**Synthesis of 1e**

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[(COE)₂RhCl]₂ (530 mg, 739 μmol) was suspended in pentane (12 mL) and treated with triisopropylphosphine (1.06 mL, 5.55 mmol). After stirring the suspension for 10 min, 3-hexyne (121 mg, 168 μL, 1.48 mmol) was added. The reaction mixture was stirred for 10 min and all volatiles were removed in vacuo. The residue was dissolved in THF (10 mL) and treated with
a stock solution of (tert-butylimino)mesitylborane in heptane (1.54 mL, 2.96 mmol, 1.93 M). The reaction mixture was stirred for 15 h at room temperature and then all volatiles were removed in vacuo. The residue was washed with pentane (4 x 5 mL) and dried under reduced pressure to yield 1e as an orange solid (526 mg, 904 μmol, 61%). Crystals of 1e suitable for X-ray diffraction were obtained by evaporation of a saturated hexane solution.

**1H NMR** (500.1 MHz, C₆D₆, 298 K): \( \delta = 6.84 \) (s, 1H, Mes-CH), 6.81 (s, 1H, Mes-CH), 3.50 (s, 3H, Mes-CH₃), 2.45 (s, 3H, Mes-CH₃), 2.41-2.33 (m, 3H, iPr-CH), 2.26 (q, \( ^3J_{HH} = 7.6 \) Hz, 2H, Et-CH₂), 2.16 (s, 3H, Mes-CH₃), 1.66-1.54 (m, 2H, Et-CH₂), 1.46 (s, 9H, tBu-CH₃), 1.25 (dd, \( ^3J_{PH} = 13.7 \) Hz, \( ^3J_{HH} = 7.2 \) Hz, 9H, iPr-CH₃), 1.18-1.13 (m, 12H, iPr-CH₃ overlapping with Et-CH₃), 1.03 (t, \( ^3J_{HH} = 7.5 \) Hz, 3H, Et-CH₃) ppm.

**13C{1H} NMR** (125.8 MHz, C₆D₆, 298 K): \( \delta = 141.6 \) (s, Mes-C₆), 139.2 (s, Mes-C₆), 137.9 (s, Mes-C₆), 131.6 (br s, Mes-C₆), 128.4 (s, Mes-CH), 127.5 (s, Mes-CH), 106.5-106.3 (m, Aza-C₆), 68.2 (br s, Aza-C₆), 56.8 (d, \( ^3J_{PC} = 2.0 \) Hz, tBu-C₆), 29.2 (d, \( ^4J_{PC} = 2.8 \) Hz, tBu-CH₃), 27.7 (d, \( ^4J_{RhC} = 0.8 \) Hz, Mes-CH₃), 24.4 (d, \( ^2J_{RhC} = 0.7 \) Hz, Et-CH₂), 23.9 (s, Mes-CH₃), 23.8 (dd, \( ^1J_{PC} = 19.8 \) Hz, \( ^2J_{RhC} = 1.3 \) Hz, iPr-CH), 21.3 (s, Mes-CH₃), 20.6 (d, \( ^2J_{PC} = 1.5 \) Hz, iPr-CH₃), 20.0 (s, Et-CH₂), 19.6 (s, iPr-CH₃), 14.8 (s, Et-CH₃), 11.2 (d, \( ^3J_{RhC} = 1.4 \) Hz, Et-CH₃) ppm.

**11B NMR** (160.5 MHz, C₆D₆, 298 K): \( \delta = 21.4 \) (br s) ppm.

**31P{1H} NMR** (202.5 MHz, C₆D₆, 298 K): \( \delta = 50.0 \) (d, \( ^4J_{RHP} = 196 \) Hz) ppm.

**HRMS (LIFDI, C₂₃H₃₁BCINPRh):** calcld: m/z = 581.2590, found: m/z = 581.2563.

UV-vis (hexane): \( \lambda_{abs} = 253, 298, 395 \) nm.

**Synthesis of 1f**

![Diagram of 1f](attachment:diagram.png)

\[ [(\text{CO})₂\text{RhCl}_2] \] (815 mg, 1.14 mmol) was suspended in pentane (15 mL) and treated with triisopropylphosphine (1.63 mL, 8.53 mmol). After stirring the suspension for 15 min, 2,4-hexadiyne (178 mg, 2.28 mmol) was added. The reaction mixture was stirred for 15 min and all volatiles were removed in vacuo. The residue was dissolved in THF (15 mL) and treated with a stock solution of (tert-butylimino)mesitylborane in heptane (2.68 mL, 6.84 mmol,
2.55 M). After stirring the reaction mixture for 15 h at ambient temperature, all volatiles were removed in vacuo. The residue was washed with pentane (5 x 5 mL) and dried under reduced pressure to yield 1f as an orange solid (936 mg, 1.62 mmol, 71%). Crystals of 1f suitable for X-ray diffraction were obtained by evaporation of a saturated hexane/benzene (10:1) solution.

$^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K): $\delta = 6.82$ (s, 1H, Mes-CH), 6.76 (s, 1H, Mes-CH), 3.45 (s, 3H, Mes-CH$_3$), 2.75-2.67 (m, 3H, iPr-CH), 2.63 (s, 3H, Mes-CH$_3$), 2.11 (s, 3H, Mes-CH$_3$), 1.64 (s, 3H, Aza-CH$_3$), 1.44 (s, 3H, CCCH$_3$) 1.35 (s, 9H, tBu-CH$_3$), 1.30-1.20 (m, 18H, iPr-CH$_3$) ppm.

$^1$H$^{31}$P NMR (500.1 MHz, C$_6$D$_6$, 298 K): $\delta = 6.819$-6.815 (m, 1H, Mes-CH), 6.76-6.75 (m, 1H, Mes-CH), 3.44 (s, 3H, Mes-CH$_3$), 2.70 (sept, $^3$J$_{HP} = 7.2$ Hz, 3H, iPr-CH), 2.63 (s, 3H, Mes-CH$_3$), 2.11 (s, 3H, Mes-CH$_3$), 1.637-1.636 (m, 3H, Aza-CH$_3$), 1.44 (s, 3H, CCCH$_3$), 1.34 (s, 9H, tBu-CH$_3$), 1.27 (d, $^3$J$_{HH} = 7.2$ Hz, 9H, iPr-CH$_3$), 1.22 (d, $^3$J$_{HH} = 7.3$ Hz, 9H, iPr-CH$_3$) ppm.

$^{13}$C$^1$H NMR (125.8 MHz, C$_6$D$_6$, 298 K): $\delta = 141.7$ (s, Mes-C$_q$), 141.2 (s, Mes-C$_q$), 138.5 (s, Mes-C$_q$), 129.9 (Mes-C$_q$, detected by HMBC), 128.4 (s, Mes-CH), 127.7 (s, Mes-CH), 102.7-102.6 (m, Aza-C$_q$), 85.48-85.46 (m, CCCH$_3$), 78.31-78.30 (m, CCCH$_3$), 56.4 (d, $^3$J$_{PC} = 1.7$ Hz, tBu-C$_q$), 49.4 (br s, Aza-C$_q$), 28.8 (d, $^4$J$_{PC} = 2.8$ Hz, tBu-CH$_3$), 27.0 (d, $^4$J$_{RHC} = 0.5$ Hz, Mes-CH$_3$), 23.2 (s, Mes-CH$_3$), 22.5 (dd, $^1$J$_{PC} = 21.4$ Hz, $^2$J$_{RHC} = 1.0$ Hz, iPr-CH), 21.3 (s, Mes-CH$_3$), 20.31-20.30 (m, iPr-CH$_3$), 19.5 (s, iPr-CH$_3$), 17.3 (d, $^2$J$_{RHC} = 0.9$ Hz, Aza-CH$_3$), 4.6 (s, CCCH$_3$) ppm.

Comment: The spectrum contains a signal corresponding to residual benzene from the crystallization process at 128.59 ppm.

$^{13}$C$^1$H, $^{31}$P NMR (75.5 MHz, C$_6$D$_6$, 298 K): $\delta = 141.7$ (s, Mes-C$_q$), 141.2 (s, Mes-C$_q$), 138.5 (s, Mes-C$_q$), 129.8 (br s, Mes-C$_q$), 102.8-102.6 (m, Aza-C$_q$), 85.5 (d, $^2$J$_{RHC} = 0.6$ Hz, CCCH$_3$), 78.3 (d, $^3$J$_{RHC} = 0.6$ Hz, CCCH$_3$), 56.4 (s, tBu-C$_q$), 49.5 (br s, Aza-C$_q$), 28.8 (s, tBu-CH$_3$), 27.0 (d, $^4$J$_{RHC} = 0.7$ Hz, Mes-CH$_3$), 23.2 (s, Mes-CH$_3$), 22.5 (d, $^2$J$_{RHC} = 1.2$ Hz, iPr-CH), 21.3 (s, Mes-CH$_3$), 20.3 (d, $^3$J$_{RHC} = 0.6$ Hz, iPr-CH$_3$), 19.5 (d, $^3$J$_{RHC} = 0.5$ Hz iPr-CH$_3$), 17.3 (d, $^2$J$_{RHC} = 1.2$ Hz, Aza-CH$_3$), 4.6 (s, CCCH$_3$), ppm.

Comment: The broad singlet corresponding to the Mes-C$_q$ nucleus bound to the boron atom could not be observed in the $^{13}$C$^1$H, $^{31}$P NMR spectrum. Due to overlapping with the signal of C$_6$D$_6$, the singlet of one Mes-CH nucleus could not be observed in the $^{13}$C$^1$H, $^{31}$P NMR spectrum.

$^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K): $\delta = 20.3$ (br s) ppm.

$^{31}$P$^1$H NMR (202.5 MHz, C$_6$D$_6$, 298 K): $\delta = 50.2$ (d, $^1$J$_{RHP} = 192$ Hz) ppm.
HRMS (LIFDI, C_{28}H_{47}BCINPRh): calcd: m/z = 577.2277, found: m/z = 577.2253.

UV-vis (hexane): $\lambda_{\text{abs}} = 267, 306, 387$ nm.

**Synthesis of 1g**

![Structure of 1g](image)

$\left\{\text{COE}\right\}_2\text{RhCl}_2$ (400 mg, 557 µmol) was suspended in pentane (12 mL) and treated with triisopropylphosphine (0.80 mL, 4.19 mmol). After stirring the suspension for 10 min, 4,4,5,5-tetramethyl-2-(2-phenylethynyl)-1,3,2-dioxaborolane (254 mg, 1.11 mmol) was added. The reaction mixture was stirred for 10 min and all volatiles were removed *in vacuo*. The residue was dissolved in THF (12 mL) and treated with a stock solution of (tert-butylimino)mesitylborane in heptane (1.16 mL, 2.22 mmol, 1.92 M). After stirring the reaction mixture for 15 h at ambient temperature, all volatiles were removed *in vacuo*. The residue was washed with pentane (7 x 5 mL) and dried under reduced pressure to yield 1g as an orange solid (490 mg, 673 µmol, 60%). Crystals of 1g suitable for X-ray diffraction were obtained by evaporation of a saturated hexane solution.

**$^1H$ NMR** (500.1 MHz, C₆D₆, 298 K): $\delta = 8.29$-$8.27$ (m, 2H, Ph-CH), 7.16-$7.12$ (m, 2H, Ph-CH), 7.10-$7.07$ (m, 1H, Ph-CH), 6.86 (s, 1H, Mes-CH), 6.81 (s, 1H, Mes-CH), 3.51 (s, 3H, Mes-CH₃), 2.73 (s, 3H, Mes-CH₃), 2.52-$2.44$ (m, 3H, iPr-CH), 2.12 (s, 3H, Mes-CH₃), 1.38-$1.33$ (m, 9H, iPr-CH₃) overlapping with 1.33 (s, 9H, tBu-CH₃), 1.11 (dd, $^3J_{PH} = 13.4$ Hz, $^3J_{HH} = 7.3$ Hz, 9H, iPr-CH₃), 0.96 (s, 6H, Bpin-CH₃), 0.90 (s, 6H, Bpin-CH₃) ppm.

**$^{13}C\{^1H\}$ NMR** (125.8 MHz, C₆D₆, 298 K): $\delta = 141.3$ (s, Mes-C₉), 139.9 (s, Mes-C₉), 138.0 (s, Mes-C₉), 133.9 (d, $^2J_{RBC} = 1.1$ Hz, Ph-C₉), 132.0 (s, Ph-CH), 131.9 (br s, Mes-C₉), 129.4 (s, Ph-CH), 128.4 (s, Mes-CH), 127.6 (s, Mes-CH), 127.2 (s, Ph-CH), 107.1-107.0 (m, Aza-C₉), 82.3 (s, Bpin-C₉), 57.9 (d, $^3J_{PC} = 1.3$ Hz, tBu-C₉), 43.1 (br s, Aza-C₉), 29.2 (d, $^4J_{PC} = 2.7$ Hz, tBu-CH₃), 27.2 (d, $^4J_{RBC} = 0.6$ Hz, Mes-CH₃), 25.7 (d, $^1J_{PC} = 20.9$ Hz, iPr-CH), 25.5 (s, Bpin-CH₃), 25.0 (s, Bpin-CH₃), 23.7 (s, Mes-CH₃), 21.3 (s, Mes-CH₃), 20.4 (s, iPr-CH₃), 19.5 (s, iPr-CH₃) ppm.

**$^{11}B$ NMR** (160.5 MHz, C₆D₆, 298 K): $\delta = 33.1$ (br s, Bpin-B), 24.8 (br s, Aza-B) ppm.
31P{1H} NMR (162.2 MHz, C6D6, 298 K): \( \delta = 57.2 \) (d, \( ^1J_{RP} = 189 \) Hz) ppm.

HRMS (LIFDI, C36H38B2ClNO2PRh): calc: m/z = 727.3129, found: m/z = 727.3090.

UV-vis (hexane): \( \lambda_{abs} = 236 \) (shoulder), 255, 398 nm.

**Synthesis of 1h**

![Diagram of 1h](image)

\[\text{[(COE)}_2\text{RhCl}]_2\] (208 mg, 290 \( \mu \)mol) was suspended in pentane (7 mL) and treated with triisopropylphosphine (0.42 mL, 2.20 mmol). After stirring the suspension for 10 min, 4-ethynyl-\( N,N \)-dimethylaniline (84.2 mg, 580 \( \mu \)mol) was added. The reaction mixture was stirred for 10 min and all volatiles were removed in vacuo. The residue was dissolved in THF (8 mL) and treated with a stock solution of (\( tert \)-butylimino)mesitylborane in heptane (0.59 mL, 1.16 mmol, 1.96 M). The reaction mixture was stirred for 15 h at ambient temperature and all volatiles were removed in vacuo. The residue was washed with pentane (5 x 4 mL) and dried under reduced pressure to yield 1h as an orange solid (330 mg, 512 \( \mu \)mol, 88\%). Crystals of 1h suitable for X-ray diffraction were obtained by evaporation of a saturated hexane/benzene (5:1) solution.

\( ^1\)H NMR (500.1 MHz, C6D6, 298 K): \( \delta = 7.97-7.94 \) (m, 2H, 4-Me2NC6H4-CH), 6.89 (s, 1H, Mes-CH), 6.88 (s, 1H, Mes-CH), 6.41-6.38 (m, 2H, 4-Me2NC6H4-CH), 3.47 (s, 3H, Mes-CH3), 3.19 (s, 1H, Aza-CH), 2.78 (s, 3H, Mes-CH3), 2.41 (s, 6H, N(CH3)2), 2.25-2.18 (m, 3H, iPr-CH) overlapping with 2.18 (s, 3H, Mes-CH3), 1.39 (s, 9H, tBu-CH3), 1.15 (dd, \( ^3J_{PH} = 13.8 \) Hz, \( ^3J_{HH} = 7.2 \) Hz, 9H, iPr-CH3), 0.96 (dd, \( ^3J_{PH} = 13.2 \) Hz, \( ^3J_{HH} = 7.2 \) Hz, 9H, iPr-CH3) ppm.

\( ^13\)C{\( ^1\)H} NMR (125.8 MHz, C6D6, 298 K): \( \delta = 151.0 \) (s, 4-Me2NC6H4-Cq), 141.6 (s, Mes-Cq), 140.5 (s, Mes-Cq), 138.1 (s, Mes-Cq), 132.4 (s, 4-Me2NC6H4-CH), 132.0 (br s, Mes-Cq), 128.6 (s, Mes-CH), 127.7 (s, Mes-CH), 121.1 (d, \( ^2J_{RH} = 1.2 \) Hz, 4-Me2NC6H4-Cq), 110.9 (s, 4-Me2NC6H4-CH), 106.1-106.0 (m, Aza-Cq), 57.0 (d, \( ^3J_{PC} = 1.1 \) Hz, tBu-Cq), 50.7 (br s, Aza-CH), 39.6 (s, N(CH3)2), 29.6 (d, \( ^4J_{PC} = 2.8 \) Hz, tBu-CH3), 26.9 (d, \( ^4J_{RHC} = 0.5 \) Hz, Mes-CH3), 25.1 (dd, \( ^1J_{PC} = 20.8 \) Hz, \( ^2J_{RHC} = 1.2 \) Hz, iPr-CH), 24.0 (s, Mes-CH3), 21.4 (s, Mes-CH3), 20.10-20.09 (m, iPr-CH), 19.2 (s, iPr-CH) ppm.
11B NMR (128.5 MHz, C6D6, 298 K): δ = 21.4 (br s) ppm.

31P{1H} NMR (202.5 MHz, C6D6, 298 K): δ = 59.6 (d, 1JRhP = 196 Hz) ppm.

HRMS (LIFDI, C32H52BClN2PRh): calc: m/z = 644.2699, found: m/z = 644.2689.
UV-vis (hexane): λabs = 248, 304, 399 nm.

**Synthesis of 1i**

![Chemical Structure](image)

\[(\text{CO})_2\text{RhCl}_2\] (233 mg, 325 μmol) was suspended in pentane (7 mL) and treated with triisopropylphosphine (0.47 mL, 2.46 mmol). After stirring the suspension for 10 min, a solution of 4-ethynyl-α,α,α-trifluorotoluene (111 mg, 106 μL, 650 μmol) in pentane (2 mL) was added. The reaction mixture was stirred for 10 min and all volatiles were removed in vacuo. The residue was dissolved in THF (8 mL) and treated with a stock solution of (tert-butylimino)mesitylborane in heptane (0.67 mL, 1.31 mmol, 1.96 M). The reaction mixture was stirred for 15 h at room temperature and all volatiles were removed in vacuo. The residue was washed with pentane (5 x 4 mL) and dried under reduced pressure to yield 1i as an orange solid (357 mg, 533 μmol, 82%). Crystals of 1i suitable for X-ray diffraction were obtained by evaporation of a saturated hexane/benzene (5:1) solution.

1H NMR (500.1 MHz, C6D6, 298 K): δ = 7.95 (d, 3JHH = 8.1 Hz, 2H, 4-F3CC6H4-CH), 7.26 (d, 3JHH = 8.2 Hz, 2H, 4-F3CC6H4-CH), 6.89 (s, 1H, Mes-CH), 6.85 (s, 1H, Mes-CH), 3.37 (s, 3H, Mes-CH3), 3.01 (s, 1H, Aza-CH), 2.69 (s, 3H, Mes-CH3), 2.17 (s, 3H, Mes-CH3) overlapping with 2.17-2.08 (m, 3H, iPr-CH), 1.22 (s, 9H, tBu-CH3), 1.05 (dd, 3JPH = 14.0 Hz, 3JHH = 7.2 Hz, 9H, iPr-CH3), 0.83 (dd, 3JPH = 13.4 Hz, 3JHH = 7.2 Hz, 9H, iPr-CH3)) ppm.

13C{1H} NMR (125.8 MHz, C6D6, 298 K): δ = 141.4 (s, Mes-Cq), 140.4 (s, Mes-Cq), 138.6 (s, Mes-Cq), 138.28-138.26 (m, 4-F3CC6H4-Cq), 131.8 (s, 4-F3CC6H4-CH) overlapping with 131.4 (q, 2JCF = 32.5 Hz, 4-F3CC6H4-Cq), 131.1 (Mes-Cq, detected by HMBC), 128.7 (s, Mes-CH), 127.8 (s, Mes-CH), 124.9 (q, 3JCF = 3.7 Hz, 4-F3CC6H4-CH), 124.6 (q, 1JCF = -272.4 Hz, CF3), 102.9-102.8 (m, Aza-Cq), 57.3 (d, 3JPC = 1.2 Hz, tBu-Cq), 49.1 (br s, Aza-CH), 29.5 (d, 4JPC = 2.8 Hz, tBu-CH3), 26.9 (d, 4JRBC = 0.5 Hz, Mes-CH3), 25.0 (dd, 1JPC = 21.3 Hz, 2JRBC = 1.2 Hz,
\mbox{iPr-CH}, 23.9 \ (s, \ \mbox{Mes-CH}), 21.3 \ (s, \ \mbox{Mes-CH}), 20.03-20.02 \ (m, \ \mbox{iPr-CH}), 19.0 \ (s, \ \mbox{iPr-CH}) \ \text{ppm.}

\textit{Comment}: The spectrum contains signals corresponding to residual THF at 67.83 and 25.82 ppm.

\textbf{\(^{11}\text{B NMR}\)} \ (160.5 MHz, C\(_6\)D\(_6\), 298 K): \(\delta = 21.2 \) (br s) ppm.

\textbf{\(^{19}\text{F NMR}\)} \ (470.6 MHz, C\(_6\)D\(_6\), 298 K): \(\delta = -62.5 \) (s) ppm.

\textbf{\(^{31}\text{P}\{^1\text{H}\} \text{NMR}\)} \ (202.5 MHz, C\(_6\)D\(_6\), 298 K): \(\delta = 60.1 \) (d, \(^{1}J_{\text{RhP}} = 195 \) Hz) ppm.

\textbf{HRMS (LIFDI, C\(_{31}\)H\(_{46}\)BCl\(_3\)NPRh)}: \textit{calc}d: \(m/z = 669.2151\), \textit{found}: \(m/z = 669.2141\).

\textbf{UV-vis (hexane): }\(\lambda_{\text{abs}} = 231 \) (shoulder), 302 (shoulder), 408 nm.

\textbf{Synthesis of 1j}

\begin{center}
\begin{tikzpicture}
\node (N) at (0,0) {N};
\node (B) at (-1,0) {B};
\node (Mes) at (0,-1) {Mes};
\node (P) at (1,-1) {P};
\node (Rh) at (1,0) {Rh};
\node (Cl) at (1,1) {Cl};
\node (tBu) at (-2,1) {tBu};
\node (4-Me\(_2\)NC\(_6\)H\(_4\)) at (1,-1.5) {4-Me\(_2\)NC\(_6\)H\(_4\)};
\node (Cl\(_6\)H\(_4\)-4-CF\(_3\)) at (2.5,-1.5) {Cl\(_6\)H\(_4\)-4-CF\(_3\)};
\draw [->] (N) -- (B);
\draw [->] (B) -- (Mes);
\draw [->] (Mes) -- (Rh);
\draw [->] (Rh) -- (Cl);
\draw [->] (Cl) -- (P);
\draw [->] (P) -- (tBu);
\draw [->] (tBu) -- (4-Me\(_2\)NC\(_6\)H\(_4\));
\draw [->] (4-Me\(_2\)NC\(_6\)H\(_4\)) -- (Cl\(_6\)H\(_4\)-4-CF\(_3\));
\end{tikzpicture}
\end{center}

\([\{(\text{COE})_2\text{RhCl}\}_2\] \ (216 mg, 301 \(\mu\)mol) was suspended in pentane \(10 \ \text{mL}\) and treated with triisopropylphosphine \(0.43 \ \text{mL}, 2.25 \ \text{mmol}\). After stirring the suspension for 10 min, \(N,N\)-dimethyl-4-\{2-[4-trifluoromethyl]phenyl\}ethynyl]benzenamine \(174 \ \text{mg}, 602 \ \mu\text{mol}\) was added. The reaction mixture was stirred for 10 min and all volatiles were removed \textit{in vacuo}. The residue was dissolved in THF \(10 \ \text{mL}\) and treated with a stock solution of \((\text{tert-butylimino})\)mesitylborane in heptane \(0.77 \ \text{mL}, 1.51 \ \text{mmol}, 1.96 \ \text{M}\). After stirring the reaction mixture for 15 h at room temperature, all volatiles were removed \textit{in vacuo}. The residue was washed with pentane \(5 \times 4 \ \text{mL}\) and dried under reduced pressure to yield \textbf{1j} as an orange solid \(380 \ \text{mg}, 482 \ \mu\text{mol}, 80\%\). Crystals of \textbf{1j} suitable for X-ray diffraction were obtained by evaporation of a saturated hexane/benzene (2:1) solution.

