Supporting Information for:

Amino-Borane Oligomers Bound to a Rh(I) Metal Fragment.

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Experimental

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk and glove-box techniques. Glassware was oven dried at 130°C overnight and flamed under vacuum prior to use. Pentane was dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.[1] CD_2Cl_2, C_6H_5F and 1,2-$C_6H_4F_2$ were distilled under vacuum from CaH_2 and stored over 3 Å molecular sieves. $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$[2] and $[H_2BNMeH]_3$[3] were made following literature procedures. $H_3B{\cdot}NMe_2H$ was purchased from Aldrich and sublimed before use (5×10^{-2} Torr, 298 K). $H_3B{\cdot}NMeH_2$[4] and $[Rh\{P(C_5H_9)_2(\eta^2\text{-}C_5H_7)\}][BAr^F{}_4]$[5] were prepared as previously described. NMR spectra were recorded on Varian Unity 500 MHz or Varian Venus 300 MHz spectrometers at room temperature unless otherwise stated. In 1,2-$C_6H_4F_2$ and C_6H_5F, ^{1}H NMR spectra were referenced to the centre of the downfield solvent multiplet (δ = 7.07 and 7.11 respectively). ^{31}P spectra were referenced against 85% H_3PO_4 (external). ^{11}B NMR spectra were referenced against $BF_3{\cdot}OEt_2$ (external). Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker MicrOTOF instrument. Microanalyses were performed by Elemental Microanalysis Ltd.

Synthesis of new complexes

Preparation of Rh(nbd){P^{i}Pr$_2$(C_5H_9)}Cl

This complex was prepared using the method of Chatt and Venanzi.[6]

^{1}H NMR (500 MHz, $CDCl_3$): δ 5.05 (s, 2H, HC=CH), 3.77 (s, 2H, nbd-CH_2), 3.75 (s, 2H, HC=CH), 2.20 - 1.37 (m, 13H, ^{i}Pr/Cyp), 1.29 (dd, 6H, *J*(PH) 13, *J*(HH) 7.3, ^{i}Pr-CH_3), 1.26 (dd, 6H, *J*(PH) 13, *J*(HH) 7.2, ^{i}Pr-CH_3).

^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$): δ 37.79 [d, *J*(RhP) 167].

Preparation of [Rh{P^{i}Pr$_2$(η^2-C_5H_7)}(η^6-C_6H_5F)][BAr$^F{}_4$]

Rh(nbd){P^{i}Pr$_2$(C_5H_9)}Cl (58 mg, 0.138 mmol) and Na[BAr$^F{}_4$] (122 mg, 0.138 mmol) were dissolved in fluorobenzene (5 mL) and stirred for 20 hours. The reaction mixture was then filtered and the solvent was then removed *in vacuo* with the resulting solid being washed twice with pentane (2 x 3 mL). Diffusion of pentane into a fluorobenzene solution of the complex gave the product as yellow crystals. Yield 107 mg, 62 %.

^{1}H NMR (500 MHz, C_6H_5F): δ 8.35 (s, 8H, BAr^F_4), 7.66 (s, 4H, BAr^F_4), 6.14 – 6.03 (m, 4H, η^6-C_6H_5F), 5.46 (m, 1H, η^6-C_6H_5F), 3.91 (d, 2H, *J*(HH) 3, HC=CH), 1.53 (m, 2H, P^iPr-CH, {^{31}P δ 122.37}, sept, *J*(HH) 7), 1.44 (br, 1H, PCyp'-CH), 1.36 (apparent triplet, *J* = 13, 2H, PCyp'-CH_2), 1.18 (apparent ddt, 2H, *J*(PH) 48, *J*(HH) 13, *J*(HH) 3, PCyp'-CH_2), 0.85 (dd, 6H, *J*(PH) 7, *J*(HH) 4, P^iPr-CH_3), 0.88 (dd, 6H, *J*(PH) 7, *J*(HH) 4, P^iPr-CH_3)

^{31}P {^{1}H} NMR (202 MHz, C_6H_5F): δ 122.37 [dd, *J*(RhP) 184, *J*(FP) 3].

ESI-MS (C_6H_5F, 60°C, 4.5kV) positive ion: m/z, 383.0775 $[M]^+$ (calcd. 383.0806)

Anal. Calcd for $C_{49}H_{38}B_1F_{25}P_1Rh_1$ (1246.1460 gmol^{-1}): C, 47.22; H, 3.07. Found: C, 47.06; H, 3.04.