\textbf{\(^1\text{H NMR}\)} \ (500.1 MHz, d\(_8\)-THF, 298 K): \(\delta = 8.30 \) (br s, 1H, 4-Me\(_2\)NC\(_6\)H\(_4\)-CH), 7.55 (br s, 1H, 4-Me\(_2\)NC\(_6\)H\(_4\)-CH), 7.24 (br s, 2H, 4-F\(_3\)CC\(_6\)H\(_4\)-CH), 7.15 (br s, 1H, 4-F\(_3\)CC\(_6\)H\(_4\)-CH), 6.97 (br s, 1H, 4-F\(_3\)CC\(_6\)H\(_4\)-CH), 6.88-6.83 (m, 4H, Mes-CH overlapping with 4-Me\(_2\)NC\(_6\)H\(_4\)-CH), 3.21 (s, 3H, Mes-CH\(_3\)), 3.05 (s, 6H, N(C\(_6\)H\(_3\))\(_2\)), 2.35 (s, 3H, Mes-CH\(_3\)), 2.27 (s, 3H, Mes-CH\(_3\)), 1.90-1.83 (m, 3H, tBu-CH), 1.19 (s, 9H, tBu-CH\(_3\)), 1.15 (dd, \(^3J_{\text{PH}} = 13.7 \) Hz, \(^3J_{\text{HH}} = 7.2 \) Hz, 9H, iPr-CH\(_3\)), 1.04 (dd, \(^3J_{\text{PH}} = 13.1 \) Hz, \(^3J_{\text{HH}} = 7.3 \) Hz, 9H, iPr-CH\(_3\)) ppm.
$^{13}$C($^1$H) NMR (125.8 MHz, d$_8$-THF, 298 K): $\delta$ = 152.2 (s, 4-Me$_2$NC$_6$H$_4$-C$_q$), 145.37-145.34 (m, 4-F$_3$CC$_6$H$_4$-C$_q$), 141.8 (s, Mes-C$_q$), 140.7 (s, Mes-C$_q$), 139.0 (s, Mes-C$_q$), 134.4 (br s, 4-Me$_2$NC$_6$H$_4$-CH), 131.5 (br s, Mes-C$_q$), 130.8 (br s, 4-F$_3$CC$_6$H$_4$-CH overlapping with 4-Me$_2$NC$_6$H$_4$-CH), 128.8 (s, Mes-CH), 128.3 (s, Mes-CH), 127.1 (q, $^2$J$_{CF}$ = 32.0 Hz, 4-F$_3$CC$_6$H$_4$-C$_q$), 127.0 (br s, 4-F$_3$CC$_6$H$_4$-CH), 125.7 (q, $^1$J$_{CF}$ = -271.3 Hz, CF$_3$), 125.6 (br s, 4-F$_3$CC$_6$H$_4$-CH), 125.2 (br s, 4-F$_3$CC$_6$H$_4$-CH), 119.1 (d, $^2$J$_{HH}$ = 0.7 Hz, 4-Me$_2$NC$_6$H$_4$-C$_q$), 111.7 (s, 4-Me$_2$NC$_6$H$_4$-CH), 101.6-101.5 (m, Aza-C$_q$), 63.8 (br s, Aza-C$_q$), 58.0 (d, $^3$J$_{PC}$ = 1.6 Hz, rBu-C$_q$), 40.1 (s, N(CH$_3$)$_2$), 29.3 (d, $^4$J$_{PC}$ = 2.8 Hz, rBu-CH$_3$), 27.3 (s, Mes-CH$_3$), 23.8 (dd, $^1$J$_{PC}$ = 20.9 Hz, $^2$J$_{HH}$ = 0.8 Hz, iPr-CH), 22.9 (s, Mes-CH$_3$), 21.4 (s, Mes-CH$_3$), 20.2 (s, iPr-CH$_3$), 19.6 (s, iPr-CH$_3$) ppm.

$^{11}$B NMR (128.5 MHz, d$_8$-THF, 298 K): $\delta$ = 22.4 (br s) ppm.

$^{19}$F NMR (470.6 MHz, d$_8$-THF, 298 K): $\delta$ = -63.5 (s) ppm.

$^{31}$P($^1$H) NMR (162.2 MHz, d$_8$-THF, 298 K): $\delta$ = 48.4 (d, $^1$J$_{PH}$ = 189 Hz) ppm.

$^1$H NMR (500.1 MHz, d$_8$-THF, 233 K): $\delta$ = 8.27-8.25 (m, 1H, 4-Me$_2$NC$_6$H$_4$-CH), 7.55-7.53 (m, 1H, 4-Me$_2$NC$_6$H$_4$-CH), 7.31 (d, $^3$J$_{HH}$ = 8.2 Hz, 1H, 4-F$_3$CC$_6$H$_4$-CH), 7.28 (d, $^3$J$_{HH}$ = 8.4 Hz, 1H, 4-F$_3$CC$_6$H$_4$-CH), 7.12 (d, $^3$J$_{HH}$ = 8.2 Hz, 1H, 4-F$_3$CC$_6$H$_4$-CH), 6.96 (d, $^3$J$_{HH}$ = 8.2 Hz, 1H, 4-F$_3$CC$_6$H$_4$-CH), 6.90-6.89 (m, 2H, Mes-CH, 4-Me$_2$NC$_6$H$_4$-CH), 6.84 (s, 1H, Mes-CH), 6.79-6.77 (m, 1H, 4-Me$_2$NC$_6$H$_4$-CH), 3.19 (s, 3H, Mes-CH$_3$), 3.07 (s, 6H, N(CH$_3$)$_2$), 2.34 (s, 3H, Mes-CH$_3$), 2.28 (s, 3H, Mes-CH$_3$), 1.17 (s, 9H, rBu-CH$_3$) overlapping with 1.04 (br s, 18H, iPr-CH$_3$) ppm.

Comment: The signal for the iPr-CH nucleus could not be observed due to overlapping with several signals.

$^{13}$C($^1$H) NMR (125.8 MHz, d$_8$-THF, 233 K): $\delta$ = 151.8 (s, 4-Me$_2$NC$_6$H$_4$-C$_q$), 145.29-145.25 (m, 4-F$_3$CC$_6$H$_4$-C$_q$), 141.6 (s, Mes-C$_q$), 140.8 (s, Mes-C$_q$), 138.9 (s, Mes-C$_q$), 134.1-134.0 (m, 4-Me$_2$NC$_6$H$_4$-CH), 131.3 (br s, Mes-C$_q$), 130.6 (s, 4-F$_3$CC$_6$H$_4$-CH), 130.5 (s, 4-Me$_2$NC$_6$H$_4$-CH), 128.8 (s, Mes-CH), 128.3 (s, Mes-CH), 126.9 (s, 4-F$_3$CC$_6$H$_4$-CH), 126.7 (q, $^2$J$_{CF}$ = 31.9 Hz, 4-F$_3$CC$_6$H$_4$-C$_q$), 125.77-125.72 (m, 4-F$_3$CC$_6$H$_4$-CH), 125.7 (q, $^1$J$_{CF}$ = -271.3 Hz, CF$_3$), 125.29-125.24 (m, 4-F$_3$CC$_6$H$_4$-CH), 118.6 (s, 4-Me$_2$NC$_6$H$_4$-C$_q$), 111.6 (s, 4-Me$_2$NC$_6$H$_4$-CH), 111.4 (s, 4-Me$_2$NC$_6$H$_4$-CH), 101.6-101.5 (m, Aza-C$_q$), 63.74-63.66 (m, Aza-C$_q$), 57.8 (d, $^3$J$_{PC}$ = 1.0 Hz, rBu-C$_q$), 40.1 (s, N(CH$_3$)$_2$), 29.02-29.01 (m, rBu-CH$_3$), 27.2 (s, Mes-CH$_3$), 23.6 (br s, iPr-CH), 23.0 (s, Mes-CH$_3$), 21.5 (s, Mes-CH$_3$), 19.4 (br s, iPr-CH$_3$) ppm.

HRMS (LIFDI, C$_{20}$H$_{55}$BClF$_5$N$_2$PRH): calcd: m/z = 788.2886, found: m/z = 788.2868.

UV-vis (hexane): $\lambda_{abs}$ = 269, 312, 395 nm.
Synthesis of I

If (936 mg, 1.62 mmol) was dissolved in benzene (12 mL) and the argon atmosphere was replaced by acetylene. After stirring the reaction mixture for 1.5 h at 86 °C, all volatiles were removed in vacuo. The residue was purified by column chromatography on silica gel with a mixture of dichloromethane and hexane (1:10) as eluent. Evaporation of the solvent from the second fraction yielded pure I as a white solid (360 mg, 1.18 mmol, 73%). Crystals of I suitable for X-ray diffraction were obtained by evaporation of a saturated hexane/dichloromethane (10:1) solution (crystal data Ia) or by evaporation of a saturated pentane/ether (10:1) solution (crystal data Ib).

$^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K): $\delta = 7.76$ (d, $^3J_{HH} = 10.9$ Hz, 1H, Aza1-CH), 6.84 (m, 2H, Mes-CH), 6.54 (d, $^3J_{HH} = 10.9$ Hz, 1H, Aza1-CH), 2.78 (s, 3H, Aza1-CH$_3$), 2.25 (s, 3H, Mes-CH$_3$), 2.21 (s, 6H, Mes-CH$_3$), 1.81 (s, 3H, CCCH$_3$), 1.30 (s, 9H, tBu-CH$_3$) ppm.

$^{13}$C{$_^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K): $\delta = $ 150.2 (s, Aza1-C$_q$), 147.3 (br s, Mes-C$_q$), 145.6 (s, Aza1-CH), 136.7 (s, Mes-C$_q$), 135.6 (s, Mes-C$_q$), 131.9 (br s, Aza1-CH), 127.8 (s, Mes-CH), 111.9 (s, Aza1-C$_q$), 88.3 (s, CCCH$_3$), 81.1 (s, CCCH$_3$), 61.7 (s, tBu-C$_q$), 34.5 (s, tBu-CH$_3$), 25.1 (s, Aza1-CH$_3$), 23.9 (s, Mes-CH$_3$), 21.3 (s, Mes-CH$_3$), 4.4 (s, CCCH$_3$) ppm.

$^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K): $\delta = $ 39.0 (br s) ppm.

Elemental analysis: % calc: C 82.63, H 9.25, N 4.59; found: C 82.40, H 9.36, N 4.68.
HRMS (ASAP, C$_{21}$H$_{28}$BN + H): calcd: m/z = 306.2388, found: m/z = 306.2377.

Synthesis of 1k
[(COE)₂RhCl]₂ (70.0 mg, 97.6 µmol) was suspended in pentane (7 mL) and treated with triisopropylphosphine (0.14 mL, 73.3 µmol). After stirring the suspension for 10 min, 1-((tert-butyl)-2-mesityl-6-methyl-5-(prop-1-yn-1-yl)-1,2-azaborinine (59.5 mg, 195 µmol) was added. The reaction mixture was stirred for 10 min and all volatiles were removed in vacuo. The residue was dissolved in THF (8 mL) and treated with a stock solution of (tert-butylimino)mesitylborane in heptane (0.20 mL, 386 µmol, 1.93 M). The reaction mixture was stirred for 15 h at room temperature and all volatiles were removed in vacuo. The residue was washed with pentane (4 x 3 mL) and dried under reduced pressure to yield 1k as an orange solid (128 mg, 159 µmol, 82%). Crystals of 1k suitable for X-ray diffraction were obtained by evaporation of a saturated hexane/benzene (5:1) solution.

$^1\text{H NMR}$ (500.1 MHz, C₆D₆, 298 K): $\delta = 9.34$ (d, $^3J_{\text{HH}} = 11.1$ Hz, 1H, Aza1-CH), 6.91 (s, 1H, Mes-CH), 6.88 (s, 1H, Mes-CH), 6.867-6.866 (m, 2H, Mes-CH), 6.61 (d, $^3J_{\text{HH}} = 11.1$ Hz, 1H, Aza1-CH), 3.57 (s, 3H, Mes-CH₃), 2.82 (s, 3H, Aza1-CH₃), 2.67 (s, 3H, Mes-CH₃), 2.43-2.36 (m, 3H, iPr-CH), 2.27 (s, 3H, Mes-CH₃), 2.24 (s, 3H, Mes-CH₃), 2.20 (s, 3H, Mes-CH₃), 2.18 (s, 3H, Mes-CH₃), 1.43 (s, 9H, tBu-CH₃), 1.38-1.37 (m, 3H, Aza-CH₃) overlapping with 1.37 (s, 9H, tBu-CH₃), 1.20 (dd, $^3J_{\text{PH}} = 13.5$ Hz, $^3J_{\text{HH}} = 7.2$ Hz, 9H, iPr-CH₃), 1.05 (dd, $^3J_{\text{PH}} = 13.0$ Hz, $^3J_{\text{HH}} = 7.3$ Hz, 9H, iPr-CH₃) ppm.

$^{13}\text{C}[^1\text{H}] \text{NMR}$ (125.8 MHz, C₆D₆, 298 K): $\delta = 148.2$ (s, Aza1-CH), 146.8 (br s, Mes-Cₐ), 146.1 (s, Aza1-Cₐ), 142.3 (s, Mes-Cₐ), 140.6 (s, Mes-Cₐ), 138.2 (s, Mes-Cₐ), 136.8 (s, Mes-Cₐ), 136.6 (s, Mes-Cₐ), 135.9 (s, Mes-Cₐ), 131.4 (br s, Mes-Cₐ), 130.5 (br s, Aza1-CH), 128.8 (s, Mes-CH), 128.0 (s, Mes-CH), 127.9 (s, Mes-CH), 127.8 (s, Mes-CH), 118.0 (d, $^2J_{\text{RMC}} = 0.7$ Hz, Aza1-Cₐ), 105.8-105.6 (m, Aza-Cₐ), 68.0 (br s, Aza-Cₐ), 61.7 (s, tBu-Cₐ), 57.0 (d, $^3J_{\text{PC}} = 1.5$ Hz, tBu-Cₐ), 34.6 (s, tBu-CH₃), 29.6 (d, $^4J_{\text{PC}} = 2.8$ Hz, tBu-CH₃), 27.7 (s, Mes-CH₃), 24.2 (s, Aza1-CH₃), 23.9 (s, Mes-CH₃), 23.6 (s, Mes-CH₃), 23.3 (s, Mes-CH₃) overlapping with 23.3-23.2 (m, iPr-CH₃), 21.3 (s, Mes-CH₃), 21.3 (s, Mes-CH₃), 19.871-19.866 (m, iPr-CH₃), 19.3 (s, iPr-CH₃), 13.8 (s, Aza-CH₃) ppm.

$^{11}\text{B NMR}$ (128.5 MHz, C₆D₆, 298 K): $\delta = 39.2$ (br s, Aza1-B), 20.3 (br s, Aza-B) ppm.

$^{31}\text{P}[^1\text{H}] \text{NMR}$ (202.5 MHz, C₆D₆, 298 K): $\delta = 49.7$ (d, $^1J_{\text{RHP}} = 194$ Hz) ppm.

HRMS (LIFDI, C₄₃H₆₉B₂Cl₅PRh): calcd: m/z = 804.4123, found: m/z = 804.4110.

UV-vis (hexane): $\lambda_{\text{abs}} = 254, 299$ (shoulder), 413 nm.
Synthesis of 11

[[(CO)₂RhCl]₂] (500 mg, 697 μmol) was suspended in pentane (12 mL) and treated with trimethylphosphine (1.00 mL, 5.24 mmol). After stirring the suspension for 15 min, 1,4-diethynylbenzene (87.9 mg, 697 μmol) was added. The reaction mixture was stirred for 15 min and all volatiles were removed in vacuo. The residue was suspended in THF (20 mL) and treated with a stock solution of (tert-butylimino)mesitylborane in heptane (1.43 mL, 2.79 mmol, 1.96 M). The reaction mixture was stirred for 15 h at ambient temperature and then all volatiles were removed in vacuo. After washing the residue with pentane (5 x 7 mL) and benzene (2 x 3 mL), residual solvent was removed under reduced pressure to yield 11 as an orange solid (243 mg, 216 μmol, 31%). Crystals of 11 suitable for X-ray diffraction were obtained by slow evaporation of a saturated benzene solution.

\[\text{Synthesis of 11}\]

\[
\begin{align*}
\text{Pr/P}_{3} & \equiv \text{RhCl} \\
\text{Mes} & \equiv \text{B-N(Bu)} \\
\text{C} & \equiv \text{C} \\
\end{align*}
\]

\[\{[(\text{CO})_{2}\text{RhCl}]_{2}\} \text{ (500 mg, 697 μmol) was suspended in pentane (12 mL) and treated with trimethylphosphine (1.00 mL, 5.24 mmol). After stirring the suspension for 15 min, 1,4-diethynylbenzene (87.9 mg, 697 μmol) was added. The reaction mixture was stirred for 15 min and all volatiles were removed in vacuo. The residue was suspended in THF (20 mL) and treated with a stock solution of (tert-butylimino)mesitylborane in heptane (1.43 mL, 2.79 mmol, 1.96 M). The reaction mixture was stirred for 15 h at ambient temperature and then all volatiles were removed in vacuo. After washing the residue with pentane (5 x 7 mL) and benzene (2 x 3 mL), residual solvent was removed under reduced pressure to yield 11 as an orange solid (243 mg, 216 μmol, 31%). Crystals of 11 suitable for X-ray diffraction were obtained by slow evaporation of a saturated benzene solution.}\]

\[\text{1H NMR (500.1 MHz, C}_{6}\text{D}_{6}, 298 K): } \delta = 7.95 \text{ (s, 4H, C}_{6}\text{H}_{4}-\text{CH), 6.91 (s, 2H, Mes-CH)}, 6.88 \text{ (s, 2H, Mes-CH), 3.42 (s, 6H, Mes-CH}_3\text{), 3.09 (s, 2H, Aza-CH), 2.75 (s, 6H, Mes-CH}_3\text{), 2.24-2.16 (m, 6H, iPr-CH) overlapping with 2.19 (s, 6H, Mes-CH}_3\text{), 1.31 (s, 18H, tBu-CH}_3\text{), 1.12 (dd, } J_{\text{PH}} = 14.0 \text{ Hz, } J_{\text{HH}} = 7.2 \text{ Hz, 18H, iPr-CH}_3\text{), 0.91 (dd, } J_{\text{PH}} = 13.4 \text{ Hz, } J_{\text{HH}} = 7.3 \text{ Hz, 18H, iPr-CH}_3\text{) ppm.}\]

\[\text{13C}^1\text{H NMR (125.8 MHz, C}_{6}\text{D}_{6}, 298 K): } \delta = 141.5 \text{ (s, Mes-}C_4\text{), 140.5 \text{ (s, Mes-}C_4\text{), 138.6 \text{ (s, Mes-}C_4\text{), 135.6 \text{ (d, } J_{\text{RH}} = 0.9 \text{ Hz, C}_{6}\text{H}_{4}-C_4\text{), 131.4 \text{ (Mes-}C_4\text{, detected by HMBC), 130.8 \text{ (s, C}_{6}\text{H}_{4}-\text{CH), 128.7 \text{ (s, Mes-CH), 127.8 \text{ (Mes-CH, detected by HSQC), 103.8-103.7 \text{ (m, Aza-}C_4\text{), 57.3 \text{ (d, } J_{\text{PC}} = 1.2 \text{ Hz, tBu-}C_4\text{), 49.4 \text{ (br s, Aza-CH), 29.6 \text{ (d, } J_{\text{PC}} = 2.7 \text{ Hz, tBu-CH}_3\text{), 26.9 \text{ (s, Mes-CH}_3\text{), 25.1 \text{ (d, } J_{\text{PC}} = 21.1 \text{ Hz, iPr-CH), 24.0 \text{ (s, Mes-CH}_3\text{), 21.3 \text{ (s, Mes-CH}_3\text{), 20.1 \text{ (d, } J_{\text{PC}} = 0.9 \text{ Hz, iPr-CH}_3\text{), 19.2 \text{ (s, iPr-CH}_3\text{) ppm.}\]

\[\text{11B NMR (128.4 MHz, C}_{6}\text{D}_{6}, 298 K): } \delta = 20.5 \text{ (br s, 2 B) ppm.}\]

\[\text{31P}^1\text{H NMR (162.0 MHz, C}_{6}\text{D}_{6}, 298 K): } \delta = 60.3 \text{ (d, } J_{\text{RHP}} = 196 \text{ Hz, 2 P) ppm.}\]

\[\text{HRMS (LIFDI, C}_{54}\text{H}_{88}\text{B}_{2}\text{Cl}_{2}\text{N}_{2}\text{P}_{2}\text{Rh}_{2}): } \text{calcld: m/z = 1124.4090, found: m/z = 1124.4094.}\]

\[\text{UV-vis (THF): } \lambda_{\text{abs}} = 242, 304 \text{ (shoulder), 409 nm.}\]
Synthesis of 2a

1a (280 mg, 519 μmol) was dissolved in benzene (12 mL) and treated with a stock solution of trimethylphosphine in benzene (1.52 mL, 1.14 mmol, 0.75 M). After stirring the reaction mixture for 30 mins, all volatiles were removed in vacuo. The residue was washed with hexane (2 mL) at −30 °C and dried under reduced pressure to yield 2a as a yellow solid (194 mg, 365 μmol, 70%). Crystals of 2a suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at −30 °C.

1H NMR (500.1 MHz, C6D6, 298 K): \( \delta = 6.80 \) (s, 2H, Mes-C\( \text{H} \)), 5.79 (t, \( ^3J_{\text{PH}} = 5.0 \) Hz, 1H, RhC\( \text{H} \)), 2.47 (s, 6H, Mes-CH\( \text{3} \)), 2.27-2.26 (m, 3H, RhC\( \text{CCCH} \)), 2.18 (s, 3H, Mes-CH\( \text{3} \)), 1.20 (s, 9H, tBu-C\( \text{H} \)), 1.12 (vtd, \( N = 6.8 \) Hz, \( ^3J_{\text{RhH}} = 0.8 \) Hz, 18H, P(CH\( \text{3} \))\( _3 \)) ppm.

13C{1H} NMR (125.8 MHz, C6D6, 298 K): \( \delta = 146.6 \) (t, \( ^3J_{\text{PC}} = 4.5 \) Hz, RhCC\( \text{CH} \)), 142.8 (br s, Mes-C\( \text{q} \)), 137.7 (t, \( ^4J_{\text{PC}} = 0.8 \) Hz, Mes-C\( \text{q} \)), 136.6 (s, Mes-C\( \text{q} \)), 128.3 (Mes-CH, detected by HSQC), 125.1 (dt, \( ^1J_{\text{RhC}} = 30.9 \) Hz, \( ^2J_{\text{PC}} = 13.0 \) Hz, RhC\( \text{H} \)), 55.4 (d, \( ^3J_{\text{RhC}} = 1.2 \) Hz, tBu-C\( \text{q} \)), 32.6 (s, tBu-\( \text{CH}_3 \)), 26.2 (t, \( ^5J_{\text{PC}} = 1.4 \) Hz, Mes-\( \text{CH}_3 \)), 24.5-24.4 (m, RhCC\( \text{CH}_3 \)), 21.4 (s, Mes-\( \text{CH}_3 \)), 14.1 (vtd, \( N = 28.9 \) Hz, \( ^2J_{\text{RhC}} = 1.3 \) Hz, P(CH\( \text{3} \))\( _3 \)) ppm.

11B NMR (160.5 MHz, C6D6, 298 K): \( \delta = 67.8 \) (br s) ppm.

31P{1H} NMR (202.5 MHz, C6D6, 298 K): \( \delta = -4.7 \) (d, \( ^1J_{\text{RhP}} = 130 \) Hz, 2 P) ppm.

HRMS (LIFDI, C22H42BClNP2Rh): calced: m/z = 531.1624, found: m/z = 531.1612.

UV-vis (hexane): \( \lambda_{abs} = 250 \) (shoulder), 290, 355 nm.

Synthesis of 2b
1b (280 mg, 465 µmol) was dissolved in benzene (8 mL) and treated with a stock solution of trimethylphosphine in benzene (1.36 mL, 1.02 mmol, 0.75 M). After stirring the reaction mixture for 1 h, all volatiles were removed in vacuo. The residue was washed with hexane (2 mL) at −30 °C and dried under reduced pressure to yield 2b as a yellow solid (197 mg, 332 µmol, 71%). Crystals of 2b suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at −30 °C.

**1H NMR** (500.1 MHz, C₆D₆, 298 K): δ = 7.42-7.40 (m, 2H, Ph-C), 7.22-7.19 (m, 2H, Ph-C), 7.13-7.10 (m, 1H, Ph-C), 6.85 (s, 2H, Mes-C), 5.80 (t, JₚH = 5.1 Hz, 1H, RhC), 2.63 (s, 6H, Mes-C), 2.19 (s, 3H, Mes-C), 1.16 (s, 9H, tBu-C), 1.14 (vtd, JNC = 6.9 Hz, 18H, P(C₃H₃)) ppm.

**13C{1H} NMR** (125.8 MHz, C₆D₆, 298 K): δ = 153.8 (t, JPC = 4.7 Hz, NCPH), 144.92-144.88 (m, Ph-C), 142.3 (br s, Mes-C), 138.1 (t, JPC = 0.7 Hz, Mes-C), 137.1 (s, Mes-C), 131.7 (dt, JRhC = 31.4 Hz, JPC = 12.8 Hz, RhC), 128.9 (t, JPC = 1.8 Hz, Ph-C), 128.5 (s, Mes-C), 127.9 (s, Ph-C), 126.1 (s, Ph-C), 56.3 (d, JRhC = 1.1 Hz, tBu-C), 32.6 (s, tBu-C), 26.6 (t, JPC = 1.3 Hz, Mes-C), 21.4 (s, Mes-C), 14.1 (vtd, N = 29.1 Hz, JRhC = 1.3 Hz, P(CH₃)) ppm.

**11B NMR** (160.5 MHz, C₆D₆, 298 K): δ = 70.2 (br s) ppm.

**31P{1H} NMR** (202.5 MHz, C₆D₆, 298 K): δ = −4.5 (d, JRhP = 128 Hz, 2 P) ppm.

**HRMS** (LIFDI, C₂₇H₄₄BClNP₂Rh): calcd: m/z = 593.1780, found: m/z = 593.1770.

**UV-vis** (hexane): λₜₜₜ = 252, 294, 348 nm.

**Synthesis of 2c**

1c (152 mg, 214 µmol) was dissolved in benzene (6 mL) and treated with a stock solution of trimethylphosphine in benzene (0.53 mL, 470 µmol, 0.887 M). After stirring the reaction mixture for 1 h, all volatiles were removed in vacuo. The residue was washed with hexane (2 x 2 mL) at −30 °C and dried under reduced pressure to yield 2c as an orange solid (102 mg,
145 μmol, 68%). Crystals of 2c suitable for X-ray diffraction were obtained by evaporation of a saturated benzene solution.

**1H NMR** (500.1 MHz, C₆D₆, 298 K): δ = 6.97 (t, 3JₚH = 5.3 Hz, 1H, RhCH), 6.83 (s, 2H, Mes-CH), 4.24-4.23 (m, 2H, C₅H₄-CH), 4.17 (s, 5H, Cp-CH), 4.01-4.00 (m, 2H, C₅H₄-CH), 2.54 (s, 6H, Mes-CH₃), 2.19 (s, 3H, Mes-CH₃), 1.26 (vtd, N = 6.8 Hz, 3JₚH = 0.9 Hz, 18H, P(CH₃)₃) ppm.

*Comment: The spectrum contains a signal corresponding to residual benzene at 7.16 (s) ppm.*

**13C{1H} NMR** (125.8 MHz, C₆D₆, 298 K): δ = 146.4 (t, 3JₚC = 4.4 Hz, NCFc), 142.7 (br s, Mes-C₄), 137.9 (t, 4JₚC = 0.8 Hz, Mes-C₄), 136.7 (s, Mes-C₄), 132.9 (dt, 1JₚC = 30.6 Hz, 2JₚC = 12.6 Hz, RhCH), 128.4 (s, Mes-CH), 95.14-95.09 (m, C₅H₄-C₄), 73.4 (t, 5JₚC = 1.7 Hz, C₅H₄-CH), 69.4 (s, C₅-CH), 66.3 (s, C₅H₄-CH), 56.1 (d, 3JₚC = 1.2 Hz, tBu-C₄), 32.8 (s, tBu-CH₃), 26.4 (t, 5JₚC = 1.2 Hz, Mes-CH₃), 21.4 (s, Mes-CH₃), 14.4 (vtd, N = 28.9 Hz, 2JₚC = 1.3 Hz, P(CH₃)₃) ppm.

*Comment: The spectrum contains a signal corresponding to residual benzene at 128.6 ppm.*

**11B NMR** (160.5 MHz, C₆D₆, 298 K): δ = 68.7 (br s) ppm.

**31P{1H} NMR** (202.5 MHz, C₆D₆, 298 K): δ = −5.5 (d, 1JₚP = 130 Hz, 2 P) ppm.

**HRMS** (LIFDI, C₃₁H₄₈BFeClNP₂Rh): *calcd:* m/z = 701.1443, *found:* m/z = 701.1432.

**UV-vis** (THF): λₘₐₓ = 255 (shoulder), 349 nm.

**Synthesis of 2d**

![Chemical structure of 2d](image)

1d (500 mg, 903 μmol) was dissolved in benzene (10 mL) and treated with a stock solution of trimethylphosphine in benzene (2.65 mL, 1.99 mmol, 0.75 M). After stirring the reaction mixture for 1 h, all volatiles were removed *in vacuo*. The residue was washed with hexane (2 mL) at −30 °C and dried under reduced pressure to yield 2d as a yellow solid (431 mg, 790 μmol, 87%). Crystals of 2d suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at −30 °C.
**1H NMR** (500.1 MHz, C₆D₆, 298 K): δ = 6.806-6.805 (m, 2H, Mes-CH), 2.50 (s, 6H, Mes-CH₃), 2.19 (s, 3H, Mes-CH₃), 2.10-2.09 (m, 3H, RhCCCH₃), 2.08-2.07 (m, 3H, RhCCCH₃), 1.22 (s, 9H, tBu-CH₃), 1.10 (vtd, N = 6.8 Hz, 3J₉H₂H = 1.0 Hz, 18H, P(CH₃)₃) ppm.

**3H²¹P NMR** (500.1 MHz, C₆D₆, 298 K): δ = 6.80 (s, 2H, Mes-CH), 2.50 (s, 6H, Mes-CH₃), 2.19 (s, 3H, Mes-CH₃), 2.10 (s, 3H, RhCCCH₃), 2.075-2.072 (m, 3H, RhCCCH₃), 1.22 (s, 9H, tBu-CH₃), 1.10 (d, 3J₉H₂H = 0.7 Hz, 18H, P(CH₃)₃) ppm.

**13C{¹H} NMR** (125.8 MHz, C₆D₆, 298 K): δ = 143.4 (Mes-C₉, detected by HMBC), 139.7 (dt, 2J₉C = 0.5 Hz, 3J₉C = 4.5 Hz, RhCCCH₃), 137.9 (t, 4J₉C = 0.7 Hz, Mes-C₉), 136.6 (s, Mes-C₉), 129.8 (dt, 1J₉C = 30.7 Hz, 2J₉C = 11.3 Hz, RhCCCH₃), 128.3 (s, Mes-CH), 55.2 (d, 3J₉C = 1.2 Hz, tBu-C₉), 33.0 (s, tBu-CH₃), 26.7 (t, 5J₉C = 0.9 Hz, Mes-CH₃), 23.8 (dt, 2J₉C = 0.5 Hz, 3J₉C = 3.3 Hz, RhCCCH₃), 21.4 (s, Mes-CH₃), 17.54-17.50 (m, RhCCCH₃), 14.7 (vtd, N = 28.2 Hz, 2J₉C = 1.4 Hz, P(CH₃)₃) ppm.

**13C{³¹P} NMR** (75.5 MHz, C₆D₆, 298 K): δ = 143.3 (br s, Mes-C₉), 139.7 (d, 2J₉C = 0.5 Hz, RhCCCH₃), 137.9 (s, Mes-C₉), 136.5 (s, Mes-C₉), 129.8 (d, 1J₉C = 30.7 Hz, RhCCCH₃), 128.3 (s, Mes-CH), 55.2 (d, 3J₉C = 1.2 Hz, tBu-C₉), 33.0 (s, tBu-CH₃), 26.7 (s, Mes-CH₃), 23.8 (d, 2J₉C = 0.5 Hz, RhCCCH₃), 21.4 (s, Mes-CH₃), 17.5 (d, 3J₉C = 2.0 Hz, RhCCCH₃), 14.7 (d, 2J₉C = 1.4 Hz, P(CH₃)₃) ppm.

**11B NMR** (160.5 MHz, C₆D₆, 298 K): δ = 68.0 (br s) ppm.

**³¹P{¹H} NMR** (202.5 MHz, C₆D₆, 298 K): δ = -5.1 (d, 1J₉P = 133 Hz, 2 P) ppm.

**HRMS** (LIFDI, C₂₅H₄₄BClNP₃Rh): *calcd*: m/z = 545.1780, *found*: m/z = 545.1757.

UV-vis (hexane): λₜₐ₉ = 254, 291 (shoulder), 352 nm.

**Synthesis of 2e**

![Chemical structure](attachment:structure.png)

**1e** (496 mg, 852 μmol) was dissolved in benzene (10 mL) and treated with a stock solution of trimethylphosphine in benzene (2.5 mL, 1.96 mmol, 0.784 M). After stirring the reaction mixture for 4 h, all volatiles were removed *in vacuo*. The residue was washed with pentane (3 x 3 mL) and dried under reduced pressure to yield **2e** as a yellow solid (386 mg, 673 μmol,
79%). Crystals of 2e suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at −30 °C.

1H NMR (500.1 MHz, C6D6, 298 K): δ = 6.81 (s, 2H, Mes-CH), 2.58 (s, 6H, Mes-CH3), 2.53 (q, 3JHH = 7.3 Hz, 2H, Et-CH2), 2.36 (qd, 3JHH = 7.6 Hz, 3JRhH = 1.2 Hz, 2H, Et-CH2), 2.18 (s, 3H, Mes-CH3), 1.34 (t, 3JHH = 7.3 Hz, 3H, Et-CH3), 1.20 (s, 9H, tBu-CH3), 1.15 (t, 3JHH = 7.3 Hz, 3H, Et-CH3) overlapping with 1.13 (vtd, N = 6.6 Hz, 3JRhH = 0.9 Hz, 18H, P(CH3)3) ppm.

1H{31P} NMR (500.1 MHz, C6D6, 298 K): δ = 6.804-6.803 (m, 2H, Mes-CH), 2.57 (s, 6H, Mes-CH3), 2.53 (q, 3JHH = 7.3 Hz, 2H, Et-CH2), 2.35 (qd, 3JHH = 7.6 Hz, 3JRhH = 1.2 Hz, 2H, Et-CH2), 2.18 (s, 3H, Mes-CH3), 1.34 (t, 3JHH = 7.6 Hz, 3H, Et-CH3), 1.20 (s, 9H, tBu-CH3), 1.15 (t, 3JHH = 7.3 Hz, 3H, Et-CH3) overlapping with 1.13 (d, 3JRhH = 0.9 Hz, 18H, P(CH3)3) ppm. Comment: The spectrum contains a signal corresponding to residual benzene at 7.156 ppm.

13C{1H} NMR (125.8 MHz, C6D6, 298 K): δ = 145.4 (t, 3JPC = 4.4 Hz, NCEt), 143.4 (br s, Mes-Cq), 138.37 (dt, 1JRhC = 32.3 Hz, 2JPC = 10.3 Hz, RhCET) overlapping with 138.36 (t, 4JPC = 0.7 Hz, Mes-Cq), 136.7 (s, Mes-Cq), 128.6 (s, Mes-CH), 54.9 (d, 3JRhC = 1.1 Hz, tBu-Cq), 32.8 (s, tBu-CH3), 30.5 (dt, 2JRhC = 0.5 Hz, 3JPC = 3.2 Hz, Et-CH2), 26.7 (s, Mes-CH3), 22.89-22.85 (m, Et-CH2), 21.3 (s, Mes-CH3), 18.4 (d, 3JRhC = 0.9 Hz, Et-CH3), 15.7 (vtd, N = 28.4 Hz, 2JRhC = 1.4 Hz, P(CH3)3), 14.8 (dt, 4JRhC = 0.4 Hz, 5JPC = 2.7 Hz, Et-CH3) ppm. Comment: The spectrum contains signals corresponding to residual hexane from crystallization at 31.97, 23.06 and 14.36 ppm.

11B NMR (160.5 MHz, C6D6, 298 K): δ = 69.4 (br s) ppm.

31P{1H} NMR (202.5 MHz, C6D6, 298 K): δ = −6.5 (d, 1JRhP = 133 Hz, 2 P) ppm.

HRMS (LIFDI, C25H48BCINP2Rh): calc: m/z = 573.2093, found: m/z = 573.2082.

UV-vis (hexane): λabs = 248 (shoulder), 285 (shoulder), 347, 413 (shoulder) nm.

Synthesis of 2f
1f (430 mg, 744 µmol) was dissolved in benzene (10 mL) and treated with a stock solution of trimethylphosphine in benzene (2.20 mL, 1.65 mmol, 0.75 M). After stirring the reaction mixture for 1 h, all volatiles were removed in vacuo and the residue was dissolved in 5 mL hexane. The yellow solution was filtrated and compound 2f crystallized at −30 °C. The yellow crystals were washed with hexane (2 x 2 mL) at −30 °C and dried under reduced pressure to yield 2f as a yellow crystalline solid (352 mg, 618 µmol, 83%). Crystals of 2f suitable for X-ray diffraction were also obtained by slow evaporation of a saturated benzene solution.

1H NMR (500.1 MHz, C₆D₆, 298 K): δ = 6.80 (s, 2H, Mes-CH), 2.52 (t, J₆PH = 2.5 Hz, 3H, RhCCCH₃), 2.46 (s, 6H, Mes-CH₂), 2.18 (s, 3H, Mes-CH₃), 1.90 (s, 3H, RhCCCH₃), 1.25 (vtd, N = 7.1 Hz, 3J₉₁H = 0.8 Hz, 18H, P(CH₃)₃), 1.17 (s, 9H, tBu-CH₃) ppm.

1H{31P} NMR (500.1 MHz, C₆D₆, 298 K): δ = 6.799-6.796 (m, 2H, Mes-CH), 2.51 (s, 3H, RhCCCH₃), 2.46 (s, 6H, Mes-CH₂), 2.18 (s, 3H, Mes-CH₃), 1.90 (s, 3H, RhCCCH₃), 1.25 (d, 3J₉₁H = 0.8 Hz, 18H, P(CH₃)₃), 1.17 (s, 9H, tBu-CH₃) ppm.

Comment: The spectrum contains signals corresponding to residual hexane from crystallization at 1.25 (m) and 0.88 (t) ppm.

13C{1H} NMR (125.8 MHz, C₆D₆, 298 K): δ = 151.8 (dt, 2J₉₁C = 0.7 Hz, 3J₉₃C = 4.5 Hz, RhCCCH₃), 143.0 (br s, Mes-C₉), 137.6 (t, 4J₉₃C = 0.8 Hz, Mes-C₉), 136.8 (s, Mes-C₉), 128.3 (s, Mes-CH), 112.7 (dt, 1J₉₃C = 30.1 Hz, 2J₉₃C = 10.9 Hz, RhCCCH₃), 94.3 (d, 3J₉₁C = 1.0 Hz, RhCCCH₃), 84.5 (dt, 2J₉₁C = 1.1 Hz, 3J₉₃C = 3.2 Hz, RhCCCH₃), 55.8 (d, 3J₉₁C = 1.2 Hz, tBu-C₉), 32.7 (s, tBu-CH₃), 26.5 (t, 5J₉₃C = 1.1 Hz, Mes-CH₃), 21.4 (s, Mes-CH₃), 21.23-21.19 (m, RhCCCH₃), 13.9 (vtd, N = 28.7 Hz, 2J₉₃C = 1.2 Hz, P(CH₃)₃), 5.5 (s, RhCCCH₃) ppm.

13C{1H, 31P} NMR (75.5 MHz, C₆D₆, 298 K): δ = 151.8 (d, 2J₉₁C = 0.8 Hz, RhCCCH₃), 137.6 (Mes-C₉), 136.8 (s, Mes-C₉), 128.3 (s, Mes-CH), 112.7 (d, 1J₉₁C = 30.1 Hz, RhCCCH₃), 94.4 (d, 3J₉₁C = 1.0 Hz, RhCCCH₃), 84.5 (d, 2J₉₁C = 1.1 Hz, RhCCCH₃), 55.8 (d, 3J₉₁C = 1.2 Hz, tBu-C₉), 32.8 (s, tBu-CH₃), 26.5 (s, Mes-CH₃), 21.4 (s, Mes-CH₃), 21.2 (d, 3J₉₁C = 2.2 Hz, RhCCCH₃), 13.9 (d, 2J₉₁C = 1.3 Hz, P(CH₃)₃), 5.5 (s, RhCCCH₃) ppm.

Comment: The spectrum contains signals corresponding to residual hexane from crystallization at 31.97, 23.06 and 14.35 ppm. The broad singlet for the Mes-C₉ nucleus bound to the boron atom could not be observed in the 13C{1H, 31P} NMR spectrum.

11B NMR (160.5 MHz, C₆D₆, 298 K): δ = 70.2 (br s) ppm.

31P{1H} NMR (202.5 MHz, C₆D₆, 298 K): δ = −3.7 (d, 1J₉₁P = 128 Hz, 2 P) ppm.

HRMS (LIFDI, C₂₅H₄₄BCIN₃R₉): calcd: m/z = 569.1780, found: m/z = 569.1767.

UV-vis (hexane): λₐₙₙ = 260, 345 nm.

23
Synthesis of 2g

1g (325 mg, 447 μmol) was dissolved in benzene (10 mL) and treated with a stock solution of trimethylphosphine in benzene (2.61 mL, 1.96 mmol, 0.75 M). After stirring the reaction mixture for 4 d, all volatiles were removed in vacuo and the residue was dissolved in 10 mL benzene. The orange solution was filtrated and the solvent was removed under reduced pressure. After washing the residue with hexane (3 x 4 mL) all volatiles were removed in vacuo to yield 2g as a yellow solid (114 mg, 158 μmol, 35%). Crystals of 2g suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at −30 °C.

1H NMR (500.1 MHz, C6D6, 298 K): δ = 7.54-7.52 (m, 2H, Ph-C6H), 7.19-7.17 (m, 2H, Mes-C6H), 7.13-7.10 (m, 1H, Ph-C6H), 6.85 (s, 2H, Mes-C6H), 2.70 (s, 6H, Mes-C6H3), 2.20 (s, 3H, Mes-C6H3), 1.37 (vtd, JRhH = 7.1 Hz, 3JRhP = 0.8 Hz, 18H, P(C6H3)3), 1.13 (s, 9H, tBu-C6H3), 0.86 (s, 12H, Bpin-C6H3) ppm.

13C{1H} NMR (125.8 MHz, C6D6, 298 K): δ = 157.1 (br s, NCPH), 143.9-143.8 (m, Ph-C6H), 143.0 (br s, Mes-C6H), 138.5 (t, 4JPC = 0.7 Hz, Mes-C6H), 137.0 (s, Mes-C6H), 131.2 (t, 5JPC = 1.8 Hz, Ph-C6H), 128.5 (s, Mes-C6H), 126.9 (s, Ph-C6H), 126.2 (s, Ph-C6H), 81.8 (s, Bpin-C6H), 56.7 (d, 3JRhC = 1.3 Hz, tBu-C6H), 33.0 (s, tBu-C6H3), 26.96-26.95 (m, Mes-C6H3), 25.0 (s, Bpin-C6H3), 21.4 (s, Mes-C6H3), 14.7 (vtd, N = 28.9 Hz, 2JRhC = 1.3 Hz, P(CH3)3) ppm.

Comment: The spectrum contains signals corresponding to residual hexane at 31.97, 23.06 and 14.35 ppm. The RhCBpin carbon nucleus was not observed in the 13C{1H} NMR spectrum.

11B NMR (160.5 MHz, C6D6, 298 K): δ = 71.3 (br s, RhBMes), 30.3 (br s, Bpin-B) ppm.

31P{1H} NMR (202.5 MHz, C6D6, 298 K): δ = −4.9 (d, 1JRhP = 128 Hz, 2 P) ppm.

HRMS (LIFDI, C33H55B2ClNO2P2Rh): calcd: m/z = 719.2632, found: m/z = 719.2620.

UV-vis (hexane): λabs = 255, 291 (shoulder), 362 nm.
Synthesis of 2l

1l (100 mg, 88.8 µmol) was dissolved in benzene (10 mL) and treated with a stock solution of trimethylphosphine in benzene (0.52 mL, 390 µmol, 0.75 M). After stirring the reaction mixture for 15 h, all volatiles were removed in vacuo. The residue was first washed with pentane (3 x 2 mL), then with benzene (3 x 2 mL), and then dried under reduced pressure to yield 2l as a yellow solid (59 mg, 53.2 µmol, 60%). Crystals of 2l suitable for X-ray diffraction were obtained by evaporation of a saturated benzene solution.

$^1$H NMR (400.6 MHz, C$_6$D$_6$, 298 K): $\delta = 7.43$ (s, 4H, C$_6$H$_4$-CH), 6.88 (s, 4H, Mes-CH), 5.92 (t, $^3$J$_{PH} = 5.0$ Hz, 2H, RhCH), 2.67 (s, 12H, Mes-CH$_3$), 2.21 (s, 6H, Mes-CH$_3$), 1.24 (s, 18H, tBu-CH$_3$), 1.17 (vt, $\nu = 6.2$ Hz, 36H, P(CH$_3$)$_3$) ppm.

$^{13}$C{${^1}$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K): $\delta = 153.7$ (RhCC$_q$, detected by HMBC), 142.3 (C$_6$H$_4$-C$_q$, detected by HMBC), 142.3 (Mes-C$_q$, detected by HMBC), 138.1 (s, Mes-C$_q$), 137.2 (s, Mes-C$_q$), 131.3 (RhCH, detected by HSQC), 128.6 (s, Mes-CH), 128.2 (C$_6$H$_4$-CH, detected by HSQC), 56.4 (d, $^3$J$_{RhP} = 1.1$ Hz, tBu-CH$_3$), 32.8 (s, tBu-CH$_3$), 26.62-26.60 (m, Mes-CH$_3$), 21.4 (s, Mes-CH$_3$), 14.1 (vt, $\nu = 29.1$ Hz, $^2$J$_{RhC} = 1.2$ Hz, P(CH$_3$)$_3$) ppm.

$^{11}$B NMR (128.5 MHz, C$_6$D$_6$, 298 K): not observed due to poor solubility.

$^{31}$P{${^1}$H} NMR (162.2 MHz, C$_6$D$_6$, 298 K): $\delta = -4.5$ (d, $^1$J$_{RhP} = 128$ Hz, 4 P) ppm.

HRMS (LIFDI, C$_{48}$H$_{82}$B$_2$Cl$_2$N$_2$P$_4$Rh$_2$): calcd: m/z = 1108.3096, found: m/z = 1108.3095.

UV-vis (THF): $\lambda_{abs} = 255$ (shoulder), 299, 344 (shoulder) nm.
Synthesis of 3a\textsuperscript{Me}

![Chemical structure](attachment:image.png)

1a (200 mg, 371 \textmu mol) and IMe (106.9 mg, 1.11 mmol) were dissolved in benzene (8 mL). After stirring the reaction mixture for 15 h, the resulting precipitate was filtered off and washed with benzene (3 x 8 mL). After removing all volatiles from the combined benzene fractions \textit{in vacuo}, the residue was washed with pentane (3 x 5 mL) and benzene (2 x 2 mL), and dried under reduced pressure to yield 3a\textsuperscript{Me} as a yellow solid (89 mg, 148 \textmu mol, 40%). Crystals of 3a\textsuperscript{Me} suitable for X-ray diffraction were obtained by evaporation of a saturated benzene-d\textsubscript{6} solution.