Preparation of [Rh{P(C_5H_9)$_2$(η^2-C_5H_7)}(η^2:η^1-$H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$)][$BAr^F_4$] (3a[$BAr^F_4$])

$H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$ (2.1 mg, 0.018 mmol, 1 eqv) was added to a solution of [Rh{P(C_5H_9)$_2$(η^2-C_5H_7)(C_6H_5F)}][BAr^F_4] (24.0 mg, 0.018 mmol) in 1,2-$C_6H_4F_2$ (3 mL). Diffusion of pentane into the solution at -35°C gave **3a[BAr^F_4]** as pale yellow crystals which were stored at -35°C. Yield 12.5 mg, 51 %. At temperatures higher than 0°C solid **3a[BAr^F_4]** melts thus a satisfactory microanalysis could not be obtained.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.34 (s, 8H, BAr^F_4), 7.69 (s, 4H, BAr^F_4), 4.19 (bs, 1H, NH), 3.79 (s, 2H, HC=CH), 2.75 (d, 6H, *J*(HH) 5, NH-CH_3), 2.67 (s, 6H, N-CH_3), 2.08 – 1.44 (m, 21H, PCyp/Cyp'), 1.23 (br dd, 2H, *J*(PH) 47, *J*(HH) 14, PCyp'-CH_2), 0.10 (br, 3H, *J*(BH) 111, BH_3) -1.94 (br, 2H, *J*(BH) 117, BH_2).

^{1}H {^{11}B} NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 0.10 (d, 3H, *J*(RhH) 21, BH_3), -1.94 (br, 2H, BH_2).

^{31}P {^{1}H} NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 114.58 [d, *J*(RhP) 170].

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ -4.33 (br).

ESI-MS (1,2-$C_6H_4F_2$, 60°C, 4.5kV) positive ion: m/z, 455.2420 $[M]^+$ (calcd. 455.2406).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.74 (s, 8H, BAr^F_4), 7.58 (s, 4H, BAr^F_4), 4.10 (bs, 1H, NH), 3.80 (s, 2H, HC=CH), 2.63 (d, 6H, *J*(HH) 5, NH-CH_3), 2.58 (s, 6H, N-CH_3), 2.23 – 1.50 (m, 21H, PCyp/Cyp'), 1.34 (br dd, 2H, *J*(PH) 47, *J*(HH) 14, PCyp'-CH_2), -0.05 (br, 3H, *J*(BH) 111, BH_3), -2.10 (br, 2H, *J*(BH) 117, BH_2).

^{1}H {^{11}B} NMR (500 MHz, CD_2Cl_2): δ -0.06 (d, 3H, *J*(RhH) 21, BH_3), -2.10 (br, 2H, BH_2).

^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2): δ 114.55 [d, *J*(RhP) 169].

^{11}B NMR (160 MHz, CD_2Cl_2): δ -4.32 (br)

^{1}H NMR (500 MHz, CD_2Cl_2, 200K): δ 7.74 (s, 8H, BAr^F_4), 7.57 (s, 4H, BAr^F_4), 4.20 (bs, 1H, NH), 3.68 (s, 2H, HC=CH), 2.56 (d, 6H, *J*(HH) 5, NH-CH_3), 2.54 (s, 6H, N-CH_3), 2.18 – 1.37 (m, 21H, PCyp/Cyp'), 1.26 (br dd, 2H, *J*(PH) 47, *J*(HH) 14, PCyp'-CH_2), -1.30 (br, 2H, BH_3), -2.32 (br, 2H, BH_2). The remaining B-H signal was not observed, presumably it was broad and/or obscured by the aliphatic signals.

^{1}H {^{11}B} NMR (500 MHz, CD_2Cl_2, 200K): δ -1.35 (v br, 2H, Rh$\underline{H}_2$BH), -2.32 (br, 2H, BH_2)

^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2, 200K): δ 113.11 [d, *J*(RhP) 169].

^{11}B NMR (160 MHz, CD_2Cl_2, 200K): δ very broad, no clear signals observed.

Preparation of [Rh{P^{i}Pr$_2$(η^2-C_5H_7)}(η^2:η^1- $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$)][$BAr^F_4$] (3b[$BAr^F_4$])

$H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$ (2.2 mg, 0.019 mmol, 1 eqv) was added to a solution of [Rh{P^{i}Pr$_2$(η^2-C_5H_7)}(C_6H_5F)][BAr^F_4] (24.0 mg, 0.019 mmol) in 1,2-$C_6H_4F_2$ (0.5 mL). Quantitative conversion to **3b[BAr^F_4]** was observed by NMR spectroscopy. Crystalline material was difficult to obtain however a single pale yellow crystal suitable for X-Ray diffraction was obtained from the diffusion of pentane into a 1,2-$C_6H_4F_2$ (3 mL) solution at -35°C.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.33 (s, 8H, BAr^F_4), 7.68 (s, 4H, BAr^F_4), 4.35 (bs, 1H, NH), 3.81 (s, 2H, HC=CH), 2.72 (d, 6H, *J*(HH) 5, NH-CH_3), 2.66 (s, 6H, N-CH_3), 1.93 (m, 2H, P^{i}Pr-CH), 1.83 (dd, 2H, *J*(HH) 14, *J*(PH) 13, PCyp'-CH_2), 1.78 (m, 1H, PCyp'-CH), 1.32 (apparent ddt, 2H, *J*(PH) 46, *J*(HH) 14, *J*(HH) 3, PCyp'-CH_2), 1.11 (dd, 6H, *J*(PH) 15, *J*(HH) 7, P^{i}Pr-CH_3), 1.07 (dd, 6H, *J*(PH) 15, *J*(HH) 7, P^{i}Pr-CH_3), 0.12 (br, 3H, *J*(BH) 110, BH_3) -2.14 (br, 2H, *J*(BH) 119, BH_2).