Comment: The residue of the filtration/extraction was identified as 1,3-dimethylimidazolium chloride by \textsuperscript{1}H NMR spectroscopy.

\textsuperscript{1}H NMR (500.1 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \(\delta = 7.06\) (s, 1H, Mes-CH), 7.02 (s, 1H, Mes-CH), 6.12 (d, \(^{3}J_{HH} = 1.8\) Hz, 1H, IMe-NCH), 6.05 (d, \(^{3}J_{HH} = 1.9\) Hz, 1H, IMe-NCH), 5.34-5.32 (m, 1H, CCH\textsubscript{2}), 4.85-4.84 (m, 1H, CCH\textsubscript{2}), 3.91 (s, 3H, IMe-CH\textsubscript{3}), 3.22 (s, 3H, IMe-CH\textsubscript{3}), 3.05 (s, 3H, Mes-CH\textsubscript{3}), 2.81 (s, 3H, Mes-CH\textsubscript{3}), 2.52-2.50 (m, 1H, CHCCH\textsubscript{2}), 2.34 (s, 3H, Mes-CH\textsubscript{3}), 1.88-1.81 (m, 3H, iPr-CH), 1.18 (dd, \(^{3}J_{HH} = 7.3\) Hz, \(^{3}J_{PH} = 12.6\) Hz, 9H, iPr-CH\textsubscript{3}), 1.04 (s, 9H, tBu-CH\textsubscript{3}), 0.77 (dd, \(^{3}J_{HH} = 7.3\) Hz, \(^{3}J_{PH} = 11.4\) Hz, 9H, iPr-CH\textsubscript{3}) ppm.

Comment: The spectrum contains signals corresponding to residual pentane at 1.25 (m) and 0.87 (t) ppm.

\textsuperscript{1}H\textsuperscript{\textsuperscript{31}P} NMR (500.1 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \(\delta = 7.06\) (s, 1H, Mes-CH), 7.02 (s, 1H, Mes-CH), 6.12 (d, \(^{3}J_{HH} = 1.8\) Hz, 1H, IMe-NCH), 6.05 (d, \(^{3}J_{HH} = 1.8\) Hz, 1H, IMe-NCH), 5.34-5.32 (m, 1H, CCH\textsubscript{2}), 4.85-4.83 (m, 1H, CCH\textsubscript{2}), 3.91 (s, 3H, IMe-CH\textsubscript{3}), 3.22 (s, 3H, IMe-CH\textsubscript{3}), 3.05 (s, 3H, Mes-CH\textsubscript{3}), 2.81 (s, 3H, Mes-CH\textsubscript{3}), 2.52-2.50 (m, 1H, CHCCH\textsubscript{2}), 2.34 (s, 3H, Mes-CH\textsubscript{3}), 1.84 (sept, \(^{3}J_{HH} = 7.2\) Hz, 3H, iPr-CH), 1.18 (d, \(^{3}J_{HH} = 7.2\) Hz, 9H, iPr-CH\textsubscript{3}), 1.04 (s, 9H, tBu-CH\textsubscript{3}), 0.77 (dd, \(^{3}J_{HH} = 7.2\) Hz, 9H, iPr-CH\textsubscript{3}) ppm.

\textsuperscript{13}C\textsuperscript{\textsuperscript{1}H} NMR (125.8 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \(\delta = 192.8\) (dd, \(^{1}J_{RhC} = 60.7\) Hz, \(^{2}J_{PC} = 16.0\) Hz, IMe-\textsubscript{q}), 188.8 (dd, \(^{1}J_{RhC} = 20.5\) Hz, \(^{2}J_{PC} = 4.8\) Hz, CCH\textsubscript{2}), 145.7 (Mes-\textsubscript{q}, detected by
After storing the filtrate at 30 °C for 8 d a yellow crystalline solid formed. The solid was washed with benzene-d₆ and dried under reduced pressure to yield 3e^{Me}.

Synthesis of 3e^{Me}

1e (25.0 mg, 43.0 μmol) and IMe (9.9 mg, 103 μmol) were dissolved in benzene (0.6 mL). After 30 mins at room temperature, the suspension was filtered, and all volatiles of the filtrate were removed in vacuo. The residue of the filtrate was treated with hexane (0.6 mL) and the resulting suspension was filtered. After storing the filtrate at −30 °C for 8 d a yellow crystalline solid formed. The solid was washed with benzene-d₆ and dried under reduced pressure to yield...
3eMe. Crystals of 3eMe suitable for X-ray diffraction were obtained by slow evaporation of a saturated hexane solution at −30 °C.

^1H NMR (500.1 MHz, C6D6, 298 K): δ = 7.073-7.070 (m, 1H, Mes-CH), 7.014-7.010 (m, 1H, Mes-CH), 6.09 (d, JHH = 1.9 Hz, 1H, IMe-NCH), 6.03 (d, JHH = 1.9 Hz, 1H, IMe-NCH), 5.32 (q, JHH = 6.5 Hz, 1H, CCHCH3), 3.80 (s, 3H, IMe-CH3), 3.51 (s, 3H, IMe-CH3), 3.03 (s, 3H, Mes-CH3), 2.78 (s, 3H, Mes-CH3), 2.35 (s, 3H, Mes-CH3), 2.27 (d, JHH = 6.5 Hz, 3H, CCHCH3), 2.13-2.06 (m, 1H, CCH2CH3), 1.80-1.73 (m, 3H, iPr-CH), 1.71-1.64 (m, 1H, CCH2CH3), 1.26-1.20 (m, 12H, iPr-CH3 overlapping with CCH2CH3), 1.01-0.97 (m, 9H, iPr-CH3) overlapping with 0.98 (s, 9H, tBu-CH3) ppm.

^13C[^1H] NMR (125.8 MHz, C6D6, 298 K): δ = 193.4 (dd, 1JRC = 59.0 Hz, 2JPC = 17.6 Hz, IMe-Cq), 183.0 (dd, 1JRC = 17.4 Hz, 2JPC = 4.2 Hz, CCHCH3), 145.5 (Mes-Cq, detected by HMBC), 139.7 (s, Mes-Cq), 138.2 (s, Mes-Cq), 134.7 (s, Mes-Cq), 127.9 (Mes-CH, detected by HSQC), 127.2 (s, Mes-CH), 122.0 (d, 3JRC = 1.4 Hz, IMe-NCH), 121.1 (d, 3JRC = 1.4 Hz, IMe-NCH), 96.04-96.03 (m, CCHCH3), 54.4 (dd, 2JRC = 1.2 Hz, 3JPC = 3.5 Hz, tBu-Cq), 39.5 (d, 3JRC = 0.8 Hz, IMe-CH3), 38.8 (d, 3JRC = 1.3 Hz, IMe-CH3), 34.1 (dd, (3JRC or 3JPC) = 0.6 Hz, (3JPC or 2JRC) = 1.8 Hz, tBu-CH3), 27.6 (s, CCH2CH3), 27.4 (dd, 1JPC = 15.9 Hz, 2JRC = 0.6 Hz, iPr-CH), 24.5 (s, Mes-CH3), 24.4 (s, Mes-CH3), 21.6 (s, Mes-CH3), 21.4 (d, 2JPC = 2.8 Hz, iPr-CH3), 19.5 (d, (3JRC or 2JPC) = 0.7 Hz, iPr-CH3), 18.2 (d, (3JRC or 4JPC) = 1.6 Hz, CCHCH3), 15.4 (d, (3JRC or 4JPC) = 0.9 Hz, CCH2CH3) ppm.

^11B NMR (160.5 MHz, C6D6, 298 K): δ = 34.7 (br s) ppm.

^31P[^1H] NMR (162.2 MHz, C6D6, 298 K): δ = 46.6 (d, 1JRP = 144 Hz) ppm.

HRMS (LIFDI, C35H58BN3PRh): calcd: m/z = 641.3511, found: m/z = 641.3498.

Synthesis of 4aPr

![Structure](image)

1a (30.0 mg, 55.6 µmol) and iPr (28.0 mg, 184 µmol) were dissolved in benzene (0.6 mL). After 6 d at room temperature the suspension was filtered. The filtrate was treated with benzene (0.2 mL), leading to precipitation of a yellow solid. The supernatant solution was removed by Pasteur pipette and the residue was washed with benzene (2 x 1 mL) and hexane (1 x 2 mL).
The residual solvent was removed in vacuo to yield \(4a^{\text{Pr}}\) as a yellow solid (10.0 mg, 15.4 \(\mu\)mol, 28\%). Crystals of \(4a^{\text{Pr}}\) suitable for X-ray diffraction were obtained by evaporation of a saturated benzene solution.

Comment: The residue of the filtration was identified as 1,3-diisopropylimidazolium chloride by \(^1H\) NMR spectroscopy.

\(\textbf{^1H NMR (500.1 MHz, C}_6\text{D}_6, 298 K): \delta = 7.11-7.10 (m, 1H, Mes-CH), 7.021-7.017 (m, 1H, Mes-CH), 6.73 (sept, \(^3J_{\text{HH}} = 6.7\) Hz, 1H, iPr-CH), 6.50 (d, \(^3J_{\text{HH}} = 2.0\) Hz, 1H, iPr-NCH), 6.44 (sept, \(^3J_{\text{HH}} = 6.6\) Hz, 1H, iPr-CH), 6.28 (d, \(^3J_{\text{HH}} = 2.2\) Hz, 1H, iPr-NCH), 6.24 (d, \(^3J_{\text{HH}} = 2.1\) Hz, 1H, iPr-NCH), 6.16 (d, \(^3J_{\text{HH}} = 2.1\) Hz, 1H, iPr-NCH), 5.40-5.31 (m, 2H, iPr-CH overlapping with CCH\(_2\)), 4.71-4.70 (m, 1H, CCH\(_2\)), 4.54 (sept, \(^3J_{\text{HH}} = 6.8\) Hz, 1H, iPr-CH), 3.08 (s, 3H, Mes-CH\(_3\)), 2.89 (s, 3H, Mes-CH\(_3\)), 2.37 (s, 3H, Mes-CH\(_3\)), 1.86 (t, \(^4J_{\text{HH}} = 3.5\) Hz, 1H, CHCCH\(_2\)), 1.43 (d, \(^3J_{\text{HH}} = 6.5\) Hz, 3H, iPr-CH\(_3\)), 1.30 (d, \(^3J_{\text{HH}} = 6.7\) Hz, 3H, iPr-CH\(_3\)), 1.26 (s, 9H, tBu-CH\(_3\)), 1.20 (d, \(^3J_{\text{HH}} = 6.8\) Hz, 3H, iPr-CH\(_3\)), 1.14 (d, \(^3J_{\text{HH}} = 6.9\) Hz, 3H, iPr-CH\(_3\)), 1.02 (d, \(^3J_{\text{HH}} = 6.9\) Hz, 3H, iPr-CH\(_3\)), 0.98 (d, \(^3J_{\text{HH}} = 6.7\) Hz, 3H, iPr-CH\(_3\)), 0.40 (d, \(^3J_{\text{HH}} = 6.8\) Hz, 3H, iPr-CH\(_3\)), 0.35 (d, \(^3J_{\text{HH}} = 6.7\) Hz, 3H, iPr-CH\(_3\)) ppm.

\(\textbf{^13C\{^1H\} NMR (125.8 MHz, C}_6\text{D}_6, 298 K): \delta = 192.4 (d, \(^1J_{\text{RHC}} = 65.7\) Hz, iPr-C\(_q\)), 186.9 (d, \(^1J_{\text{RHC}} = 24.5\) Hz, CCH\(_2\)), 183.8 (d, \(^1J_{\text{RHC}} = 48.3\) Hz, iPr-C\(_q\)), 147.7 (Mes-C\(_q\), detected by HMBC), 140.2 (s, Mes-C\(_q\)), 136.8 (s, Mes-C\(_q\)), 133.9 (s, Mes-C\(_q\)), 127.9 (Mes-CH, detected by HSQC), 127.0 (s, Mes-CH), 117.4 (d, \(^3J_{\text{RHC}} = 1.8\) Hz, iPr-NCH), 116.4 (d, \(^3J_{\text{RHC}} = 0.8\) Hz, iPr-NCH), 115.3 (d, \(^3J_{\text{RHC}} = 1.1\) Hz, iPr-NCH), 114.8 (d, \(^3J_{\text{RHC}} = 1.4\) Hz., iPr-NCH), 85.9 (s, CCH\(_2\)), 54.6 (d, \(^2J_{\text{RHC}} = 0.7\) Hz, tBu-C\(_q\)), 52.8 (s, iPr-CH), 50.9 (s, iPr-CH), 50.497 (s, iPr-CH) overlapping with 50.488 (s, iPr-CH), 36.1 (s, tBu-CH\(_3\)), 34.0 (br s, CHCCH\(_2\)), 25.0 (s, iPr-CH\(_3\)), 24.9 (s, iPr-CH\(_3\)), 24.1 (s, iPr-CH\(_3\)), 23.8 (s, Mes-CH\(_3\)), 23.5 (s, iPr-CH\(_3\)), 23.4 (s, Mes-CH\(_3\)), 22.8 (s, iPr-CH\(_3\)), 22.6 (s, iPr-CH\(_3\)), 22.1 (s, iPr-CH\(_3\)), 22.0 (s, iPr-CH\(_3\)), 21.6 (s, Mes-CH\(_3\)) ppm.

\(\textbf{^11B NMR (160.5 MHz, C}_6\text{D}_6, 298 K): \delta = 31.7 \text{ (br s)} \) ppm.

HRMS (LIFDI, C\(_{34}\)H\(_{53}\)BN\(_3\)Rh): \textit{calcd: m/z = 647.3600, found: m/z = 647.3594.}

UV-vis (THF): \(\lambda_{\text{abs}} = 380, 430 \text{ nm.}\)
Synthesis of 4e^{Pr}

1e (30.0 mg, 51.6 μmol) and iPr (25.9 mg, 170 μmol) were dissolved in benzene (0.6 mL). After 4 d at room temperature, the suspension was filtered, and all volatiles of the filtrate were removed in vacuo. The residue of the filtrate was washed with hexane (3 x 1 mL) and dried under reduced pressure to yield 4e^{Pr} as an orange solid (9.0 mg, 13.1 μmol, 25%). Crystals of 4e^{Pr} suitable for X-ray diffraction were obtained by evaporation of a saturated hexane solution.

$^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K): δ = 7.122-7.119 (m, 1H, Mes-CH), 7.061-7.059 (m, 1H, Mes-CH), 6.58-6.50 (m, 2H, iPr-CH) overlapping with iPr-NCH), 6.36-6.28 (m, 2H, iPr-CH overlapping with iPr-NCH), 6.26 (d, $^3$J$_{HH}$ = 2.0 Hz, 1H, iPr-NCH), 6.16 (d, $^3$J$_{HH}$ = 2.1 Hz, 1H, iPr-NCH), 5.40 (sept, $^3$J$_{HH}$ = 6.8 Hz, 1H, iPr-CH), 4.94 (qd, $^3$J$_{HH}$ = 6.3 Hz, $^3$J$_{Rh}$ = 1.6 Hz, 1H, CCHCH$_3$), 4.50 (sept, $^3$J$_{HH}$ = 6.8 Hz, 1H, iPr-CH), 3.08 (s, 3H, Mes-CH$_3$), 2.88 (s, 3H, Mes-CH$_3$), 2.39 (s, 3H, Mes-CH$_3$), 2.30 (d, $^3$J$_{HH}$ = 6.3 Hz, 3H, CCHCH$_3$), 1.94-1.86 (m, 1H, CCH$_2$CH$_3$), 1.48 (d, $^3$J$_{HH}$ = 6.5 Hz, 3H, iPr-CH$_3$), 1.34-1.26 (m, 7H, CCH$_2$CH$_3$ overlapping with two iPr-CH$_3$), 1.24 (s, 9H, tBu-CH$_3$), 1.17-1.14 (m, 6H, iPr-CH$_3$ overlapping with another iPr-CH$_3$), 1.00 (d, $^3$J$_{HH}$ = 6.9 Hz, 3H, iPr-CH$_3$), 0.73 (t, $^3$J$_{HH}$ = 7.4 Hz, 3H, CCH$_2$CH$_3$), 0.43 (d, $^3$J$_{HH}$ = 6.8 Hz, 3H, iPr-CH$_3$), 0.32 (d, $^3$J$_{HH}$ = 6.7 Hz, 3H, iPr-CH$_3$) ppm.

$^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K): δ = 192.3 (d, $^1$J$_{RHC}$ = 67.2 Hz, iPr-C$_q$), 184.7 (d, $^1$J$_{RHC}$ = 48.4 Hz, iPr-C$_q$), 179.2 (d, $^1$J$_{RHC}$ = 26.5 Hz, CCHCH$_3$), 146.8 (br s, Mes-C$_q$), 139.7 (s, Mes-C$_q$), 137.3 (s, Mes-C$_q$), 133.8 (s, Mes-C$_q$), 127.7 (s, Mes-CH), 127.2 (s, Mes-CH), 117.6 (d, $^3$J$_{RHC}$ = 1.9 Hz, iPr-NCH), 116.6 (d, $^3$J$_{RHC}$ = 0.8 Hz, iPr-NCH), 115.1 (d, $^3$J$_{RHC}$ = 0.9 Hz, iPr-NCH), 114.6 (d, $^3$J$_{RHC}$ = 1.4 Hz, iPr-NCH), 95.2 (s, CCHCH$_3$), 54.6 (d, $^2$J$_{RHC}$ = 0.7 Hz, tBu-C$_q$), 52.6 (s, iPr-CH), 50.6 (d, $^3$J$_{RHC}$ = 0.8 Hz, iPr-CH), 50.2 (s, iPr-CH), 49.7 (d, $^3$J$_{RHC}$ = 1.3 Hz, iPr-CH), 49.3 (br s, CCH$_2$CH$_3$), 36.2 (s, tBu-CH$_3$), 27.4 (s, CCH$_2$CH$_3$), 24.9 (s, iPr-CH$_3$), 24.6 (s, iPr-CH$_3$), 24.5 (s, iPr-CH$_3$), 24.3 (s, iPr-CH$_3$), 23.70 (s, Mes-CH$_3$), 23.68 (s, Mes-CH$_3$), 23.4 (s, iPr-CH$_3$), 22.5 (s, iPr-CH$_3$), 22.1 (s, iPr-CH$_3$), 21.75 (s, iPr-CH$_3$), 21.66 (s, Mes-CH$_3$), 18.3 (d, $^3$J$_{RHC}$ = 3.5 Hz, CCHCH$_3$), 13.5 (s, CCH$_2$CH$_3$) ppm.
Comment: The spectrum contains signals corresponding to residual hexane at 31.97, 23.06 and 14.35 and residual benzene at 128.59 ppm.

$^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K): $\delta = 32.3$ (br s) ppm.

HRMS (LIFDI, C$_{37}$H$_{61}$BN$_3$Rh): calcd: m/z = 689.4070, found: m/z = 689.4058.

UV-vis (THF): $\lambda_{abs} = 351$ (shoulder), 449 nm.

**Synthesis of 5**

$^{1}H$ NMR (500.1 MHz, C$_6$D$_6$, 298 K): $\delta = 6.95$ (s, 1H, Mes-CH), 6.87 (s, 1H, Mes-CH), 5.10 (q, $J_{HH} = 6.7$ Hz, 1H, CCHCH$_3$), 3.36 (s, 3H, Mes-CH$_3$), 2.33 (s, 3H, Mes-CH$_3$) overlapping with 2.32 (d, $J_{HH} = 6.8$ Hz, 3H, CCHCH$_3$), 2.28-2.20 (m, 3H, iPr-CH) overlapping with 2.22 (s, 3H, Mes-CH$_3$), 2.11-2.10 (m, 1H, NH), 1.95-1.88 (m, 1H, Et-CH$_2$), 1.38 (s, 9H, tBu-CH$_3$), 1.21-1.16 (m, 19H, iPr-CH$_3$ overlapping with Et-CH$_2$), 1.03 (t, $J_{HH} = 7.5$ Hz, 3H, Et-CH$_3$) ppm.

$^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K): $\delta = 168.2$ (dd, $J_{HH} = 20.5$ Hz, $J_{PC} = 4.7$ Hz, CCHCH$_3$), 140.4 (s, Mes-C$_q$), 139.0 (s, Mes-C$_q$), 137.1 (s, Mes-C$_q$), 135.3 (Mes-C$_q$, detected by HMBC), 128.3 (Mes-CH, detected by HSQC), 127.8 (Mes-CH, detected by HSQC), 101.97-101.95 (m, CCHCH$_3$), 58.2 (BCEt, detected by HMBC), 54.7 (d, $J_{HH} = 0.5$ Hz, tBu-C$_q$), 30.3 (d, $J_{HH} = 1.1$ Hz, iPr-CH), 25.0 (s, Et-CH$_2$), 23.6 (s, Mes-CH$_3$), 21.3 (s, Mes-CH$_3$), 20.8 (s, iPr-CH$_3$), 19.2 ($J_{HH} = 1.3$ Hz, iPr-CH$_3$), 16.5 (d, $J_{HH} = 1.1$ Hz, CCHCH$_3$), 13.3 (dd, $J_{HH} = 0.7$ Hz, $J_{PC} = 1.6$ Hz, Et-CH$_3$) ppm.

$^{1}$H NMR (30.0 mg, 51.6 $\mu$mol) was dissolved in benzene-d$_6$ (0.6 mL). After 4 d at 80 °C, all volatiles were removed in vacuo and the residue was washed with hexane (3 x 1 mL). Drying under reduced pressure yielded 5 as a yellow solid. Crystals of 5 suitable for X-ray diffraction were obtained by slow evaporation of a saturated pentane solution at −30 °C.

Comment: Crystals of 6 suitable for X-ray diffraction were obtained by evaporation of the hexane filtrate/washing solution.
$^{11}$B NMR (128.5 MHz, C₆D₆, 298 K): $\delta = 29.3$ (br s) ppm.

$^{31}$P{¹H} NMR (202.5 MHz, C₆D₆, 298 K): $\delta = 53.9$ (d, $^1J_{RhP} = 181$ Hz) ppm.

**Irradiation of 5**

The irradiation of a solution of 5 in benzene-d₆ with a mercury-xenon vapor lamp for 2 h led to complete conversion to a compound with a major signal in the $^{11}$B NMR spectrum at 40.4 ppm and a doublet at 47.6 ppm ($^1J_{RhP} = 169$ Hz) in the $^{31}$P NMR spectrum, in addition to traces of side products. After removing all volatiles *in vacuo* the residue was dissolved in pentane. Crystals of 7 suitable for X-ray diffraction were obtained by slow evaporation of this solution at −30 °C.

**Synthesis of 1b(IMe)**

![Chemical Structure](image)

1b (30.0 mg, 49.8 μmol) and IMe (4.8 mg, 49.9 μmol) were dissolved in benzene (0.6 mL). After 2 h at room temperature, all volatiles were removed *in vacuo*. The residue was washed with hexane (3 x 1.5 mL), dried under reduced pressure and dissolved in benzene-d₆ (0.6 mL). After 6 d at room temperature, an orange solid precipitated. The supernatant solution was removed by Pasteur pipette. The residue was washed with benzene (ca. 0.3 mL) and dried under reduced pressure to yield 1b(IMe).

$^1$H NMR (500.1 MHz, C₆D₆, 298 K): $\delta = 8.14$-$8.12$ (m, 2H, Ph-CH), 7.13-$7.06$ (m, 3H, Ph-CH), 6.92 (s, 2H, Mes-CH), 5.78 (s, 2H, IMe-NCH), 3.60 (s, 3H, Mes-CH₃), 3.38 (s, 6H, IMe-CH₃), 3.02 (s, 1H, Aza-CH), 2.75 (s, 3H, Mes-CH₃), 2.21 (s, 3H, Mes-CH₃), 1.33 (s, 9H, tBu-CH₃) ppm.

$^{13}$C{¹H} NMR (125.8 MHz, C₆D₆, 298 K): $\delta = 181.7$ (d, $^1J_{RhC} = 68.1$ Hz, IMe-C₄), 141.8 (s, Mes-C₆), 140.9 (s, Mes-C₆), 138.1 (s, Mes-C₆), 135.5 (s, Ph-C₆), 132.2 (Mes-C₆, detected by HMBC), 131.1 (s, Ph-CH), 129.1 (s, Ph-CH), 128.7 (s, Mes-CH), 127.9 (Ph-CH, detected by HSQC), 127.7 (s, Mes-CH), 121.4 (s, IMe-NCH), 103.5 (d, $^1J_{RhC} = 14.6$ Hz, Aza-C₄), 56.4 (s,
\( \text{tBu-C}_3 \), 47.7 (br s, Aza-CH), 37.8 (s, IMe-CH\textsubscript{3}), 29.6 (s, tBu-CH\textsubscript{3}), 26.7 (s, Mes-CH\textsubscript{3}), 24.0 (s, Mes-CH\textsubscript{3}), 21.3 (s, Mes-CH\textsubscript{3}) ppm.

**\( ^{11}\text{B NMR} \)** (128.5 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \( \delta = 20.3 \) (br s) ppm.

**Reaction of 1a with PEt\textsubscript{3}**

1a (21.0 mg, 38.9 \( \mu \)mol) was dissolved in benzene-\textsubscript{d\textsubscript{6}} (0.5 mL) and PEt\textsubscript{3} (0.03 mL, 207 \( \mu \)mol) was added. After 30 mins at room temperature, complete conversion to compound 2a(PEt\textsubscript{3}) was observed by \( ^{11}\text{B} \) and \( ^{31}\text{P} \) NMR spectroscopy (assigned on the basis of similarity to 2a).

\( ^{11}\text{B NMR} \) (128.5 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \( \delta = 68.1 \) (br s) ppm.

\( ^{31}\text{P}\{^1\text{H}\} \text{NMR} \) (162.2 MHz, C\textsubscript{6}D\textsubscript{6}, 298 K): \( \delta = 12.5 \) (d, \( ^1\text{J}_{\text{Rh-P}} = 127 \) Hz, 2P) ppm.

*Comment:* The \( ^{31}\text{P}\{^1\text{H}\} \text{NMR} \) spectrum contains signals corresponding to P\textsubscript{\textit{Pr}}\textsubscript{3} at 19.5 ppm and PEt\textsubscript{3} at -19.7 ppm.

**Reaction of 1a with PCy\textsubscript{3}**

1a (20.0 mg, 37.1 \( \mu \)mol) and PCy\textsubscript{3} (21.3 mg, 76.0 \( \mu \)mol) were dissolved in toluene (0.6 mL). The reaction mixture was heated at 80 °C for 2 d and then all volatiles were removed in vacuo. The residue was dissolved again in toluene (0.6 mL) and heated at 80 °C for 1 d. Again all volatiles were removed in vacuo, the residue was dissolved in toluene (0.6 mL) and heated at 80 °C for 8 h. Almost complete conversion to compound 1a(PCy\textsubscript{3}) was observed (assigned by \( ^{11}\text{B} \) and \( ^{31}\text{P} \) NMR spectroscopy on the basis of similarity to 1a).

\( ^{11}\text{B NMR} \) (128.5 MHz, toluene, 298 K): \( \delta = 20.0 \) (br s) ppm.

\( ^{31}\text{P}\{^1\text{H}\} \text{NMR} \) (162.2 MHz, toluene, 298 K): \( \delta = 49.0 \) (d, \( ^1\text{J}_{\text{Rh-P}} = 197 \) Hz) ppm.

*Comment:* The \( ^{31}\text{P}\{^1\text{H}\} \text{NMR} \) spectrum contains signals corresponding to starting material 1a at 60.4 (d, \( ^1\text{J}_{\text{Rh-P}} = 197 \) Hz) ppm, P\textsubscript{\textit{Pr}}\textsubscript{3} at 18.8 ppm and PCy\textsubscript{3} at 9.0 ppm.
NMR spectra

Figure S1. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1a

Figure S2. $^1$H{$^{31}$P} NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1a.
Figure S3. $^{13}$C$\{^1\text{H}\}$ NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1a.

Figure S4. $^{13}$C$\{^1\text{H}, ^{31}\text{P}\}$ NMR (75.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1a.
Figure S5. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1a.

Figure S6. $^{31}$P{$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1a.
Figure S7. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1c.

Figure S8. $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1c.
Figure S9. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1c.

Figure S10. $^{31}$P{$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1c.
Figure S11. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1d.

Figure S12. $^1$H$^{31}$P NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1d.
Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1d.

Figure S14. $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (75.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1d.
Figure S15. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1d.

Figure S16. $^{31}$P{$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1d.
Figure S17. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1e.

Figure S18. $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1e.
Figure S19. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1e.

Figure S20. $^{31}$P($^1$H) NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1e.
Figure S21. $^1$H NMR (500.1 MHz, C₆D₆, 298 K) spectrum of 1f.

Figure S22. $^1$H{$^{31}$P} NMR (500.1 MHz, C₆D₆, 298 K) spectrum of 1f.
Figure S23. $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1f.

Figure S24. $^{13}$C($^1$H, $^{31}$P) NMR (75.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1f.
Figure S25. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1f.

Figure S26. $^{31}$P{^1}H NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1f.
Figure S27. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1g.

Figure S28. $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1g.
Figure S29. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1g.

Figure S30. $^{31}$P{$^1$H} NMR (162.2 MHz, C$_6$D$_6$, 298 K) spectrum of 1g.
Figure S31. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1h.

Figure S32. $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1h.
**Figure S33.** $^{11}$B NMR (128.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1h.

**Figure S34.** $^{31}$P{$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1h.
**Figure S35.** $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1i.

**Figure S36.** $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1i.
**Figure S37.** $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1i.

**Figure S38.** $^{19}$F NMR (470.6 MHz, C$_6$D$_6$, 298 K) spectrum of 1i.
Figure S39. $^{31}$P/$^1$H NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1i.

Figure S40. $^1$H NMR (500.1 MHz, d$_8$-THF, 298 K) spectrum of 1j.
Figure S41. $^{13}$C($^1$H) NMR (125.8 MHz, $d_8$-THF, 298 K) spectrum of 1j.

Figure S42. $^{11}$B NMR (128.5 MHz, $d_8$-THF, 298 K) spectrum of 1j.
Figure S43. $^{19}$F NMR (470.6 MHz, d$_8$-THF, 298 K) spectrum of 1j.

Figure S44. $^{31}$P{$_1^1$H} NMR (162.0 MHz, d$_8$-THF, 298 K) spectrum of 1j.
Figure S45. $^1$H NMR (500.1 MHz, $d_8$-THF, 233 K) spectrum of 1j.

Figure S46. $^{13}$C\{1H\} NMR (125.8 MHz, $d_8$-THF, 233 K) spectrum of 1j.
Figure S47. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 1k.

Figure S48. $^{13}$C{^1}H NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 1k.
Figure S49. $^{11}$B NMR (128.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1k.

Figure S50. $^{31}$P{^1}H NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 1k.
Figure S51. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 11.

Figure S52. $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 11.
Figure S53. $^{11}$B NMR (128.4 MHz, C$_6$D$_6$, 298 K) spectrum of 1l.

Figure S54. $^{31}$P{$^1$H} NMR (162.0 MHz, C$_6$D$_6$, 298 K) spectrum of 1l.
Figure S55. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2a.

Figure S56. $^{13}$C{$_1^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 2a.
Figure S57. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2a.

Figure S58. $^{31}$P{$_1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2a.
Figure S59. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2b.

Figure S60. $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 2b.
Figure S61. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2b.

Figure S62. $^{31}$P{$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2b.
Figure S63. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2c.

Figure S64. $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 2c.
Figure S65. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2c.

Figure S66. $^{31}$P{$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2c.
Figure S67. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2d.

Figure S68. $^1$H{$^{31}$P} NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2d.
Figure S69. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 2d.

Figure S70. $^{13}\text{C}\{^1\text{H}, ^{31}\text{P}\}$ NMR (75.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2d.
Figure S71. $^{11}$B NMR (160.5 MHz, $\text{C}_6\text{D}_6$, 298 K) spectrum of 2d.

Figure S72. $^{31}\text{P}\{^1\text{H}\}$ NMR (202.5 MHz, $\text{C}_6\text{D}_6$, 298 K) spectrum of 2d.
Figure S73. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2e.

Figure S74. $^1$H$^{^{31}}$P NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2e.
Figure S75. $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 2e.

Figure S76. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2e.
Figure S77. $^{31}$P{$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2e.

Figure S78. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2f.
Figure S79. $^1$H{$^{31}$P} NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2f.

Figure S80. $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 2f.
Figure S81. $^{13}$C\{$^1$H, $^{31}$P\} NMR (75.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2f.

Figure S82. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2f.
Figure S83. $^{31}$P [$^1$H] NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2f.

Figure S84. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 2g.
Figure S85. $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 2g.

Figure S86. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2g.
Figure S87. $^{31}$P-$^1$H NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 2g.

Figure S88. $^1$H NMR (400.6 MHz, C$_6$D$_6$, 298 K) spectrum of 2l.
**Figure S89.** $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 2l.

**Figure S90.** $^{31}$P($^1$H) NMR (162.2 MHz, C$_6$D$_6$, 298 K) spectrum of 2l.
Figure S91. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 3a$^{Me}$.

Figure S92. $^1$H-$^{31}$P NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 3a$^{Me}$.
**Figure S93.** $^{13}$C($^1$H) NMR (125.8 MHz, C₆D₆, 298 K) spectrum of 3a$^{Me}$.

**Figure S94.** $^{13}$C($^1$H, $^{31}$P) NMR (75.5 MHz, C₆D₆, 298 K) spectrum of 3a$^{Me}$. 
Figure S95. $^{11}$B NMR (128.5 MHz, C$_6$D$_6$, 298 K) spectrum of 3a$^{Me}$.

Figure S96. $^{31}$P{${}^1$H} NMR (162.2 MHz, C$_6$D$_6$, 298 K) spectrum of 3a$^{Me}$. 
Figure S97. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 3e$^{Me}$.

Figure S98. $^{13}$C($^1$H) NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of 3e$^{Me}$. 
Figure S99. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 3e$_{\text{Me}}$.

Figure S100. $^{31}$P{$^1$H} NMR (162.2 MHz, C$_6$D$_6$, 298 K) spectrum of 3e$_{\text{Me}}$. 
Figure S101. $^1$H NMR (500.1 MHz, C₆D₆, 298 K) spectrum of 4a$^{iPr}$.

Figure S102. $^{13}$C{$^1$H} NMR (125.8 MHz, C₆D₆, 298 K) spectrum of 4a$^{iPr}$.
Figure S103. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of 4a$^{iPr}$.

Figure S104. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of 4e$^{iPr}$. 
Figure S105. $^{13}$C\{H\} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of $4\text{e}^{iPr}$.

Figure S106. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of $4\text{e}^{iPr}$. 
Figure S107. $^1$H NMR (500.1 MHz, $\text{C}_6\text{D}_6$, 298 K) spectrum of 5.

Figure S108. $^{13}\text{C}\{^1\text{H}\}$ NMR (125.8 MHz, $\text{C}_6\text{D}_6$, 298 K) spectrum of 5.
Figure S109. $^{11}$B NMR (128.5 MHz, C$_6$D$_6$, 298 K) spectrum of 5.

Figure S110. $^{31}$P{$^1$H} NMR (202.5 MHz, C$_6$D$_6$, 298 K) spectrum of 5.
Figure S111. $^1$H NMR (400.6 MHz, C$_6$D$_6$, 298 K) spectrum of 7 with impurities.

Figure S112. $^{11}$B NMR (128.5 MHz, C$_6$D$_6$, 298 K) spectrum of 7.
Figure S113. $^{31}$P{$^1$H} NMR (162.2 MHz, C$_6$D$_6$, 298 K) spectrum of 7.

Figure S114. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of I.
Figure S115. $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of I.

Figure S116. $^{11}$B NMR (160.5 MHz, C$_6$D$_6$, 298 K) spectrum of I.
Figure S117. $^1$H NMR (500.1 MHz, C$_6$D$_6$, 298 K) spectrum of II.

Figure S118. $^{13}$C{$^1$H} NMR (125.8 MHz, C$_6$D$_6$, 298 K) spectrum of II.
Figure S119. $^{11}$B NMR (128.5 MHz, C₆D₆, 298 K) spectrum of II.

Figure S120. $^{11}$B NMR (128.5 MHz, C₆D₆, 298 K) spectrum of the reaction of 1a with PEt₃.
**Figure S121.** $^{31}\text{P}^{(1)}\text{H}$ NMR (162.2 MHz, C$_6$D$_6$, 298 K) spectrum of the reaction of 1a with PEt$_3$.

**Figure S122.** $^{11}\text{B}$ NMR (128.5 MHz, toluene, 298 K) spectrum of the reaction of 1a with PCy$_3$. 
Figure S123. $^{31}$P{$^1$H} NMR (162.2 MHz, toluene, 298 K) spectrum of the reaction of 1a with PCy$_3$.

Figure S124. $^1$H NMR (400.1 MHz, CD$_2$Cl$_2$, 298 K) spectrum of 1,3-diisopropylimidazolium chloride.
Figure S125. $^1$H NMR (400.3 MHz, CD$_2$Cl$_2$, 298 K) spectrum of 1,3-dimethylimidazolium chloride.
UV-Vis spectra

The UV-vis absorption spectra of 1a, 1c, 1d, 1e, 1f, 1g, 1h, 1i, 1j, 1k, 1l, 2a, 2b, 2c, 2d, 2e, 2f, 2g, 2l and 3aMe were measured on a JASCO V-660 UV-vis spectrometer. The UV-vis absorption spectra of 4aPr and 4ePr were measured on a METTLER TOLEDO UV-vis Excellence UV5 spectrophotometer.

Figure S126. UV-vis absorption spectra of 1a, 1c and 1d in hexane.
Figure S127. UV-vis absorption spectra of 1e, 1f and 1g in hexane.

Figure S128. UV-vis absorption spectra of 1h, 1i and 1j in hexane.
Figure S129. UV-vis absorption spectra of 1k in hexane and of 1l in THF.

Figure S130. UV-vis absorption spectra of 2a and 2b in hexane and of 2c in THF.
Figure S 131. UV-vis absorption spectra of 2d, 2e and 2f in hexane.

Figure S132. UV-vis absorption spectra of 2g in hexane and of 2l in THF.
Figure S133. UV-vis absorption spectrum of $3a^{Me}$ in THF.

Figure S134. UV-vis absorption spectra of $4a^{iPr}$ and $4e^{iPr}$ in THF.
Crystal structure determination

The crystal data of $1c$, $1d$, $1g$, $1i$, $1j$, $1k$, $2b$, $2c$, $2e$, $2f$, $2g$, $2l$, $3a^{Pr}$, $3e^{Me}$, $4a^{Pr}$, $4e^{Pr}$, $5$, $6$, $7$ and I (Ia) were collected on a BRUKER D8 QUEST diffractometer with a CMOS area detector and multi-layer mirror monochromated Mo$_{K\alpha}$ radiation. The crystal data of $1a$, $1e$, $1f$, $1l$, $2a$, $2d$, $3a^{Me}$ and I(Ib) were collected on a BRUKER X8-APEX II diffractometer with a CCD area detector and multi-layer mirror monochromated Mo$_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,\textsuperscript{11} refined with the SHELXL program\textsuperscript{12} and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations. All hydrogen atoms were assigned to idealized geometric positions unless otherwise stated.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 1997139-1997165, 1997341 and 2012450. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

The hydrogen atoms of the azaborete four-membered ring system CH moieties of the compounds $1a$, $1c$, $1h$, $1i$ and $1l$ were refined with different refinement options (HFIX 43, HFIX 13 and freely refined). The different options showed no significant variations (less than double the standard deviations) concerning the bond distances and angles of the corresponding CH carbon atom to the surrounding heavier atoms (heavier than H). These hydrogen atoms were refined using the HFIX 13 command.

The hydrogen atoms of the allene CH moieties of the compounds $3a^{Me}$, $3a^{Pr}$, $3e^{Me}$ and $4a^{Pr}$ were refined with different refinement options (HFIX 43, HFIX 13 and freely refined). The different options showed no significant differences (less than the standard deviations) among each other concerning the bond distances and angles of the corresponding CH carbon atom to the surrounding heavier atoms (heavier than H). These hydrogen atoms were refined using the HFIX 43 command.

**Refinement details for 1d:** The two most disagreeable reflections were omitted.
**Refinement details for 1e:** The structure was refined using the TWIN keyword. The BASF parameter was refined to 46.9%.

**Refinement details for 1g:** The most disagreeable reflection was omitted. The displacement parameters of atoms B1_1 and B1_10 of the residues RESI 1 and RESI 10 were constrained to the same value with the EADP keyword. The displacement parameters of atoms B1_1 > C6_10 of the residues RESI 1 and RESI 10 were restrained to the same value with the similarity restraint SIMU. The Uii displacement parameters of atoms B1_1 > C6_10 of the residues RESI 1 and RESI 10 were restrained with the ISOR keyword to approximate isotropic behavior. The atomic displacement parameters of atoms B1_1 > C6_10 were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. A standard value of 0.003 was used). The 1-2 and 1-3 distances in the residues RESI 1 and RESI 10 were restrained to the same values with the SAME keyword.

**Refinement details for 1h:** The most disagreeable reflection was omitted.

**Refinement details for 1i:** The most disagreeable reflection was omitted.

**Refinement details for 2d:** The displacement parameters of atoms C1_1 > C4_10 of the residues RESI 1 and RESI 10 were restrained to the same value with the similarity restraint SIMU. The Uii displacement parameters of atoms C1_1 > C4_10 were restrained with the ISOR keyword to approximate isotropic behavior. The atomic displacement parameters of atoms C1_1 > C4_10 were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.002 for both parameters s1 and s2 were used). The 1-2 and 1-3 distances in RESI 1 and RESI 10 residues were restrained to the same values with the SAME keyword. The BUMP command was used to avoid short intramolecular H-H contacts.

**Refinement details for 2f:** The most disagreeable reflection was omitted. The displacement parameters of atoms C1_3 > C4_10 of the residues RESI 1, RESI 3, RESI 4, RESI 5 and RESI 10 were restrained to the same value with the similarity restraint SIMU. The Uii displacement parameters of atoms C1_3 > C4_10 were restrained with the ISOR keyword to approximate isotropic behavior. The atomic displacement parameters of atoms C1_3 > C4_10 were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all
bonds in the connectivity list. Standard values of 0.002 for both parameters s1 and s2 were used). The 1-2 and 1-3 distances in RESI 1 and RESI 10 residues were restrained to the same values with the SAME keyword.

**Refinement details for 2g:** The most disagreeable reflection was omitted.

**Refinement details for 2l:** The displacement parameters of atoms C1_1 > C3_2 of the residues RESI 1 and RESI 2 were restrained to the same value with the similarity restraint SIMU. The 1-2 and 1-3 distances in RESI 1 and RESI 2 residues were restrained to the same values with the SAME keyword.

**Refinement details for 3a**<sup>Pr</sup>: The most disagreeable reflection was omitted.

**Refinement details for 4a**<sup>Pr</sup>: The two most disagreeable reflections were omitted.

**Refinement details for 4e**<sup>Pr</sup>: The displacement parameters of atoms C1_1 > C4_10 of the residues RESI 1 and RESI 10 were restrained to the same value with the similarity restraint SIMU. The Uii displacement parameters of atoms C1_1 > C4_10 were restrained with the ISOR keyword to approximate isotropic behavior. The atomic displacement parameters of atoms C1_1 > C4_10 were restrained with the RIGU keyword in the ShelXL input ('enhanced rigid bond' restraint for all bonds in the connectivity list. Standard values of 0.004 for both parameters s1 and s2 were used).

**Refinement details for 5:** The most disagreeable reflection was omitted. All hydrogen atoms except H1 were assigned to idealized positions. The coordinates of H1 were refined freely.

**Refinement details for 6:** All hydrogen atoms except H2, H3 and H4 were assigned to idealized positions. The coordinates of H2, H3 and H4 were refined freely.

**Refinement details for 7:** All hydrogen atoms except H2, H4, H30 and H32 were assigned to idealized positions. The coordinates of H2, H4, H30 and H32 were refined freely. The BUMP instruction was used to avoid short intramolecular H-H contacts. The structure was refined using the TWIN keyword. The BASF parameter was refined to 12.6%. The four most disagreeable reflections were omitted.
Refinement details for 1a: The four most disagreeable reflections were omitted.

Crystal data for 1a: C_{25}H_{45}BCINPRh, \( M_r = 539.76 \), yellow block, 0.156x0.122x0.069 mm\(^3\), triclinic space group \( P \bar{1} \), \( a = 7.2623(5) \) Å, \( b = 8.3682(6) \) Å, \( c = 23.6179(17) \) Å, \( \alpha = 81.735(2)^\circ \), \( \beta = 87.228(2)^\circ \), \( \gamma = 72.334(2)^\circ \), \( V = 1353.41(17) \) Å\(^3\), \( Z = 2 \), \( \rho_{\text{calc}} = 1.324 \) g·cm\(^{-3}\), \( \mu = 0.801 \) mm\(^{-1}\), \( F(000) = 568 \), \( T = 100(2) \) K, \( R_I = 0.0494 \), \( wR^2 = 0.0733 \), 5548 independent reflections \([20 \leq 52.794^\circ]\) and 284 parameters.

Crystal data for 1c: C_{34}H_{51}BCIFeNPRh, \( M_r = 709.74 \), orange block, 0.37x0.314x0.295 mm\(^3\), monoclinic space group \( P2_1/c \), \( a = 18.500(3) \) Å, \( b = 10.9446(14) \) Å, \( c = 16.701(5) \) Å, \( \beta = 99.868(18)^\circ \), \( V = 3331.5(13) \) Å\(^3\), \( Z = 4 \), \( \rho_{\text{calc}} = 1.415 \) g·cm\(^{-3}\), \( \mu = 1.083 \) mm\(^{-1}\), \( F(000) = 1480 \), \( T = 100(2) \) K, \( R_I = 0.0189 \), \( wR^2 = 0.0443 \), 6810 independent reflections \([20 \leq 52.744^\circ]\) and 373 parameters.

Crystal data for 1d: C_{26}H_{47}BCINPRh, \( M_r = 553.78 \), orange block, 0.237x0.162x0.053 mm\(^3\), monoclinic space group \( P2_1/n \), \( a = 8.4198(13) \) Å, \( b = 22.107(5) \) Å, \( c = 15.400(3) \) Å, \( \beta = 100.678(15)^\circ \), \( V = 2816.8(9) \) Å\(^3\), \( Z = 4 \), \( \rho_{\text{calc}} = 1.306 \) g·cm\(^{-3}\), \( \mu = 0.771 \) mm\(^{-1}\), \( F(000) = 1168 \), \( T = 100(2) \) K, \( R_I = 0.0361 \), \( wR^2 = 0.0550 \), 5761 independent reflections \([20 \leq 52.744^\circ]\) and 294 parameters.

Crystal data for 1e: C_{28}H_{51}BCINPRh, \( M_r = 581.83 \), orange block, 0.37x0.283x0.234 mm\(^3\), monoclinic space group \( P2_1 \), \( a = 13.155(4) \) Å, \( b = 13.567(4) \) Å, \( c = 17.300(5) \) Å, \( \beta = 95.737(13)^\circ \), \( V = 3072.0(15) \) Å\(^3\), \( Z = 4 \), \( \rho_{\text{calc}} = 1.258 \) g·cm\(^{-3}\), \( \mu = 0.711 \) mm\(^{-1}\), \( F(000) = 1232 \), \( T = 100(2) \) K, \( R_I = 0.0189 \), \( wR^2 = 0.0477 \), 12580 independent reflections \([20 \leq 52.744^\circ]\) and 624 parameters.