^{1}H {^{11}B} NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 0.12 (d, 3H, *J*(RhH) 19, BH_3), -2.12 (br, 2H, BH_2).

^{31}P {^{1}H} NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 123.03 [d, *J*(RhP) 176].

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ -4.26 (br).

ESI-MS (1,2-$C_6H_4F_2$, 60°C, 4.5kV) positive ion: m/z, 403.2066 $[M]^+$ (Calcd. 403.2092).

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.74 (s, 8H, BAr^F_4), 7.58 (s, 4H, BAr^F_4), 4.13 (bs, 1H, NH), 3.82 (s, 2H, HC=CH), 2.62 (d, 6H, *J*(HH) 6, NH-CH_3), 2.59 (br s, 6H, N-CH_3), 2.08 (m, 2H, P^{i}Pr-CH), 1.95 (br m, 1H, PCyp'-CH), 1.94 (dd, 2H, *J*(HH) 13, *J*(PH) 12, PCyp'-CH_2), 1.44 (apparent ddt, 2H, *J*(PH) 46, *J*(HH) 14, *J*(HH) 3, PCyp'-CH_2), 1.24 (dd, 6H, *J*(PH) 14, *J*(HH) 7, P^{i}Pr-CH_3), 1.18 (dd, 6H, *J*(PH) 14, *J*(HH) 7, P^{i}Pr-CH_3), -0.02 (br, 3H, *J*(BH) 110, BH_3), -2.26 (br, 2H, *J*(BH) 119, BH_2).

^{1}H {^{11}B} NMR (500 MHz, CD_2Cl_2): -0.03 (d, 3H, *J*(RhH) 21, BH_3), -2.25 (br, 2H, BH_2).

^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2): δ 123.44 [d, *J*(RhP) 176].

^{11}B NMR (160 MHz, CD_2Cl_2): δ -4.29 (br).

^{1}H NMR (500 MHz, CD_2Cl_2, 200K): δ 7.74 (s, 8H, BAr^F_4), 7.56 (s, 4H, BAr^F_4), 4.25 (bs, 1H, NH), 3.70 (s, 2H, HC=CH), 2.58 – 2.53 (m, 12H, NH-CH_3 , N-CH_3), 1.99 (m, 2H, P^{i}Pr-CH), 1.88 (br m, 1H, PCyp CH), 1.82 (dd, 2H, *J*(HH) 13, *J*(PH) 12, PCyp'-CH_2), 1.37 (br dd, 2H, *J*(PH) 46, *J*(HH) 13 PCyp'-CH_2), 1.14 (dd, 6H, *J*(PH) 14, *J*(HH) 7, P^{i}Pr-CH_3), 1.09 (dd, 6H, *J*(PH) 14, *J*(HH) 7, P^{i}Pr-CH_3), -1.34 (br, 2H, BH_3), -2.48 (br, 2H, BH_2). The remaining B-H signal was not observed, presumably it was broad and/or obscured by the aliphatic signals.

^{1}H {^{11}B} NMR (500 MHz, CD_2Cl_2, 200K): -1.35 (v br, 2H, Rh$\underline{H}_2$BH), -2.49 (br, 2H, BH_2).

^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2, 200K): δ 121.59 [d, *J*(RhP) 172].

^{11}B NMR (160 MHz, CD_2Cl_2, 200K): δ very broad, no clear signals observed.

Preparation of [Rh{P(C_5H_9)$_2$(η^2-C_5H_7)}(η^1:η^1:η^1-H_2BNMeH)$_3$][BAr^F_4] (4a[BAr^F_4])

$[H_2BNMeH]_3$ (3.5 mg, 0.027 mmol, 1.5 eqv) was added to a solution of [Rh{P(C_5H_9)$_2$(η^2-C_5H_7)}(C_6H_5F)][BAr^F_4] (24.0 mg, 0.018 mmol) in 1,2-$C_6H_4F_2$ (3 mL). The solution was stirred for 24 hours. Diffusion of pentane into the solution at 20°C gave **4a[BAr^F_4]** as pale yellow crystals. Yield 10.5 mg, 43 %.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.34 (s, 8H, BAr^F_4), 7.69 (s, 4H, BAr^F_4), 3.81 (s, 2H, HC=CH), 3.26 (br s, 3H, NH), 2.73 (d, *J*(HH) 5, 9H, N-CH_3), 2.17 – 1.44 (m, 21H, PCyp/Cyp'), 1.16 (apparent ddt, 2H, *J*(PH) 49, *J*(HH) 14, *J*(HH) 3, PCyp'-CH_2), -3.16 (br, 3H, Rh$\underline{H}$BH). The RhHB$\underline{H}$ signal was not unequivocally identified, presumably it was broad and/or obscured by the aliphatic signals.