Crystal data for 1f: C_{28}H_{47}BCINPRh, \( M_r = 577.80 \), orange block, 0.299x0.246x0.224 mm\(^3\), monoclinic space group \( P2_1/n \), \( a = 17.729(7) \) Å, \( b = 9.767(4) \) Å, \( c = 19.228(8) \) Å, \( \beta = 115.848(10)^\circ \), \( V = 2996(2) \) Å\(^3\), \( Z = 4 \), \( \rho_{\text{calc}} = 1.281 \) g·cm\(^{-3}\), \( \mu = 0.728 \) mm\(^{-1}\), \( F(000) = 1216 \), \( T = 100(2) \) K, \( R_I = 0.0264 \), \( wR^2 = 0.0588 \), 6125 independent reflections \([20 \leq 52.746^\circ]\) and 312 parameters.

Crystal data for 1g: C_{36}H_{58}B_{2}ClNO_{2}PRh, \( M_r = 727.78 \), orange block, 0.303x0.284x0.172 mm\(^3\), monoclinic space group \( P2_1/n \), \( a = 11.385(5) \) Å, \( b = 27.454(4) \) Å, \( c = 12.146(2) \) Å,
\( \beta = 95.31(3) ^\circ \), \( V = 3779.9(19) \, \text{Å}^3 \), \( Z = 4 \), \( \rho_{\text{calc}} = 1.279 \, \text{g} \cdot \text{cm}^{-3} \), \( \mu = 0.595 \, \text{mm}^{-1} \), \( F(000) = 1536 \), \( T = 100(2) \, \text{K} \), \( R_I = 0.0423 \), \( wR^2 = 0.0830 \), 7727 independent reflections \([20 \leq 52.742 ^\circ]\) and 493 parameters.

Crystal data for \( \text{Ih} \): \( \text{C}_{27}\text{H}_{52}\text{BCl}_2\text{N}_2\text{PRh} \), \( M_I = 644.89 \), orange block, 0.286×0.194×0.158 mm\(^3\), monoclinic space group \( P2_1/cn \), \( a = 8.3899(14) \, \text{Å} \), \( b = 20.844(4) \, \text{Å} \), \( c = 19.120(3) \, \text{Å} \), \( \beta = 93.632(11) ^\circ \), \( V = 3336.9(10) \, \text{Å}^3 \), \( Z = 4 \), \( \rho_{\text{calc}} = 1.284 \, \text{g} \cdot \text{cm}^{-3} \), \( \mu = 0.662 \, \text{mm}^{-1} \), \( F(000) = 1360 \), \( T = 100(2) \, \text{K} \), \( R_I = 0.0277 \), \( wR^2 = 0.0609 \), 6821 independent reflections \([20 \leq 52.742 ^\circ]\) and 357 parameters.

Crystal data for \( \text{Ii} \): \( \text{C}_{31}\text{H}_{46}\text{BClF}_3\text{NPRh} \), \( M_I = 669.83 \), orange block, 0.329×0.179×0.143 mm\(^3\), monoclinic space group \( P2_1/c \), \( a = 14.758(4) \, \text{Å} \), \( b = 11.7829(18) \, \text{Å} \), \( c = 19.206(7) \, \text{Å} \), \( \beta = 107.324(9) ^\circ \), \( V = 3188.3(16) \, \text{Å}^3 \), \( Z = 4 \), \( \rho_{\text{calc}} = 1.395 \, \text{g} \cdot \text{cm}^{-3} \), \( \mu = 0.708 \, \text{mm}^{-1} \), \( F(000) = 1392 \), \( T = 100(2) \, \text{K} \), \( R_I = 0.0226 \), \( wR^2 = 0.0481 \), 6509 independent reflections \([20 \leq 52.738 ^\circ]\) and 364 parameters.

Crystal data for \( \text{Ij} \): \( \text{C}_{39}\text{H}_{55}\text{BClF}_3\text{N}_2\text{PRh} \), \( M_I = 788.99 \), orange block, 0.268×0.259×0.102 mm\(^3\), monoclinic space group \( P2_1/c \), \( a = 16.099(7) \, \text{Å} \), \( b = 12.139(3) \, \text{Å} \), \( c = 20.044(6) \, \text{Å} \), \( \beta = 96.049(12) ^\circ \), \( V = 3895(2) \, \text{Å}^3 \), \( Z = 4 \), \( \rho_{\text{calc}} = 1.345 \, \text{g} \cdot \text{cm}^{-3} \), \( \mu = 0.592 \, \text{mm}^{-1} \), \( F(000) = 1648 \), \( T = 103(2) \, \text{K} \), \( R_I = 0.0341 \), \( wR^2 = 0.0636 \), 7955 independent reflections \([20 \leq 52.744 ^\circ]\) and 447 parameters.

Crystal data for \( \text{Ik} \): \( \text{C}_{43}\text{H}_{69}\text{B}_2\text{ClN}_2\text{PRh} \), \( M_I = 804.95 \), orange block, 0.29×0.285×0.256 mm\(^3\), triclinic space group \( P \overline{1} \), \( a = 9.269(3) \, \text{Å} \), \( b = 12.103(3) \, \text{Å} \), \( c = 20.168(7) \, \text{Å} \), \( \alpha = 106.938(10) ^\circ \), \( \beta = 91.473(14) ^\circ \), \( \gamma = 96.900(13) ^\circ \), \( V = 2144.3(11) \, \text{Å}^3 \), \( Z = 2 \), \( \rho_{\text{calc}} = 1.247 \, \text{g} \cdot \text{cm}^{-3} \), \( \mu = 0.529 \, \text{mm}^{-1} \), \( F(000) = 856 \), \( T = 101(2) \, \text{K} \), \( R_I = 0.0236 \), \( wR^2 = 0.0561 \), 8743 independent reflections \([20 \leq 52.744 ^\circ]\) and 471 parameters.

Crystal data for \( \text{Il} \): \( \text{C}_{39}\text{H}_{56}\text{BClNPRh} \), \( M_I = 718.98 \), orange block, 0.14×0.102×0.041 mm\(^3\), monoclinic space group \( P2_1/c \), \( a = 18.735(7) \, \text{Å} \), \( b = 25.249(11) \, \text{Å} \), \( c = 8.208(4) \, \text{Å} \), \( \beta = 102.644(12) ^\circ \), \( V = 3788(3) \, \text{Å}^3 \), \( Z = 4 \), \( \rho_{\text{calc}} = 1.261 \, \text{g} \cdot \text{cm}^{-3} \), \( \mu = 0.590 \, \text{mm}^{-1} \), \( F(000) = 1516 \), \( T = 100(2) \, \text{K} \), \( R_I = 0.0423 \), \( wR^2 = 0.0659 \), 7762 independent reflections \([20 \leq 52.746 ^\circ]\) and 409 parameters.
Crystal data for 2a: C_{22}H_{12}BClNP_{2}Rh, M_{r} = 531.67, yellow block, 0.426×0.28×0.182 mm³, orthorhombic space group Pbcn, a = 10.096(3) Å, b = 18.272(9) Å, c = 28.341(2) Å, V = 5228(3) Å³, Z = 8, \(\rho_{\text{calc}} = 1.351 \text{ g·cm}^{-3}\), \(\mu = 0.886 \text{ mm}^{-1}\), \(F(000) = 2224\), \(T = 100(2)\) K, \(R_{I} = 0.0250\), \(wR^{2} = 0.0578\), 5152 independent reflections [20≤52.04°] and 266 parameters.

Crystal data for 2b: C_{27}H_{24}BClNP_{2}Rh, M_{r} = 593.74, yellow block, 0.25×0.243×0.216 mm³, monoclinic space group P2_{1}/n, a = 9.117(3) Å, b = 18.699(4) Å, c = 17.128(6) Å, \(\beta = 92.047(16)^{\circ}\), V = 2918.0(15) Å³, Z = 4, \(\rho_{\text{calc}} = 1.352 \text{ g·cm}^{-3}\), \(\mu = 0.802 \text{ mm}^{-1}\), \(F(000) = 1240\), \(T = 101(2)\) K, \(R_{I} = 0.0222\), \(wR^{2} = 0.0479\), 5966 independent reflections [20≤52.744°] and 310 parameters.

Crystal data for 2c: C_{31}H_{48}BClFeNP_{2}Rh, M_{r} = 701.66, yellow needle, 0.417×0.164×0.088 mm³, monoclinic space group P2_{1}/n, a = 11.621(3) Å, b = 38.859(7) Å, c = 14.802(4) Å, \(\beta = 99.837(7)^{\circ}\), V = 6586(3) Å³, Z = 8, \(\rho_{\text{calc}} = 1.415 \text{ g·cm}^{-3}\), \(\mu = 1.141 \text{ mm}^{-1}\), \(F(000) = 2912\), \(T = 100(2)\) K, \(R_{I} = 0.0307\), \(wR^{2} = 0.0497\), 13475 independent reflections [20≤52.744°] and 709 parameters.

Crystal data for 2d: C_{23}H_{44}BClNP_{2}Rh, M_{r} = 545.70, yellow block, 0.415×0.30×0.272 mm³, monoclinic space group P2_{1}/c, a = 13.118(5) Å, b = 14.618(8) Å, c = 28.215(10) Å, \(\beta = 92.720(16)^{\circ}\), V = 5404(4) Å³, Z = 8, \(\rho_{\text{calc}} = 1.341 \text{ g·cm}^{-3}\), \(\mu = 0.859 \text{ mm}^{-1}\), \(F(000) = 2288\), \(T = 100(2)\) K, \(R_{I} = 0.0237\), \(wR^{2} = 0.0575\), 10634 independent reflections [20≤52.044°] and 591 parameters.

Crystal data for 2e: C_{25}H_{48}BClNP_{2}Rh, M_{r} = 573.75, yellow block, 0.265×0.216×0.121 mm³, triclinic space group P 1̅, a = 9.9075(19) Å, b = 10.1161(14) Å, c = 14.978(4) Å, \(\alpha = 84.197(7)^{\circ}\), \(\beta = 79.842(10)^{\circ}\), \(\gamma = 77.786(7)^{\circ}\), V = 1441.0(5) Å³, Z = 2, \(\rho_{\text{calc}} = 1.322 \text{ g·cm}^{-3}\), \(\mu = 0.809 \text{ mm}^{-1}\), \(F(000) = 604\), \(T = 100(2)\) K, \(R_{I} = 0.0192\), \(wR^{2} = 0.0479\), 5907 independent reflections [20≤52.744°] and 294 parameters.

Crystal data for 2f: C_{90}H_{147}B_{3}Cl_{3}N_{3}P_{6}Rh_{3}, M_{r} = 1904.43, yellow block, 0.321×0.242×0.228 mm³, triclinic space group P 1̅, a = 12.921(2) Å, b = 20.038(5) Å, c = 21.929(4) Å, \(\alpha = 107.641(11)^{\circ}\), \(\beta = 104.548(13)^{\circ}\), \(\gamma = 103.913(12)^{\circ}\), V = 4919.3(17) Å³.
Crystal data for 2g: C$_{33}$H$_{55}$B$_2$ClNO$_3$P$_2$Rh, $M_r = 719.70$, yellow block, 0.226×0.22×0.18 mm$^3$, monoclinic space group $P2_1/c$, $a = 9.831(6)$ Å, $b = 19.140(9)$ Å, $c = 19.599(10)$ Å, $\beta = 101.13(3)^\circ$, $V = 3618(3)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.321$ g·cm$^{-3}$, $\mu = 0.663$ mm$^{-1}$, $F(000) = 1512$, $T = 100(2)$ K, $R_I = 0.0346$, $wR^2 = 0.0753$, 20119 independent reflections [20≤52.744$^\circ$] and 1054 parameters.

Crystal data for 2l: C$_{30}$H$_{47}$BCIN$_3$P$_2$Rh, $M_r = 632.79$, yellow block, 0.266×0.258×0.098 mm$^3$, monoclinic space group $C2/l$, $a = 22.645(8)$ Å, $b = 18.484(6)$ Å, $c = 17.744(3)$ Å, $\beta = 122.497(8)^\circ$, $V = 6264(3)$ Å$^3$, $Z = 8$, $\rho_{calc} = 1.342$ g·cm$^{-3}$, $\mu = 0.752$ mm$^{-1}$, $F(000) = 2648$, $T = 101(2)$ K, $R_I = 0.0295$, $wR^2 = 0.0574$, 6403 independent reflections [20≤52.744$^\circ$] and 338 parameters.

Crystal data for 3a$^{Me}$: C$_{30}$H$_{52}$BN$_3$PRh, $M_r = 599.43$, orange block, 0.315×0.244×0.174 mm$^3$, monoclinic space group $P2_1/n$, $a = 12.009(6)$ Å, $b = 18.218(8)$ Å, $c = 14.765(13)$ Å, $\beta = 107.74(2)^\circ$, $V = 3077(3)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.294$ g·cm$^{-3}$, $\mu = 0.630$ mm$^{-1}$, $F(000) = 1272$, $T = 100(2)$ K, $R_I = 0.0676$, $wR^2 = 0.0922$, 6284 independent reflections [20≤52.744$^\circ$] and 339 parameters.

Crystal data for 3a$^{Pr}$: C$_{34}$H$_{60}$BN$_3$PRh, $M_r = 655.54$, orange block, 0.20×0.155×0.09 mm$^3$, orthorhombic space group $P2_12_12_1$, $a = 11.529(4)$ Å, $b = 16.437(5)$ Å, $c = 18.831(5)$ Å, $V = 3568.4(18)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.220$ g·cm$^{-3}$, $\mu = 0.549$ mm$^{-1}$, $F(000) = 1400$, $T = 100(2)$ K, $R_I = 0.0305$, $wR^2 = 0.0708$, 7016 independent reflections [20≤52.042$^\circ$] and 377 parameters.

Crystal data for 3e$^{Me}$: C$_{36}$H$_{65}$BN$_3$PRh, $M_r = 684.60$, yellow plate, 0.212×0.13×0.034 mm$^3$, monoclinic space group $P2_1/c$, $a = 11.713(2)$ Å, $b = 16.0270(19)$ Å, $c = 20.498(4)$ Å, $\beta = 106.075(7)^\circ$, $V = 3697.5(11)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.230$ g·cm$^{-3}$, $\mu = 0.532$ mm$^{-1}$, $F(000) = 1468$, $T = 100(2)$ K, $R_I = 0.0366$, $wR^2 = 0.0692$, 7569 independent reflections [20≤52.744$^\circ$] and 396 parameters.

Crystal data for 4a$^{Pr}$: C$_{36}$H$_{65}$BN$_3$Rh, $M_r = 647.55$, yellow needle, 0.266×0.119×0.056 mm$^3$, monoclinic space group $P2_1/n$, $a = 11.060(3)$ Å, $b = 18.039(3)$ Å, $c = 17.701(2)$ Å,
\[ \beta = 94.498(12)^\circ, \quad V = 3520.7(13) \, \text{Å}^3, \quad Z = 4, \quad \rho_{\text{calc}} = 1.222 \, \text{g} \cdot \text{cm}^{-3}, \quad \mu = 0.514 \, \text{mm}^{-1}, \]
\[ F(000) = 1376, \quad T = 100(2) \, \text{K}, \quad R_I = 0.0292, \quad wR^2 = 0.0577, \quad 7203 \text{ independent reflections} \quad [20 \leq 52.744^\circ] \text{ and 384 parameters.} \]

Crystal data for 4\(\text{e}^{\text{Pr}}\): \(\text{C}_{37}\text{H}_{61}\text{BN}_3\text{Rh}, \quad M_t = 689.62, \quad \text{orange block, 0.31} \times 0.257 \times 0.11 \, \text{mm}^3, \quad \text{monoclinic space group} \quad P2_1/n, \quad a = 11.969(2) \, \text{Å}, \quad b = 19.828(4) \, \text{Å}, \quad c = 15.990(3) \, \text{Å}, \quad \beta = 91.168(6)^\circ, \quad V = 3793.9(12) \, \text{Å}^3, \quad Z = 4, \quad \rho_{\text{calc}} = 1.207 \, \text{g} \cdot \text{cm}^{-3}, \quad \mu = 0.481 \, \text{mm}^{-1}, \]
\[ F(000) = 1472, \quad T = 100(2) \, \text{K}, \quad R_I = 0.0237, \quad wR^2 = 0.0517, \quad 7745 \text{ independent reflections} \quad [20 \leq 52.744^\circ] \text{ and 453 parameters.} \]

Crystal data for 5: \(\text{C}_{28}\text{H}_{51}\text{BCINPRh}, \quad M_t = 581.83, \quad \text{yellow needles, 0.417} \times 0.279 \times 0.156 \, \text{mm}^3, \quad \text{monoclinic space group} \quad P2_1/n, \quad a = 11.254(4) \, \text{Å}, \quad b = 9.024(2) \, \text{Å}, \quad c = 29.373(8) \, \text{Å}, \quad \beta = 98.317(13)^\circ, \quad V = 2951.7(14) \, \text{Å}^3, \quad Z = 4, \quad \rho_{\text{calc}} = 1.309 \, \text{g} \cdot \text{cm}^{-3}, \quad \mu = 0.740 \, \text{mm}^{-1}, \]
\[ F(000) = 1232, \quad T = 100(2) \, \text{K}, \quad R_I = 0.0553, \quad wR^2 = 0.0688, \quad 5800 \text{ independent reflections} \quad [20 \leq 52.04^\circ] \text{ and 315 parameters.} \]

Crystal data for 6: \(\text{C}_{28}\text{H}_{51}\text{BCINPRh}, \quad M_t = 581.83, \quad \text{orange needle, 0.512} \times 0.077 \times 0.057 \, \text{mm}^3, \quad \text{monoclinic space group} \quad P2_1/c, \quad a = 14.740(3) \, \text{Å}, \quad b = 15.319(4) \, \text{Å}, \quad c = 14.833(3) \, \text{Å}, \quad \beta = 116.828(9)^\circ, \quad V = 2988.9(12) \, \text{Å}^3, \quad Z = 4, \quad \rho_{\text{calc}} = 1.293 \, \text{g} \cdot \text{cm}^{-3}, \quad \mu = 0.730 \, \text{mm}^{-1}, \]
\[ F(000) = 1232, \quad T = 100(2) \, \text{K}, \quad R_I = 0.0438, \quad wR^2 = 0.0981, \quad 6124 \text{ independent reflections} \quad [20 \leq 52.74^\circ] \text{ and 321 parameters.} \]

Crystal data for 7: \(\text{C}_{28}\text{H}_{51}\text{BCINPRh}, \quad M_t = 581.83, \quad \text{orange block, 0.121} \times 0.093 \times 0.069 \, \text{mm}^3, \quad \text{orthorhombic space group} \quad Pca2_1, \quad a = 21.577(5) \, \text{Å}, \quad b = 8.0109(19) \, \text{Å}, \quad c = 34.845(8) \, \text{Å}, \quad V = 6023(2) \, \text{Å}^3, \quad Z = 8, \quad \rho_{\text{calc}} = 1.283 \, \text{g} \cdot \text{cm}^{-3}, \quad \mu = 0.725 \, \text{mm}^{-1}, \quad F(000) = 2464, \quad T = 100(2) \, \text{K}, \quad R_I = 0.0695, \quad wR^2 = 0.1221, \quad 13278 \text{ independent reflections} \quad [20 \leq 54.206^\circ] \text{ and 634 parameters.} \]

Crystal data for \(\text{I}(\text{Ia})\): \(\text{C}_{21}\text{H}_{28}\text{BN}, \quad M_t = 305.25, \quad \text{colourless plate, 0.412} \times 0.224 \times 0.106 \, \text{mm}^3, \quad \text{monoclinic space group} \quad P2_1/c, \quad a = 16.329(5) \, \text{Å}, \quad b = 9.070(3) \, \text{Å}, \quad c = 13.365(3) \, \text{Å}, \quad \beta = 110.285(5)^\circ, \quad V = 1856.8(8) \, \text{Å}^3, \quad Z = 4, \quad \rho_{\text{calc}} = 1.092 \, \text{g} \cdot \text{cm}^{-3}, \quad \mu = 0.061 \, \text{mm}^{-1}, \]
\[ F(000) = 664, \quad T = 100(2) \, \text{K}, \quad R_I = 0.0497, \quad wR^2 = 0.1248, \quad 3811 \text{ independent reflections} \quad [20 \leq 52.744^\circ] \text{ and 216 parameters.} \]
Crystal data for I(Ib): C$_{21}$H$_{28}$BN, $M_r = 305.25$, colourless plate, 0.291×0.157×0.108 mm$^3$, orthorhombic space group $Pca2_1$, $a = 12.670(8)$ Å, $b = 11.135(6)$ Å, $c = 13.004(8)$ Å, $V = 1834.6(18)$ Å$^3$, $Z = 4$, $\rho_{calc} = 1.105$ g·cm$^{-3}$, $\mu = 0.062$ mm$^{-1}$, $F(000) = 664$, $T = 100(2)$ K, $R_I = 0.0484$, $wR^2 = 0.0961$, 3484 independent reflections [$2\theta \leq 52.724^\circ$] and 216 parameters.

Figure S135. Crystallographically-derived molecular structures of complexes 1a (top left), 1c (top right), 1d (bottom left) and 1e (bottom right) with atomic displacement ellipsoids at the 50% probability level. Some ellipsoids and all hydrogen atoms are omitted for clarity.
Figure S136. Crystallographically-derived molecular structures of complexes 1f (top left), 1g (top right), 1h (bottom left) and 1i (bottom right) with atomic displacement ellipsoids at the 50% probability level. Some ellipsoids and all hydrogen atoms are omitted for clarity.

Figure S137. Crystallographically-derived molecular structures of complexes 1j (left), 1k (right) and 1l (below) with atomic displacement ellipsoids at the 50% probability level. Co-crystallised solvent molecules, some ellipsoids and all hydrogen atoms are omitted for clarity.
Figure S138. Crystallographically-derived molecular structures of complexes 2b (left), 2c (below) and 2d (right) with atomic displacement ellipsoids at the 50% probability level. Some ellipsoids and all hydrogen atoms are omitted for clarity.

Figure S139. Crystallographically-derived molecular structures of complexes 2e (left), 2f (right) and 2g (below) with atomic displacement ellipsoids at the 50% probability level. Co-crystallised solvent molecules, some ellipsoids and all hydrogen atoms are omitted for clarity.
Figure S140. Crystallographically-derived molecular structures of complexes 3\textsuperscript{aPr} (left) and 4\textsuperscript{ePr} (right) with atomic displacement ellipsoids at the 50% probability level. Some ellipsoids and most hydrogen atoms are omitted for clarity.

Figure S141. Crystallographically-derived molecular structures of complex 3\textsuperscript{eMe} with atomic displacement ellipsoids at the 50% probability level. Co-crystallised solvent molecules, some ellipsoids and most hydrogen atoms are omitted for clarity.
Figure S142. Crystallographically-derived molecular structure of compound I(a) with atomic displacement ellipsoids at the 50% probability level. Some ellipsoids and all hydrogen atoms are omitted for clarity.
Computational details

All calculations were performed with the Orca 4.1.1 software. The structures were optimized with the PBE0 functional. The def2-TZVP basis set and its corresponding effective core potential (def2-ECP) were used for Rh, while def2-SVP was applied to all other atoms. Dispersion corrections were taking into account in the geometry optimizations by using Grimme’s D3 model together with the Becke-Johnson (BJ) damping function. In order to speed up the calculations, we included the resolution of the identity approximation for Coulomb integrals (RI-J) and the chain of spheres numerical integration for Hartree-Fock exchange, COSX. Hessian calculations were then performed for all optimized structures at the same level of theory. All geometries were characterized as minimum energy structures as all of their vibrational frequencies are real. Additionally, single-point calculations were performed at the PBE0-D3(BJ)/def2-QZVPP and TPSSH-D3(BJ)/def2-QZVPP levels. Solvation effects were taken into account using the Solvation Model for Density (SMD) with benzene (ε = 2.28) as solvent. A concentration correction of ΔG°→* = RTln(24.46) = 1.89 kcal mol⁻¹ (T = 298.15 K) was included in the free energies of all species in order to account for the change in standard states in going from gas phase (1 atm) to the condensed phase (1 M) and to properly describe associative/dissociative steps. Images of the 3D structures were obtained with CYLview.