^{1}H {^{11}B} NMR (500 MHz, 1,2-$C_6H_4F_2$): 2.63 (br d, 3H, *J* 9, RhHB$\underline{H}$), -3.17 (br, 3H, Rh$\underline{H}$BH).

^{31}P {^{1}H} NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 113.07 [d, *J*(RhP) 161].

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ -5.34 (br).

ESI-MS (1,2-$C_6H_4F_2$, 60°C, 4.5kV) positive ion: m/z, 468.2497 $[M]^+$ (calcd. 468.2533)

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.74 (s, 8H, BAr^F_4), 7.58 (s, 4H, BAr^F_4), 3.81 (s, 2H, HC=CH), 3.10 (bs, 3H, NH), 2.62 (d, *J*(HH) 5, 9H, N-CH_3), 2.37 – 1.42 (m, 21H, PCyp/Cyp'), 1.15 (apparent ddt, 2H, *J*(PH) 49, *J*(HH) 14, *J*(HH) 3, PCyp'-CH_2), -3.30 (br, 3H, Rh$\underline{H}$BH). The RhHB$\underline{H}$ signal was not unequivocally identified, presumably it was broad and/or obscured by the aliphatic signals.

^{1}H {^{11}B} NMR (500 MHz, CD_2Cl_2): δ 2.40 (br d, 3H, *J* 10, RhHB$\underline{H}$), -3.30 (br, 3H, Rh$\underline{H}$BH).

^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2): δ 112.61 [d, *J*(RhP) 161].

^{11}B NMR (160 MHz, CD_2Cl_2): δ -5.57 (br dd, *J*(BH) 117, 83).

^{1}H NMR (500 MHz, CD_2Cl_2, 200K): δ 7.73 (s, 8H, BAr^F_4), 7.55 (s, 4H, BAr^F_4), 3.69 (s, 2H, HC=CH), 3.19 (bs, 3H, NH), 2.57 (v br, 9H, N-CH_3), 2.24 – 1.30 (m, 21H, PCyp/Cyp'), 1.09 (br dd, 2H, *J*(PH) 49, *J*(HH) 14, PCyp'-CH_2), -1.08 (br, 2H, Rh<u>H</u>BH), -8.31 (br, 1H, Rh<u>H</u>BH). The remaining RhHB<u>H</u> signals were not unequivocally identified, presumably they are broad and/or obscured by the aliphatic signals.

^{1}H {^{11}B} NMR (500 MHz, CD_2Cl_2, 200K): δ -1.08 (br, 2H, Rh<u>H</u>BH), -8.31 (br, 1H, Rh<u>H</u>BH).

^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2, 200K): δ 111.29 [d, *J*(RhP) 159].

^{11}B NMR (160 MHz, CD_2Cl_2, 200K): δ very broad, no clear signal observed.

Anal. Calcd for $C_{50}H_{55}B_4F_{24}N_3P_1Rh_1.C_6H_4F_2$ (1445.170 $gmol^{-1}$): C, 46.54; H, 4.11; N, 2.91. Found: C, 46.16; H, 4.05; N, 2.81.

Preparation of [Rh{$P^iPr_2(\eta^2\text{-}C_5H_7)$}($\eta^1$:$\eta^1$:$\eta^1$-$H_2BNMeH)_3$][$BAr^F_4$] (4b[$BAr^F_4$])

$[H_2BNMeH]_3$ (3.5 mg, 0.027 mmol, 1.5 eqv) was added to a solution of [Rh{$P^iPr_2(\eta^2\text{-}C_5H_7)$}($C_6H_5F$)][$BAr^F_4$] (24.0 mg, 0.019 mmol) in 1,2-$C_6H_4F_2$ (3 mL). The solution was stirred for 24 hours. Quantitative conversion to **4b[BAr^F_4]** was observed by NMR spectroscopy from *in situ* generated samples. Crystalline material was difficult to obtain however a single pale yellow crystal suitable for X-Ray diffraction was obtained from the diffusion of pentane into a 1,2-$C_6H_4F_2$ (3 mL) solution at -35°C.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.33 (s, 8H, BAr^F_4), 7.68 (s, 4H, BAr^F_4), 3.81 (s, 2H, HC=CH), 3.31 (br s, 3H, NH), 2.71 (d, *J*(HH) 6, 9H, N-CH_3), 1.98 (m, 2H, P^iPr-CH), 1.81 (br m, 1H, PCyp'-CH), 1.76 (virtual triplet, 2H, *J*(HH) ~ *J*(PH) 13, PCyp'-CH_2), 1.34 – 1.15 (m, 12H, P^iPr-CH_3) 1.26 – 1.05 (partially obscured multiplet, 2H, PCyp'-CH_2), -3.32 (collapsed quartet, 3H, *J*(BH) 87, Rh<u>H</u>BH). The remaining RhHB<u>H</u> signal was not unequivocally identified, presumably it is broad and/or obscured by the aliphatic signals.