By collecting the Gibbs free energies of all structures in which calculations were performed, we were able to construct a free energy map involving the Rh₃[PPr₃]₄-azaborole complex 1a, the respective azaborole complex 2a featuring two PMe₃ ligands, and a variety of related species featuring distinct numbers (and types) of coordinating phosphines. We expect that, in solution, a complex equilibrium involving at least some of these species will be present, and a full description of the reaction from 1a to 2a should take into account all possible connections within the derived reaction network. We approached this problem by initially identifying in the map the thermodynamically preferred pathway, in which high-energy intermediates are avoided. We then performed calculations for identifying transition states (TS) along the thermodynamically preferred pathway. These were characterized by having one imaginary frequency mode in the Hessian calculation. In order to verify the connectivity of the TS, we performed additional geometry optimizations along the imaginary mode and intrinsic reaction coordinate (IRC) calculations.

All species in the map are related to the complexes where R¹ and R² are Me and H, respectively. The structures were labelled as 1, representing the azaborole, or 2, related to the corresponding azaborole complexes. These can be followed by the letters A, B, or the combinations AB or B₂. A stands for PPr₃, while B represents PMe₃. Therefore, while 1 is the Rh₃[π⁴-azaborole chloride complex without any coordinating phosphine, 2AB is the azaborole system in which the Rh features two coordinating phosphines: one PPr₃ and one PMe₃. All molecular structures involved in the construction of the free energy map are shown in Figures S139 and S140. A flowchart depicting the reaction network is shown in Figure S141, and a mechanistic proposal for the transformation of 1A into 2B₂ is given in Figure S142. Free energy values are given in kcal mol⁻¹ as relative to that of the reactant, 1A.
Figure S143. Images of the molecular structures of all species of type 1 taken into account in the free energy map. Geometries were optimized at the PBE0-D3(BJ)/def2-SVP,def2-TZVP(Rh) level of theory. The number in parenthesis are the respective free energies obtained at the PBE0-D3(BJ)/def2-QZVPP+SMD(Benzene) level.
Figure S144. Images of the molecular structures of all species of type 2 taken into account in the free energy map. Geometries were optimized at the PBE0-D3(BJ)/def2-SVP,def2-TZVP(Rh) level of theory. The number in parenthesis are the respective free energies obtained at the PBE0-D3(BJ)/def2-QZVPP+SMD(Benzene) level.
**Figure S145.** Free energy map illustrating distinct pathways connecting 1A and 2B₂. Each circle represents an intermediate, whose free energy (kcal mol⁻¹) is also shown. Green circles are low-energy intermediates whose energies are at most 10 kcal mol⁻¹ higher than that of 1A. Yellow circles represent intermediates with moderate free energies. Red circles indicate high-energy intermediates. The black lines highlight the thermodynamically preferred pathway connecting 1A and 2B₂. All energies are at the PBE0-D3(BJ)/def2-QZVPP+SMD level of theory.
Figure S146. Relative Gibbs free energy profile (T = 298.15 K) of a proposed mechanistic pathway connecting 1A and 2B₂ at the PBE0-D3(BJ)/def2-QZVPP+SMD (black curve) and TPSSh-D3(BJ)/def2-QZVPP+SMD (red curve) levels of theory.
**Cartesian coordinates**

**PMe₃**

E(PBE0-D3(BJ)/def2-QZVPP+SMD): -460.900770 Eₜₜ
E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -461.217266 Eₜₜ

ΔΔG(298): 0.086349 Eₜₜ

Lowest frequency: 187.58 cm⁻¹

|   |   |   |   |
|---|---|---|---|
| P | 1.563305000 | 12.888692000 | 9.181026000 |
| C | 2.688000000 | 13.377363000 | 7.794656000 |
| H | 3.245086000 | 12.496434000 | 7.440349000 |
| H | 3.422815000 | 14.111218000 | 8.158511000 |
| H | 2.137841000 | 13.814817000 | 6.944224000 |
| C | 0.380781000 | 11.819362000 | 8.244674000 |
| H | -0.003795000 | 12.307638000 | 7.333585000 |
| H | -0.469862000 | 11.559535000 | 8.892869000 |
| H | 0.879571000 | 10.880242000 | 7.959920000 |
| C | 0.552072000 | 14.435594000 | 9.283805000 |
| H | 0.180827000 | 14.759198000 | 8.296725000 |
| H | 1.162190000 | 15.243230000 | 9.715828000 |
| H | -0.308894000 | 14.273038000 | 9.949322000 |

**PiPr₃**

E(PBE0-D3(BJ)/def2-QZVPP+SMD): -696.594465 Eₜₜ
E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -697.229504 Eₜₜ

ΔΔG(298.15): 0.248698 Eₜₜ

Lowest frequency: 53.55 cm⁻¹

|   |   |   |   |
|---|---|---|---|
| P | 6.142848000 | 3.328984000 | 3.225734000 |
| C | 4.449714000 | 2.497452000 | 3.153518000 |
| H | 3.832087000 | 3.218522000 | 3.719467000 |
| C | 4.462397000 | 1.202240000 | 3.962107000 |
H  3.434217000  0.852916000  4.152231000
H  4.961491000  1.327964000  4.935355000
H  4.980340000  0.398947000  3.415535000
C  3.783276000  2.288859000  1.797609000
H  2.768719000  1.877037000  1.936328000
H  4.337109000  1.577035000  1.172176000
H  3.677250000  3.224454000  1.230179000
C  7.380921000  2.131272000  2.483681000
H  8.214487000  2.820064000  2.260361000
C  7.901335000  1.166973000  3.546394000
H  8.780244000  0.618007000  3.170089000
H  7.146821000  0.419868000  3.830853000
H  8.196198000  1.704434000  4.460263000
C  7.017263000  1.413897000  1.189777000
H  7.902498000  0.907815000  0.768747000
H  6.633801000  2.104633000  0.424546000
H  6.255545000  0.637328000  1.357506000
C  5.998106000  4.630541000  1.880661000
H  5.626148000  4.161729000  0.952847000
C  7.349639000  5.277810000  1.589228000
H  7.222215000  6.133596000  0.906471000
H  8.057944000  4.585928000  1.111386000
H  7.815044000  5.659678000  2.513094000
C  4.995448000  5.687524000  2.337315000
H  4.862518000  6.460544000  1.562794000
H  5.351534000  6.186164000  3.253205000
H  4.003057000  5.264452000  2.556939000
E(PBE0-D3(BJ)/def2-QZVPP+SMD): -1274.000389 E\(_h\)
E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -1275.083890 E\(_h\)
\(\Delta\Delta G(298.15): 0.321545 E\(_h\)\)

Lowest frequency: 27.48 cm\(^{-1}\)

| C     | 5.478500000 | 5.240764000 | 6.342528000 |
|-------|-------------|-------------|-------------|
| N     | 6.480362000 | 5.048011000 | 7.341453000 |
| B     | 6.199537000 | 3.536955000 | 7.339958000 |
| Cl    | 7.482134000 | 3.545393000 | 3.414921000 |
| C     | 4.793646000 | 6.481405000 | 5.905865000 |
| H     | 4.293859000 | 6.281982000 | 4.947784000 |
| H     | 5.488893000 | 7.318378000 | 5.764902000 |
| H     | 4.022121000 | 6.781678000 | 6.633187000 |
| C     | 5.158231000 | 3.835211000 | 6.227324000 |
| H     | 4.404421000 | 3.361647000 | 5.599741000 |
| Rh    | 7.024296000 | 4.313377000 | 5.484507000 |
| C     | 6.249940000 | 6.804096000 | 9.015617000 |
| H     | 6.802013000 | 7.478007000 | 9.687564000 |
| H     | 5.642776000 | 6.124438000 | 9.632483000 |
| H     | 5.572335000 | 7.418818000 | 8.405307000 |
| C     | 8.184045000 | 5.222049000 | 9.044829000 |
| H     | 8.788308000 | 5.912241000 | 9.652625000 |
| H     | 8.866065000 | 4.604706000 | 8.441996000 |
| H     | 7.628963000 | 4.552156000 | 9.715626000 |
| C     | 7.235935000 | 6.016146000 | 8.151675000 |
| C     | 5.831281000 | 2.196382000 | 9.471060000 |
| C     | 6.649764000 | 2.423862000 | 8.343443000 |
| C     | 8.047283000 | 6.954952000 | 7.257741000 |
| H     | 8.625387000 | 7.653601000 | 7.881583000 |
| H     | 7.413216000 | 7.549100000 | 6.585456000 |
| H     | 8.755910000 | 6.384206000 | 6.637725000 |
C 6.210548000 1.255476000 10.433656000
H 5.562436000 1.088483000 11.299791000
C 7.397474000 0.531101000 10.319011000
C 8.185057000 0.741711000 9.183552000
H 9.106072000 0.163235000 9.063360000
C 7.832461000 1.665562000 8.196671000
C 8.718143000 1.817036000 6.992046000
H 9.590581000 1.151653000 7.052242000
H 9.099768000 2.846707000 6.884952000
H 8.174793000 1.585690000 6.062576000
C 4.569929000 2.988114000 9.682612000
H 3.832926000 2.420400000 10.268849000
H 4.103807000 3.278923000 8.729575000
H 4.775816000 3.918472000 10.239555000
C 7.837817000 -0.417100000 11.396587000
H 8.462750000 -1.227557000 10.993965000
H 6.981114000 -0.869400000 11.917590000
H 8.438281000 0.112232000 12.156128000

**1A**

E(PBE0-D3(BJ)/def2-QZVPP+SMD): -1970.677980 E_h

E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -1972.397863 E_h

Δ∆G(298.15): 0.594676

Lowest frequency: 22.47 cm⁻¹

C 5.690609000 5.550545000 6.280383000
P 6.217524000 3.266574000 3.305181000
N 6.763977000 5.159363000 7.142135000
B 6.117815000 3.769879000 7.242689000
Cl 9.136006000 4.564104000 4.517720000
C 5.289875000 6.918523000 5.863551000
| Atom | X          | Y          | Z          |
|------|------------|------------|------------|
| H    | 4.448915000 | 6.845752000 | 5.160969000 |
| H    | 6.113445000 | 7.455981000 | 5.374406000 |
| H    | 4.956076000 | 7.509551000 | 6.732627000 |
| C    | 5.033171000 | 4.279869000 | 6.271192000 |
| H    | 4.078209000 | 4.016527000 | 5.822799000 |
| Rh   | 6.900498000 | 4.294591000 | 5.228365000 |
| C    | 7.050690000 | 6.403165000 | 9.207528000 |
| H    | 7.747110000 | 6.999857000 | 9.815778000 |
| H    | 6.718180000 | 5.544621000 | 9.810346000 |
| H    | 6.174077000 | 7.029869000 | 8.980739000 |
| C    | 8.885995000 | 4.976119000 | 8.262159000 |
| H    | 9.624058000 | 5.492977000 | 8.893331000 |
| H    | 9.378421000 | 4.644570000 | 7.336376000 |
| H    | 8.518922000 | 4.096333000 | 8.808572000 |
| C    | 7.739128000 | 5.926369000 | 7.926263000 |
| C    | 5.401304000 | 2.476627000 | 9.310329000 |
| C    | 6.330329000 | 2.585306000 | 8.244205000 |
| C    | 8.286061000 | 7.106542000 | 7.125684000 |
| H    | 9.112312000 | 7.569615000 | 7.684913000 |
| H    | 7.528221000 | 7.883920000 | 6.957594000 |
| H    | 8.676688000 | 6.756718000 | 6.158179000 |
| C    | 5.524206000 | 1.444096000 | 10.237526000 |
| H    | 4.804081000 | 1.379215000 | 11.060124000 |
| C    | 6.539721000 | 0.485491000 | 10.142207000 |
| C    | 7.438763000 | 0.594257000 | 9.085286000 |
| H    | 8.240004000 | -0.145624000 | 8.986391000 |
| C    | 7.355769000 | 1.626812000 | 8.142058000 |
| C    | 8.383061000 | 1.674631000 | 7.048814000 |
| H    | 9.382167000 | 1.910743000 | 7.448197000 |
| H    | 8.148187000 | 2.446150000 | 6.299346000 |
| H    | 8.459702000 | 0.705686000 | 6.531381000 |
| Element | X-Coordinate | Y-Coordinate | Z-Coordinate |
|---------|--------------|--------------|--------------|
| C       | 4.273399000  | 3.462058000  | 9.452581000  |
| H       | 3.712273000  | 3.292505000  | 10.382540000 |
| H       | 3.568724000  | 3.384690000  | 8.609665000  |
| H       | 4.634001000  | 4.502294000  | 9.459625000  |
| C       | 6.644835000  | -0.620381000 | 11.151560000 |
| H       | 7.496551000  | -1.281412000 | 10.937745000 |
| H       | 5.732036000  | -1.238148000 | 11.164107000 |
| H       | 6.775026000  | 0.220018000  | 12.169754000 |
| C       | 4.948647000  | 1.941256000  | 3.626345000  |
| H       | 4.103831000  | 2.545058000  | 3.999912000  |
| C       | 5.351223000  | 1.005745000  | 4.762669000  |
| H       | 4.495436000  | 0.371184000  | 5.043243000  |
| H       | 5.665559000  | 1.564108000  | 5.655054000  |
| H       | 6.176175000  | 0.338984000  | 4.476741000  |
| C       | 4.484311000  | 1.178228000  | 2.392366000  |
| H       | 3.609781000  | 0.555566000  | 2.641468000  |
| H       | 5.268298000  | 0.500127000  | 2.023664000  |
| H       | 4.193525000  | 1.843110000  | 1.565157000  |
| C       | 7.617949000  | 2.582802000  | 2.282390000  |
| H       | 8.344014000  | 3.408565000  | 2.380574000  |
| C       | 8.259888000  | 1.375852000  | 2.957847000  |
| H       | 9.232031000  | 1.162924000  | 2.486642000  |
| H       | 7.640806000  | 0.470467000  | 2.859630000  |
| H       | 8.448903000  | 1.564113000  | 4.024181000  |
| C       | 7.353730000  | 2.335236000  | 0.802162000  |
| H       | 8.293941000  | 2.024383000  | 0.318320000  |
| H       | 7.007787000  | 3.235842000  | 0.274993000  |
| H       | 6.619045000  | 1.536082000  | 0.627986000  |
| C       | 5.367049000  | 4.444962000  | 2.139996000  |
| H       | 5.222535000  | 3.902809000  | 1.189913000  |
| C       | 6.277253000  | 5.644332000  | 1.894089000  |
H    5.825437000  6.320025000  1.149915000
H    7.272330000  5.353186000  1.528839000
H    6.430681000  6.208202000  2.827468000
C    4.001574000  4.883828000  2.652391000
H    3.579095000  5.652269000  1.985573000
H    4.082154000  5.322563000  3.658259000
H    3.280352000  4.054288000  2.697940000

1AB

E(PBE0-D3(BJ)/def2-QZVPP+SMD): -2431.592893 E$_h$
E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -2433.632648 E$_h$

$\Delta \Delta G(298.15)$: 0.707554 E$_h$

Lowest frequency: 14.03 cm$^{-1}$

C    5.731192000  5.660653000  6.654880000
P    5.624512000  3.417937000  3.569625000
N    6.921885000  5.180477000  7.285241000
B    6.296834000  3.764695000  7.263703000
Cl   7.405339000  6.820017000  4.186429000
C    5.239248000  7.053248000  6.510455000
H    4.322757000  7.036443000  5.905861000
H    5.972665000  7.698030000  6.009684000
H    4.984440000  7.466859000  7.499452000
C    5.088076000  4.418437000  6.538167000
H    4.082413000  4.239525000  6.175050000
Rh   6.825442000  4.503803000  5.209892000
C    6.931245000  6.110656000  9.531992000
H    7.513065000  6.681586000  10.271231000
H    6.661624000  5.142055000  9.978228000
H    6.005765000  6.669624000  9.330125000
C    8.967760000  5.050927000  8.591829000
|   |          |          |          |          |
|---|----------|----------|----------|----------|
| H | 9.579275000 | 5.561090000 | 9.349968000 |
| H | 9.586387000 | 4.888304000 | 7.703011000 |
| H | 8.659531000 | 4.078762000 | 8.997769000 |
| C | 7.755738000 | 5.908053000 | 8.254433000 |
| C | 5.374860000 | 2.323721000 | 9.178627000 |
| C | 6.437907000 | 2.549499000 | 8.262723000 |
| C | 8.213959000 | 7.257486000 | 7.698231000 |
| H | 9.020551000 | 7.659015000 | 8.328885000 |
| H | 7.401857000 | 7.996206000 | 7.692564000 |
| H | 8.573276000 | 7.158623000 | 6.664225000 |
| C | 5.409497000 | 1.224601000 | 10.038089000 |
| H | 4.574223000 | 1.071553000 | 10.729724000 |
| C | 6.462493000 | 0.306491000 | 10.028998000 |
| C | 7.518310000 | 0.546309000 | 9.152580000 |
| H | 8.366176000 | -0.146986000 | 9.131947000 |
| C | 7.522003000 | 1.645717000 | 8.286309000 |
| C | 8.701482000 | 1.830430000 | 7.380402000 |
| H | 9.549272000 | 2.290141000 | 7.914727000 |
| H | 8.432483000 | 2.490216000 | 6.543310000 |
| H | 9.055792000 | 0.866408000 | 6.984256000 |
| C | 4.172428000 | 3.225533000 | 9.252422000 |
| H | 3.561775000 | 2.990759000 | 10.136132000 |
| H | 3.532502000 | 3.107175000 | 8.364501000 |
| H | 4.455481000 | 4.287794000 | 9.299590000 |
| C | 6.421160000 | -0.921413000 | 10.890287000 |
| H | 7.427388000 | -1.246498000 | 11.193041000 |
| H | 5.957960000 | -1.760573000 | 10.343837000 |
| H | 5.825415000 | -0.756819000 | 11.800910000 |
| C | 4.132387000 | 2.476267000 | 4.222001000 |
| H | 3.522951000 | 3.300987000 | 4.619330000 |
| C | 4.451258000 | 1.532947000 | 5.379489000 |
H 3.54611500 1.35470100 5.98135700
H 5.22592500 1.92897600 6.04767700
H 4.79414600 0.55559700 5.01606700
C 3.28689900 1.76740500 3.17033100
H 2.35024800 1.41664200 3.63242800
H 3.79565200 0.87686100 2.77476900
H 3.01414300 2.41180400 2.32346500
C 6.48487200 2.19297100 2.43147100
H 7.44588500 2.69472100 2.24639800
C 6.77864200 0.88609400 3.16169900
H 7.54004800 0.30700400 2.61486900
H 5.87997100 0.25702400 3.22255100
H 7.14114700 1.05603500 4.18590000
C 5.86859700 1.91548500 1.05883500
H 6.59038600 1.33941700 0.45636000
H 5.63263400 2.82701700 0.49590900
H 4.95144800 1.31602300 1.12157400
C 4.83237700 4.62928500 2.38850200
H 4.14498900 4.03401000 1.76265600
C 5.84893500 5.33071100 1.49349900
H 5.31557900 5.98801000 0.78728400
H 6.46167800 4.63996900 0.89709400
H 6.51682100 5.95665800 2.10529400
C 4.02953100 5.66999100 3.16101900
H 3.50115600 6.33199900 2.45602900
H 4.71401600 6.28823200 3.76199800
H 3.27243700 5.22236600 3.82226600
P 8.94790600 4.03930300 4.24690900
C 9.68436300 2.36251100 4.02470600
H 9.10536400 1.78973000 3.29214800
H 9.69506100 1.80476300 4.96822500

128
|   |          |          |          |
|---|----------|----------|----------|
| H | 10.714965000 | 2.461090000 | 3.648788000 |
| C | 9.227264000  | 4.683036000 | 2.548556000 |
| H | 10.268760000 | 4.483510000 | 2.253476000 |
| H | 9.016732000  | 5.760241000 | 2.556163000 |
| H | 8.555884000  | 4.203126000 | 1.826546000 |
| C | 10.314798000 | 4.872396000 | 5.140130000 |
| H | 11.227887000 | 4.871445000 | 4.525723000 |
| H | 10.519966000 | 4.346013000 | 6.081027000 |
| H | 10.011934000 | 5.905499000 | 5.354562000 |

**1B**

\( E(\text{PBE0-D3(BJ)/def2-QZVPP+SMD}): -1734.977790 \text{ E}_h \)

\( E(\text{TPSSh-D3(BJ)/def2-QZVPP+SMD}): -1736.376795 \text{ E}_h \)

\( \Delta \Delta G(298.15): 0.430267 \text{ E}_h \)

Lowest frequency: 21.80 cm\(^{-1}\)
| Atomic Symbol | X Coord   | Y Coord   | Z Coord   |
|---------------|-----------|-----------|-----------|
| H             | 5.379296  | 7.349798  | 8.490812  |
| C             | 8.136553  | 5.261732  | 8.826393  |
| H             | 8.779599  | 5.971718  | 9.367738  |
| H             | 8.763837  | 4.683009  | 8.132657  |
| H             | 7.695887  | 4.563777  | 9.551234  |
| C             | 7.060459  | 6.021390  | 8.057989  |
| C             | 6.030215  | 2.349635  | 9.640015  |
| C             | 6.556172  | 2.405922  | 8.331811  |
| C             | 7.727792  | 7.021984  | 7.117055  |
| H             | 8.325453  | 7.734808  | 7.705990  |
| H             | 6.992627  | 7.601738  | 6.541022  |
| H             | 8.388165  | 6.502034  | 6.407496  |
| C             | 6.511958  | 1.409469  | 10.553461 |
| H             | 6.085426  | 1.383068  | 11.561239 |
| C             | 7.516703  | 0.504630  | 10.211524 |
| C             | 8.006492  | 0.541576  | 8.904267  |
| H             | 8.772597  | -0.180069 | 8.603493  |
| C             | 7.542475  | 1.463462  | 7.960681  |
| C             | 8.093637  | 1.406091  | 6.565320  |
| H             | 8.798127  | 0.570023  | 6.447875  |
| H             | 8.615159  | 2.333201  | 6.278441  |
| H             | 7.280034  | 1.269985  | 5.835505  |
| C             | 4.957220  | 3.301408  | 10.093864 |
| H             | 4.209044  | 2.785956  | 10.715296 |
| H             | 4.431467  | 3.766111  | 9.246546  |
| H             | 5.381408  | 4.113491  | 10.708665 |
| C             | 8.051397  | -0.464270 | 11.225942 |
| H             | 8.669806  | -1.243235 | 10.757648 |
| H             | 7.238326  | -0.960486 | 11.778930 |
| H             | 8.676361  | 0.055802  | 11.971538 |
| C             | 4.579516  | 2.761888  | 2.975173  |
\[ \begin{align*}
H & \quad 3.860779000 \quad 3.586542000 \quad 3.083489000 \\
C & \quad 7.341210000 \quad 1.973226000 \quad 2.889722000 \\
H & \quad 8.378364000 \quad 2.284826000 \quad 3.084402000 \\
C & \quad 6.554414000 \quad 4.583891000 \quad 1.988097000 \\
H & \quad 6.360419000 \quad 4.136078000 \quad 1.000703000 \\
H & \quad 4.319841000 \quad 1.974066000 \quad 3.695639000 \\
H & \quad 4.513534000 \quad 2.353390000 \quad 1.954675000 \\
H & \quad 7.219175000 \quad 1.674782000 \quad 1.837140000 \\
H & \quad 7.106910000 \quad 1.119519000 \quad 3.540149000 \\
H & \quad 5.900601000 \quad 5.454556000 \quad 2.136139000 \\
H & \quad 7.598607000 \quad 4.921704000 \quad 2.058998000 \\
\end{align*} \]

**1B\text{2}**

E(PBE0-D3(BJ)/def2-QZVPP+SMD): -2195.906039 \( \text{E}_h \)

E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -2197.623329 \( \text{E}_h \)

\( \Delta \Delta G(298.15) \): 0.540329 \( \text{E}_h \)