^{1}H {^{11}B} NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 2.62 (br d, 3H, *J* 10, RhHB<u>H</u>), -3.32 (br, 3H, Rh<u>H</u>BH).

^{31}P {^{1}H} NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 120.7 [d, *J*(RhP) 165].

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ -5.24 (br dd, *J*(BH) 118, 87).

ESI-MS (1,2-$C_6H_4F_2$, 60°C, 4.5kV) positive ion: m/z, 416.2230 $[M]^+$ (calcd. 416.2218)

^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.73 (s, 8H, BAr^F_4), 7.58 (s, 4H, BAr^F_4), 3.85 (s, 2H, HC=CH), 3.18 (bs, 3H, NH), 2.62 (d, *J*(HH) 5, 9H, N-CH_3), 2.08 (m, 2H, P^{i}Pr-CH), 1.97 (br m, 1H, PCyp'-CH), 1.82 (virtual triplet, 2H, *J*(HH) ~ *J*(PH) 13, PCyp'-CH_2), 1.34 -1.19 (m, 12H, P^{i}Pr-CH_3), 1.28 – 1.08 (partially obscured multiplet, 2H, PCyp'-CH_2), -3.44 (collapsed quartet, 3H, *J*(BH) 87, RhHBH). The remaining RhHBH signal was not unequivocally identified, presumably it is broad and/or obscured by the aliphatic signals.

^{1}H {^{11}B} NMR (500 MHz, CD_2Cl_2): δ 2.40 (br d, 3H, *J* 9, RhHBH), -3.43 (br, 3H, RhHBH).

^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2): δ 120.70 [d, *J*(RhP) 163].

^{11}B NMR (160 MHz, CD_2Cl_2): δ -5.45 (dd, *J*(HH) 118, 87).

^{1}H NMR (500 MHz, CD_2Cl_2, 200K): δ 7.73 (s, 8H, BAr^F_4), 7.55 (s, 4H, BAr^F_4), 3.73 (s, 2H, HC=CH), 3.20 (bs, 3H, NH), 2.56 (v br, 9H, N-CH_3), 2.00 (m, 2H, P^{i}Pr-CH), 1.90 (br m, 1H, PCyp'-CH), 1.70 (virtual triplet, 2H, *J*(HH) ~ *J*(PH) 13, PCyp'-CH_2), 1.16 (dd, 12H, *J*(HH) 7, *J*(PH) 14, P^{i}Pr-CH_3) 1.23 – 0.97 (partially obscured multiplet, 2H, PCyp'-CH_2), -1.11 (br, 2H, RhHBH), -8.80 (v br, 1H, RhHBH). The remaining RhHBH signals were not unequivocally identified, presumably they are broad and/or obscured by the aliphatic signals.

^{1}H {^{11}B} NMR (500 MHz, CD_2Cl_2, 200K): δ -1.11 (br, 2H, RhHBH), -8.85 (br, 1H, RhHBH).

^{31}P {^{1}H} NMR (202 MHz, CD_2Cl_2, 200K): δ 119.33 [d, *J*(RhP) 162].

^{11}B NMR (160 MHz, CD_2Cl_2, 200K): δ very broad, no clear signal observed.

Selected NMR spectra

* = free oligomer resonances

= new BH resonance as a result of performing $^{1}H\{^{11}B\}$ NMR spectroscopy experiment

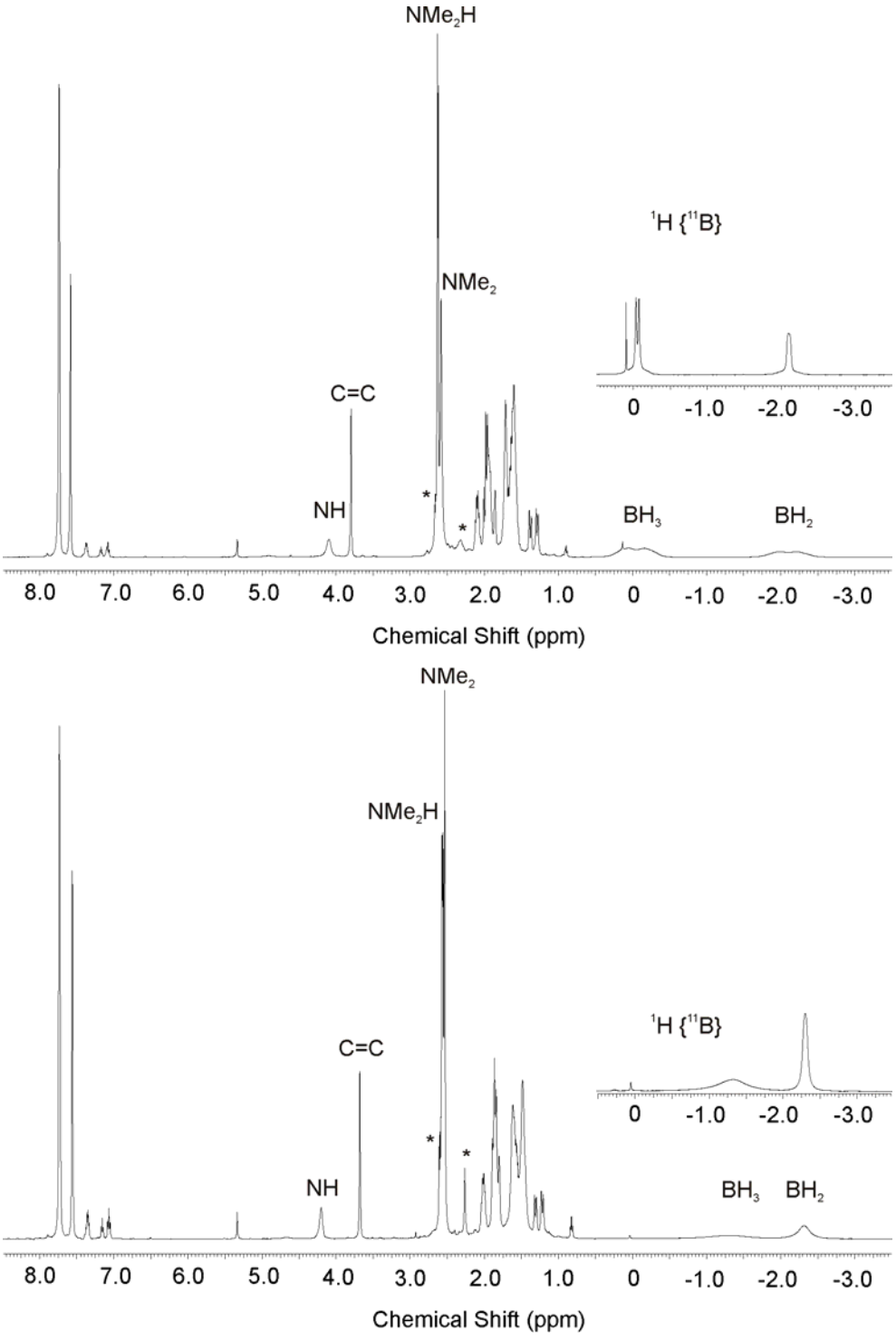

Figure S1: ^{1}H NMR (CD_2Cl_2) spectra of **3a[BAr$^{F}_{4}$]** at room temperature (top) and 200K (bottom).