Lowest frequency: 3.95 cm\(^{-1} \)

\[ \begin{align*}
C & \quad 5.501126000 \quad 5.241629000 \quad 6.522311000 \\
P & \quad 5.656673000 \quad 4.190789000 \quad 3.284065000 \\
N & \quad 6.694891000 \quad 4.972001000 \quad 7.314360000 \\
B & \quad 6.322207000 \quad 3.505506000 \quad 7.325174000 \\
Cl & \quad 7.764252000 \quad 6.679023000 \quad 4.420237000 \\
C & \quad 4.723706000 \quad 6.504547000 \quad 6.424172000 \\
H & \quad 3.877871000 \quad 6.335853000 \quad 5.743598000 \\
H & \quad 5.334934000 \quad 7.322296000 \quad 6.019201000 \\
H & \quad 4.303842000 \quad 6.812057000 \quad 7.397347000 \\
C & \quad 5.161240000 \quad 3.842931000 \quad 6.393371000 \\
H & \quad 4.263149000 \quad 3.933800000 \quad 5.981778000 \\
Rh & \quad 6.818544000 \quad 4.522058000 \quad 5.182325000 \\
C & \quad 6.750603000 \quad 5.656271000 \quad 9.649336000 \\
\end{align*} \]
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | 6.747980000 | -0.144142000 | 12.525530000 |
| C       | 3.829787000 | 4.209009000   | 3.465815000  |
| H       | 3.512548000 | 5.140136000   | 3.954802000  |
| C       | 5.840944000 | 2.603172000   | 2.375790000  |
| H       | 6.855835000 | 2.498465000   | 1.970849000  |
| C       | 5.860541000 | 5.449319000   | 1.976963000  |
| H       | 5.220363000 | 5.217159000   | 1.112390000  |
| P       | 8.828175000 | 3.611866000   | 4.226386000  |
| C       | 9.080503000 | 1.808214000   | 3.958185000  |
| H       | 8.318975000 | 1.442132000   | 3.256984000  |
| H       | 8.959732000 | 1.260260000   | 4.900239000  |
| H       | 10.075545000 | 1.598158000 | 3.533741000  |
| C       | 9.206994000 | 4.229033000   | 2.533180000  |
| H       | 10.231244000 | 3.948668000 | 2.243135000  |
| H       | 9.101517000 | 5.323659000   | 2.550667000  |
| H       | 8.511260000 | 3.809302000   | 1.794907000  |
| C       | 10.386391000 | 4.130738000 | 5.049341000  |
| H       | 11.263441000 | 3.788200000 | 4.479068000  |
| H       | 10.444924000 | 3.742221000 | 6.073687000  |
| H       | 10.370452000 | 5.230404000 | 5.085553000  |
| H       | 5.659089000 | 1.775152000   | 3.076119000  |
| H       | 5.125548000 | 2.542685000   | 1.541556000  |
| H       | 6.909826000 | 5.512000000   | 1.666386000  |
| H       | 5.594888000 | 6.425841000   | 2.404112000  |
| H       | 3.354249000 | 4.143674000   | 2.475416000  |
| H       | 3.496360000 | 3.360925000   | 4.077122000  |
E(PBE0-D3(BJ)/def2-QZVPP+SMD): -1273.963495 \text{E}_h
E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -1275.045605 \text{E}_h
\Delta \Delta G(298.15): 0.321487 \text{E}_h
Lowest frequency: 24.57 \text{cm}^{-1}

|  |  |  |  |
|---|---|---|---|
| Rh | 2.064469000 | 11.928019000 | 10.953095000 |
| N  | 4.677752000 | 10.720421000 | 10.774376000 |
| B  | 3.289232000 | 10.392170000 | 10.749865000 |
| C  | 3.676224000 | 12.811803000 | 10.451246000 |
| H  | 3.639612000 | 13.864310000 | 10.137524000 |
| C  | 4.813787000 | 12.072146000 | 10.378204000 |
| C  | 6.053520000 | 12.571359000 | 9.702429000 |
| H  | 6.273802000 | 11.979574000 | 8.799812000 |
| H  | 6.945872000 | 12.530473000 | 10.344295000 |
| H  | 5.908207000 | 13.614842000 | 9.393063000 |
| C  | 5.155272000 | 8.642287000  | 11.934799000 |
| H  | 4.650980000 | 8.033816000  | 11.170609000 |
| H  | 4.422097000 | 8.907598000  | 12.710587000 |
| H  | 5.941133000 | 8.031412000  | 12.401914000 |
| Cl | 2.159993000 | 12.026189000 | 13.186308000 |
| C  | 5.773894000 | 9.901030000  | 11.329581000 |
| C  | 6.779445000 | 9.471195000  | 10.257989000 |
| H  | 6.272723000 | 8.902703000  | 9.463192000  |
| H  | 7.542735000 | 8.817833000  | 10.707971000 |
| H  | 7.300650000 | 10.319177000 | 9.797143000  |
| C  | 6.463557000 | 10.679813000 | 12.456801000 |
| H  | 7.204187000 | 10.041327000 | 12.962162000 |
| H  | 5.719210000 | 11.010352000 | 13.194958000 |
| H  | 6.991819000 | 11.568913000 | 12.088585000 |
| C  | 2.441310000 | 9.189313000  | 10.228233000 |
| C  | 1.568298000 | 8.416480000  | 11.029004000 |
2A

E(PBE0-D3(BJ)/def2-QZVPP+SMD): -1970.646038 \text{E}_h

E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -1972.365675 \text{E}_h

\Delta\Delta G(298.15): 0.595201 \text{E}_h

Lowest frequency: 14.83 cm$^{-1}$

Rh  2.436951000  12.497162000  10.795465000
N   4.533205000  10.591039000  10.461436000
B   3.104330000  10.664911000  10.372426000
C   4.249822000  12.894518000  10.200643000
H   4.545756000  13.895112000  9.870071000
C   5.109171000  11.857791000  10.175428000
|   |   |   |   |
|---|---|---|---|
| C | 6.503053000 | 11.985449000 | 9.638970000 |
| H | 6.614074000 | 11.416523000 | 8.700381000 |
| H | 7.277702000 | 11.624774000 | 10.330923000 |
| H | 6.715526000 | 13.041403000 | 9.420435000 |
| C | 4.373710000 | 8.444434000 | 11.692573000 |
| H | 3.851335000 | 7.886266000 | 10.906583000 |
| H | 3.625156000 | 8.887587000 | 12.365294000 |
| H | 4.971537000 | 7.730716000 | 12.786430000 |
| Cl | 2.926824000 | 12.349073000 | 13.051851000 |
| C | 5.309297000 | 9.515231000 | 11.132888000 |
| C | 6.284330000 | 8.818296000 | 10.177894000 |
| H | 5.734230000 | 8.323041000 | 9.364761000 |
| H | 6.845706000 | 8.049350000 | 10.724532000 |
| H | 7.013623000 | 9.502885000 | 9.729580000 |
| C | 6.040923000 | 10.120085000 | 12.339915000 |
| H | 6.549689000 | 9.323130000 | 12.904052000 |
| H | 5.314950000 | 10.618402000 | 12.997774000 |
| H | 6.795889000 | 10.863647000 | 12.056344000 |
| C | 2.172482000 | 9.468061000 | 9.966428000 |
| C | 1.166216000 | 8.926158000 | 10.801142000 |
| C | 0.537846000 | 7.736124000 | 10.436506000 |
| H | -0.206492000 | 7.300247000 | 11.110728000 |
| C | 0.855359000 | 7.064168000 | 9.249297000 |
| C | 1.771147000 | 7.663264000 | 8.386868000 |
| H | 2.009796000 | 7.177783000 | 7.434695000 |
| C | 2.428956000 | 8.851411000 | 8.723358000 |
| C | 0.768416000 | 9.606918000 | 12.080346000 |
| H | 1.626331000 | 10.019325000 | 12.629833000 |
| H | 0.214210000 | 8.927238000 | 12.743096000 |
| H | 0.107176000 | 10.466552000 | 11.873389000 |
| C | 0.273875000 | 5.714588000 | 8.945365000 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | 3.110792000 | 12.729807000 | 6.470279000 |
| H       | 4.167564000 | 13.328860000 | 7.761677000 |
| C       | 2.603742000 | 15.610257000 | 8.406585000 |
| H       | 3.217259000 | 16.230174000 | 7.733946000 |
| H       | 3.187494000 | 15.435564000 | 9.322886000 |
| H       | 1.721038000 | 16.205852000 | 8.681617000 |
| H       | -0.195216000 | 10.733102000 | 9.429758000 |

**2AB**

E\((\text{PBE0-D3(BJ)/def2-QZVPP+SMD})\): -2431.593403 \(E_h\)

E\((\text{TPSSh-D3(BJ)/def2-QZVPP+SMD})\): -2433.630659 \(E_h\)

\(\Delta\Delta G(298.15): 0.706085 \ E_h\)

Lowest frequency: 19.73 cm\(^{-1}\)

| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| Rh      | 2.266240000 | 12.543397000 | 11.304706000 |
| P       | 2.891304000 | 12.792442000 | 13.599408000 |
| N       | 4.609060000 | 10.863660000 | 10.614218000 |
| B       | 3.175162000 | 10.834559000 | 10.749344000 |
| C       | 4.090523000 | 13.130862000 | 10.769811000 |
| H       | 4.304990000 | 14.182978000 | 10.532002000 |
| C       | 5.041945000 | 12.219953000 | 10.476090000 |
| P       | 1.452154000 | 13.123316000 | 9.227290000 |
| C       | 6.330174000 | 12.612380000 | 9.808034000 |
| H       | 6.303596000 | 12.407842000 | 8.723089000 |
| H       | 7.230140000 | 12.118005000 | 10.196437000 |
| H       | 6.467207000 | 13.695815000 | 9.936664000 |
| C       | 4.889315000 | 8.406930000 | 11.052052000 |
| H       | 4.236747000 | 8.017154000 | 10.262258000 |
| H       | 4.292838000 | 8.502512000 | 11.968294000 |
| H       | 5.675853000 | 7.662359000 | 11.244491000 |
| Cl      | -0.100395000 | 12.085512000 | 11.741510000 |
C 5.568309000   9.726889000   10.663449000
C 6.250010000   9.476254000   9.308176000
H 5.510711000   9.172600000   8.556489000
H 6.977168000   8.656173000   9.408832000
H 6.788192000   10.349939000   8.925520000
C 6.619735000   10.001250000   11.749191000
H 5.510711000   9.172600000   8.556489000
H 6.977168000   8.656173000   9.408832000
H 6.788192000   10.349939000   8.925520000
C 6.619735000   10.001250000   11.749191000
H 5.510711000   9.172600000   8.556489000
H 6.977168000   8.656173000   9.408832000
H 6.788192000   10.349939000   8.925520000
2B

E(PBE0-D3(BJ)/def2-QZVPP+SMD): -1734.955494 Eₕ
E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -1736.353106 Eₕ

ΔΔG(298.15): 0.430947 Eₕ

Lowest frequency: 23.89 cm⁻¹
| Atoms | X         | Y         | Z         |
|-------|-----------|-----------|-----------|
| Cl    | -0.625356000 | 12.258422000 | 9.113947000 |
| C     | 5.301546000  | 10.183390000 | 10.017144000 |
| C     | 6.609525000  | 10.958021000 | 9.822037000  |
| H     | 6.456005000  | 11.849036000 | 9.195055000  |
| H     | 7.334958000  | 10.309436000 | 9.309100000  |
| H     | 7.066671000  | 11.273318000 | 10.766882000 |
| C     | 5.514637000  | 9.051303000  | 11.026079000 |
| H     | 6.343871000  | 8.400345000  | 10.708322000 |
| H     | 4.609164000  | 8.433660000  | 11.110899000 |
| H     | 5.762487000  | 9.445968000  | 12.022634000 |
| C     | 2.028503000  | 9.435382000  | 12.843080000 |
| C     | 1.998395000  | 8.857058000  | 11.665250000 |
| C     | 1.462901000  | 7.578122000  | 11.839655000 |
| H     | 1.460498000  | 7.140530000  | 12.843080000 |
| C     | 0.944332000  | 6.844137000  | 10.775269000 |
| C     | 0.893881000  | 7.461346000  | 9.522055000  |
| H     | 0.438946000  | 6.927234000  | 8.682572000  |
| C     | 1.403401000  | 8.741246000  | 9.305297000  |
| C     | 2.531501000  | 9.567874000  | 12.879778000 |
| H     | 3.615272000  | 9.408091000  | 12.997939000 |
| H     | 2.042757000  | 9.186752000  | 13.787459000 |
| H     | 2.371145000  | 10.655661000 | 12.833491000 |
| C     | 0.460305000  | 5.437494000  | 10.963713000 |
| H     | 1.053423000  | 4.736142000  | 10.356622000 |
| H     | -0.589372000 | 5.321531000  | 10.648957000 |
| H     | 0.544165000  | 5.122466000  | 12.013571000 |
| C     | 1.261583000  | 9.360526000  | 7.946214000  |
| H     | 0.624309000  | 10.257057000 | 8.010403000  |
| H     | 0.804505000  | 8.658373000  | 7.235798000  |
| H     | 2.232718000  | 9.671045000  | 7.532605000  |
| C     | 4.113440000  | 13.918525000 | 8.616899000  |

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| 2B₂   |   |
|-------|---|
| E(PBE0-D3(BJ)/def2-QZVPP+SMD): -2195.921711 Eₜ   |   |
| E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -2197.636540 Eₜ |   |
| ΔΔG(298.15): 0.540769 Eₜ  |   |
| Lowest frequency: 27.66 cm⁻¹ |   |

| Rh     | 2.220995000 | 12.563237000 | 11.218253000 |
| P      | 2.799338000 | 12.624172000 | 13.443408000 |
| N      | 4.605215000 | 10.830256000 | 10.817131000 |
| B      | 3.165925000 | 10.852440000 | 10.786368000 |
| C      | 4.112192000 | 13.099281000 | 10.869130000 |
| H      | 4.373772000 | 14.157412000 | 10.713076000 |
| C      | 5.084900000 | 12.173083000 | 10.729569000 |
| P      | 1.511611000 | 13.258216000 | 9.121689000  |
| C      | 6.479485000 | 12.543603000 | 10.306837000 |
| H      | 6.643983000 | 12.353547000 | 9.232165000  |
| H      | 7.284179000 | 12.024434000 | 10.842738000 |
| H      | 6.612271000 | 13.621705000 | 10.475107000 |
| C      | 4.722479000 | 8.361861000  | 11.217472000 |
H   4.130578000  8.019121000  10.361370000
H   4.050288000  8.477944000  12.079509000
H   5.449912000  7.575182000  11.466631000
Cl  -0.147991000  12.559231000 11.803166000
C    5.502115000  9.652541000 10.938184000
C    6.307785000  9.426287000  9.650643000
H    5.629882000  9.308919000  8.794740000
H    6.900211000  8.502836000  9.737632000
H    7.002907000 10.243847000  9.427263000
C    6.438892000  9.816519000 12.145152000
H    7.211506000  9.033570000 12.125194000
H    5.870505000  9.704681000 13.078448000
H    6.950202000 10.784456000 12.182611000
C    2.272236000  9.654046000 10.283279000
C    1.446474000  8.887193000 11.139470000
C    0.893200000  7.692570000 10.681639000
H    0.294797000  7.088650000 11.371534000
C    1.124159000  7.214440000  9.386734000
C    1.864339000  8.019934000  8.523650000
H    2.053890000  7.679366000  7.500527000
C    2.422378000  9.232244000  8.943902000
C    1.191533000  9.318101000 12.551439000
H    2.132478000  9.583787000 13.060030000
H    0.698628000  8.527913000 13.135150000
H    0.556714000 10.219518000 12.563710000
C    0.633490000  5.856550000  8.974070000
H    0.840476000  5.656053000  7.913001000
H   -0.448839000  5.740788000  9.144970000
H    1.135002000  5.072273000  9.563308000
C    3.194769000 10.037952000  7.935782000
H    2.508808000 10.550392000  7.240312000
|    | X-Coordinate | Y-Coordinate | Z-Coordinate |
|----|--------------|--------------|--------------|
| H  | 3.841732000  | 9.397527000  | 7.317008000  |
| H  | 3.820102000  | 10.800909000 | 8.415862000  |
| C  | 4.296173000  | 11.807539000 | 14.088544000 |
| H  | 4.139658000  | 10.720630000 | 14.125639000 |
| H  | 4.534093000  | 12.177775000 | 15.096762000 |
| H  | 5.123153000  | 12.025340000 | 13.401357000 |
| C  | 1.531028000  | 12.228596000 | 14.697166000 |
| H  | 0.585776000  | 12.690959000 | 14.380807000 |
| H  | 1.840004000  | 12.600389000 | 15.685595000 |
| H  | 1.372239000  | 11.143133000 | 14.744833000 |
| C  | 3.137958000  | 14.395406000 | 13.778886000 |
| H  | 3.967857000  | 14.718722000 | 13.136371000 |
| H  | 3.395675000  | 14.566941000 | 14.835713000 |
| H  | 2.246562000  | 14.985708000 | 13.519507000 |
| C  | 2.713160000  | 13.657882000 | 7.801089000  |
| H  | 3.208498000  | 12.748821000 | 7.440128000  |
| H  | 3.483024000  | 14.320074000 | 8.221014000  |
| H  | 2.213924000  | 14.162351000 | 6.959399000  |
| C  | 0.191499000  | 12.292473000 | 8.314191000  |
| H  | -0.182960000 | 12.796948000 | 7.410385000  |
| H  | -0.611665000 | 12.189779000 | 9.058438000  |
| H  | 0.553634000  | 11.285802000 | 8.065172000  |
| C  | 0.704467000  | 14.885744000 | 9.381947000  |
| H  | 0.324485000  | 15.300444000 | 8.434715000  |
| H  | 1.427015000  | 15.586426000 | 9.825541000  |
| H  | -0.121408000 | 14.733615000 | 10.090965000 |
$1B_2^+$

$E(\text{PBE0-D3(BJ)/def2-QZVPP+SMD})$: -2195.910206 $E_h$

$E(\text{TPSSh-D3(BJ)/def2-QZVPP+SMD})$: -2197.623433 $E_h$

$\Delta \Delta G(298)$: 0.539615 $E_h$

Lowest frequency: 28.97 cm$^{-1}$

| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| Rh      | 2.278486000 | 12.595975000 | 11.353379000 |
| P       | 3.302804000 | 12.976231000 | 13.379147000 |
| N       | 4.658740000 | 10.666423000 | 11.524707000 |
| B       | 3.403011000 | 10.951729000 | 10.723133000 |
| C       | 4.054078000 | 12.493899000 | 10.345699000 |
| H       | 4.188281000 | 13.135494000 | 9.470128000  |
| C       | 5.122090000 | 11.680106000 | 10.690016000 |
| P       | 0.995722000 | 12.833413000 | 9.428260000  |
| C       | 6.494874000 | 11.813955000 | 10.115562000 |
| H       | 6.903847000 | 10.879445000 | 9.712075000  |
| H       | 7.177198000 | 12.156096000 | 10.911025000 |
| H       | 6.494860000 | 12.574351000 | 9.324037000  |
| C       | 4.356666000 | 8.571628000  | 12.684902000 |
| H       | 3.523136000 | 8.242125000  | 12.049815000 |
| H       | 3.946027000 | 9.135407000  | 13.533106000 |
| H       | 4.861004000 | 7.677482000  | 13.079532000 |
| Cl      | 0.203808000 | 12.889471000 | 12.514084000 |
| C       | 5.343784000 | 9.418561000  | 11.883773000 |
| C       | 5.802517000 | 8.565981000  | 10.690340000 |
| H       | 4.956506000 | 8.322769000  | 10.033200000 |
| H       | 6.228180000 | 7.620663000  | 11.059497000 |
| H       | 6.585275000 | 9.055399000  | 10.096371000 |
| C       | 6.547035000 | 9.747108000  | 12.771667000 |
| H       | 7.036784000 | 8.821528000  | 13.110200000 |
| H       | 6.229416000 | 10.308751000 | 13.662573000 |
| H       | 7.300544000 | 10.342226000 | 12.236993000 |
### TS1

E(PBE0-D3(BJ)/def2-QZVPP+SMD): -2195.910206 \(E_h\)

E(TPSSh-D3(BJ)/def2-QZVPP+SMD): -2197.623433 \(E_h\)

\(\Delta\Delta G(298)\): 0.539615 \(E_h\)

Lowest frequency: 163.04i \(\text{cm}^{-1}\)

| Atom | X     | Y     | Z     |
|------|-------|-------|-------|
| Rh   | 2.297302000 | 12.570398000 | 11.325936000 |
| P    | 3.260074000  | 12.934690000 | 13.374735000 |
| N    | 4.680521000  | 10.676438000 | 11.446450000 |
| B    | 3.345523000  | 10.890145000 | 10.841335000 |
| C    | 4.099517000  | 12.610072000 | 10.391946000 |
| H    | 4.254072000  | 13.345686000 | 9.593459000  |
| C    | 5.139300000  | 11.764058000 | 10.674206000 |
| P    | 1.059931000  | 12.850292000 | 9.361933000  |
| C    | 6.520307000  | 11.918816000 | 10.127578000 |
| H    | 6.885629000  | 11.024532000 | 9.603394000  |
| H    | 7.234145000  | 12.141162000 | 10.938025000 |
H   6.540295000  12.763663000  9.426472000
C   4.424825000  8.594533000  12.644514000
H   3.604966000  8.233293000  12.008609000
H   3.994320000  9.159408000  13.482221000
H   4.949557000  7.719665000  13.054667000
Cl  0.179638000  12.823930000  12.444818000
C   5.395631000  9.458424000  11.840920000
C   5.889589000  8.604742000  10.663658000
H   5.048218000  8.302210000  10.025394000
H   6.370429000  7.691537000  11.045949000
H   6.635128000  9.128868000  10.050958000
C   6.580562000  9.820723000  12.740578000
H   7.082843000  8.907239000  13.093509000
H   6.240073000  10.381891000  13.623048000
H   7.329865000  10.424871000  12.21135000
C   2.581428000  9.819271000  9.956221000
C   1.467066000  9.125600000  10.489160000
C   0.761588000  8.219481000  9.687869000
H  -0.094873000  7.694181000  10.121629000
C   1.110689000  7.969219000  8.361161000
C   2.228434000  8.635167000  7.853983000
H   2.548265000  8.432576000  6.826787000
C   2.967598000  9.541858000  8.620999000
C   0.983733000  9.354957000 11.892084000
H   1.800208000  9.319654000 12.626652000
H   0.239336000  8.598876000 12.177770000
H   0.521405000 10.350129000 11.998121000
C   0.303994000  7.041996000  7.497268000
H   0.948588000  6.422260000  6.854267000
H  -0.366648000  7.610778000  6.830231000
H  -0.325015000  6.370288000  8.099790000
| Atoms | X       | Y       | Z       |
|-------|---------|---------|---------|
| C     | 4.172927| 10.1834 | 7.99022 |
| H     | 4.253628| 9.9085  | 6.92893 |
| H     | 5.099259| 9.86128 | 8.48467 |
| H     | 4.145137| 11.2788 | 8.07218 |
| C     | 5.05248 | 13.2883 | 13.4883 |
| H     | 5.62790 | 12.3945 | 13.2233 |
| H     | 5.31755 | 13.6124 | 14.5061 |
| H     | 5.29840 | 14.0845 | 12.7728 |
| C     | 2.97657 | 11.7039 | 14.6917 |
| H     | 1.90178 | 11.4732 | 14.7117 |
| H     | 3.30379 | 12.0759 | 15.6744 |
| H     | 3.52931 | 10.7892 | 14.4430 |
| C     | 2.56786 | 14.4704 | 14.1006 |
| H     | 2.76219 | 15.3046 | 13.4106 |
| H     | 3.02815 | 14.6877 | 15.0768 |
| H     | 1.48046 | 14.3495 | 14.1969 |
| C     | 1.81820 | 12.8366 | 7.69476 |
| H     | 2.07378 | 11.8052 | 7.41887 |
| H     | 2.73353 | 13.4442 | 7.68474 |
| H     | 1.11120 | 13.2418 | 6.95424 |
| C     | -0.41596| 11.8070 | 9.12278 |
| H     | -1.02913| 12.1771 | 8.28677 |
| H     | -0.99295| 11.8323 | 10.0579 |
| H     | -0.09851| 10.7724 | 8.92604 |
| C     | 0.35866 | 14.5417 | 9.43956 |
| H     | -0.29021| 14.7493 | 8.57433 |
| H     | 1.17725 | 15.2764 | 9.46943 |
| H     | -0.21801| 14.6224 | 10.3715 |
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