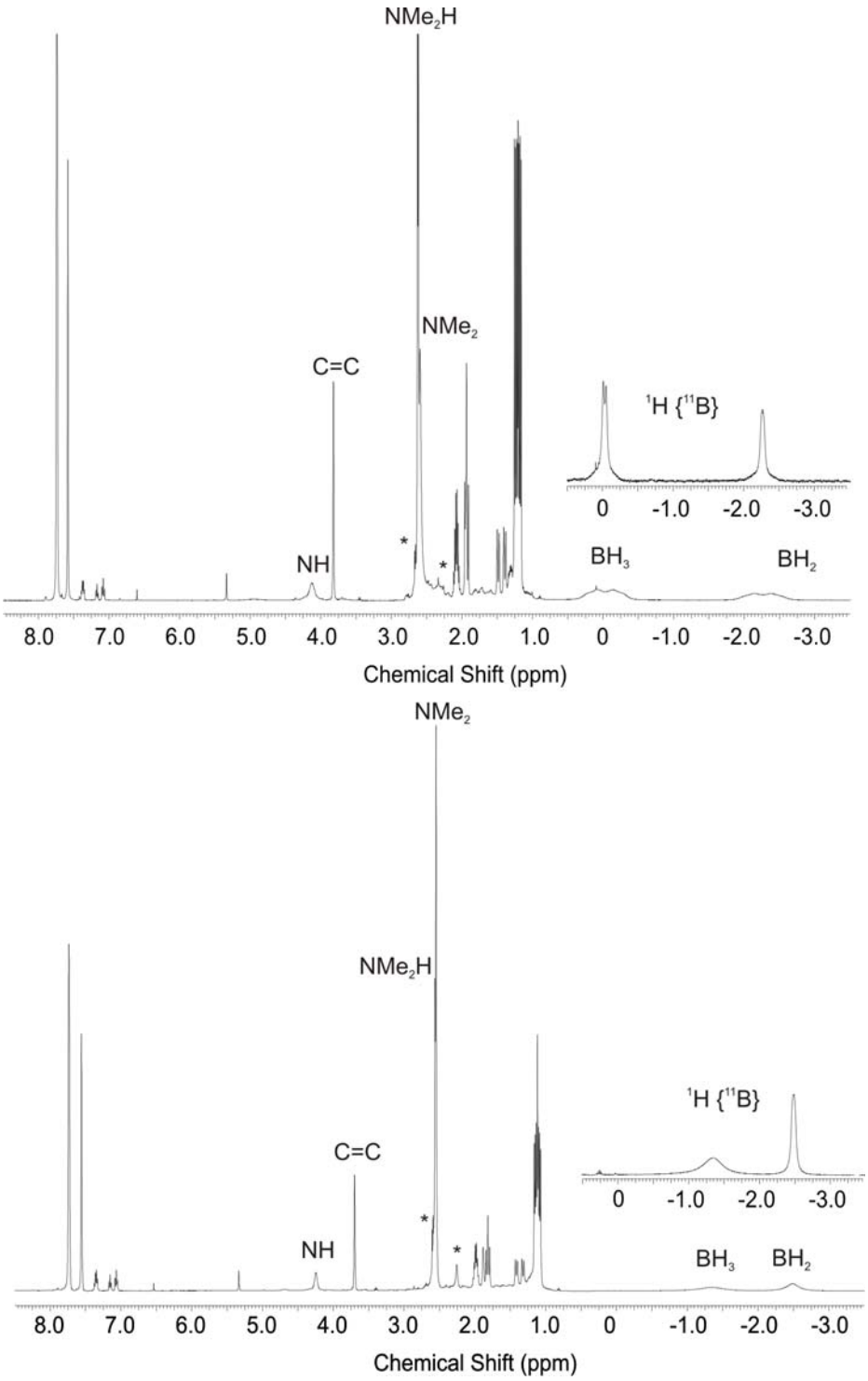

Figure S2: ^{1}H NMR (CD_2Cl_2) spectra of **3b[BAr$^F_4$]** at room temperature (top) and 200K (bottom).

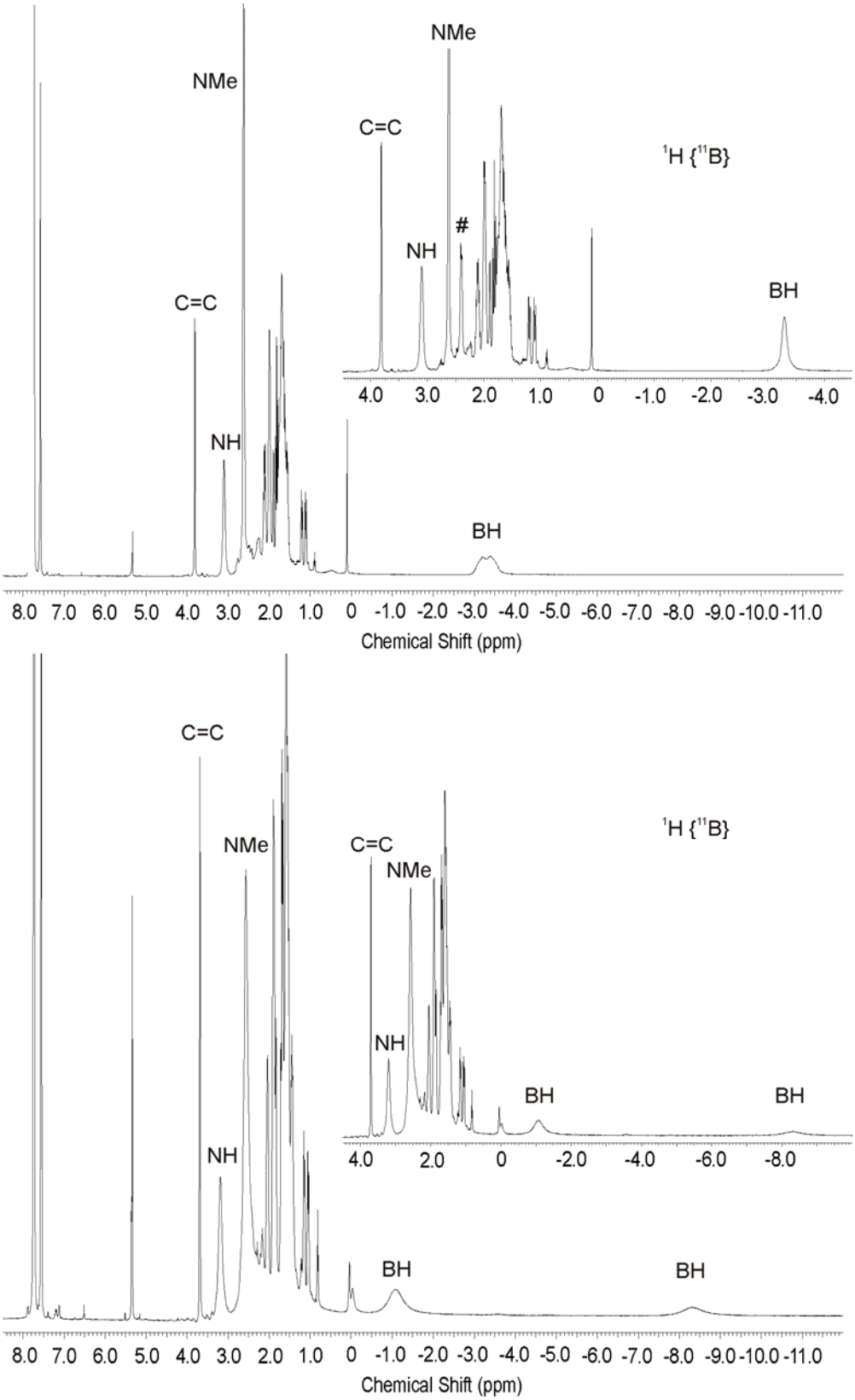

Figure S3: ^1H NMR (CD_2Cl_2) spectra of **4a[BAr$^F_4$]** at room temperature (top) and 200K (bottom).

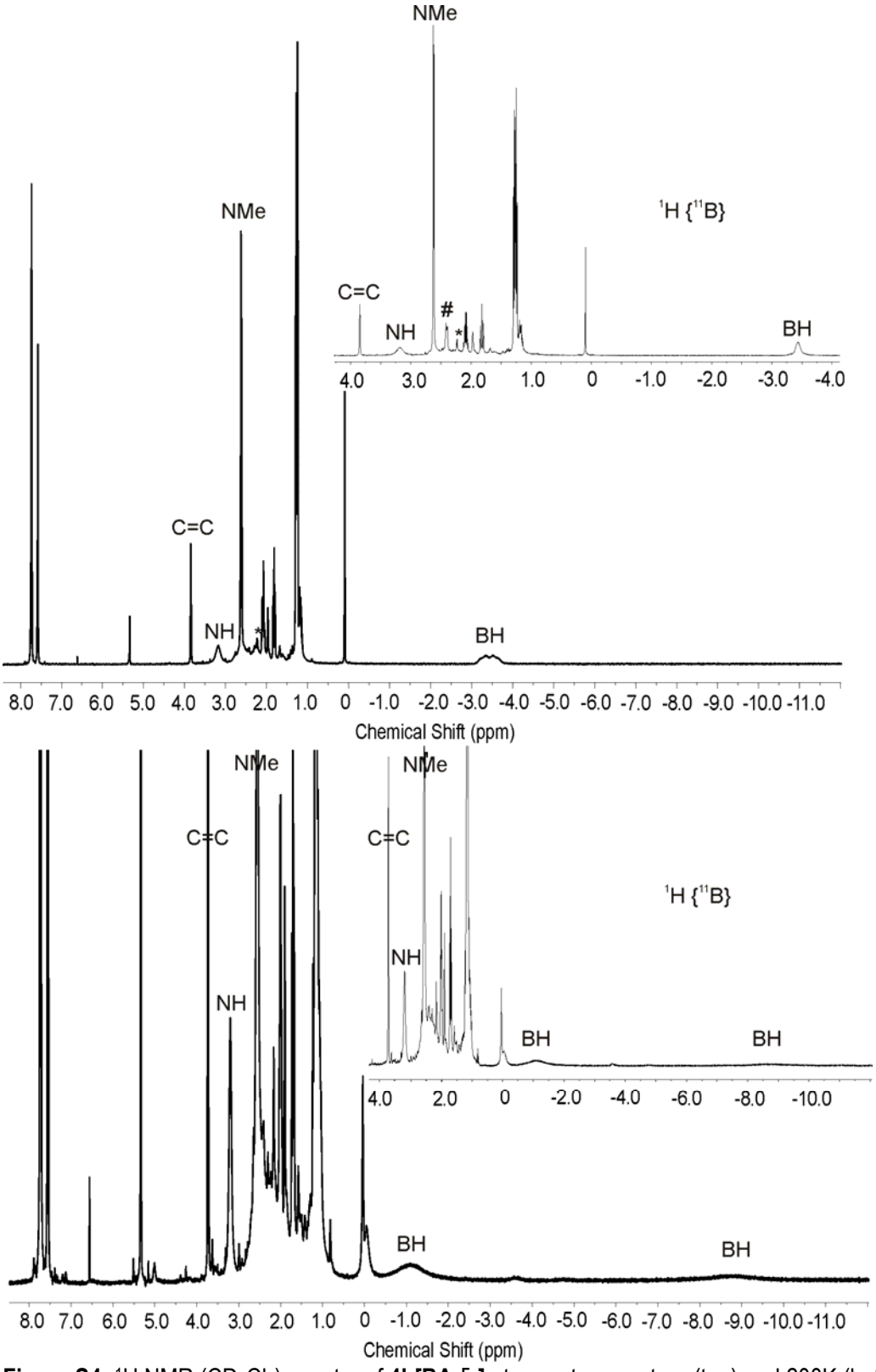

Figure S4: ^{1}H NMR (CD_2Cl_2) spectra of **4b[BAr$^F_4$]** at room temperature (top) and 200K (bottom).

Dehydrocoupling

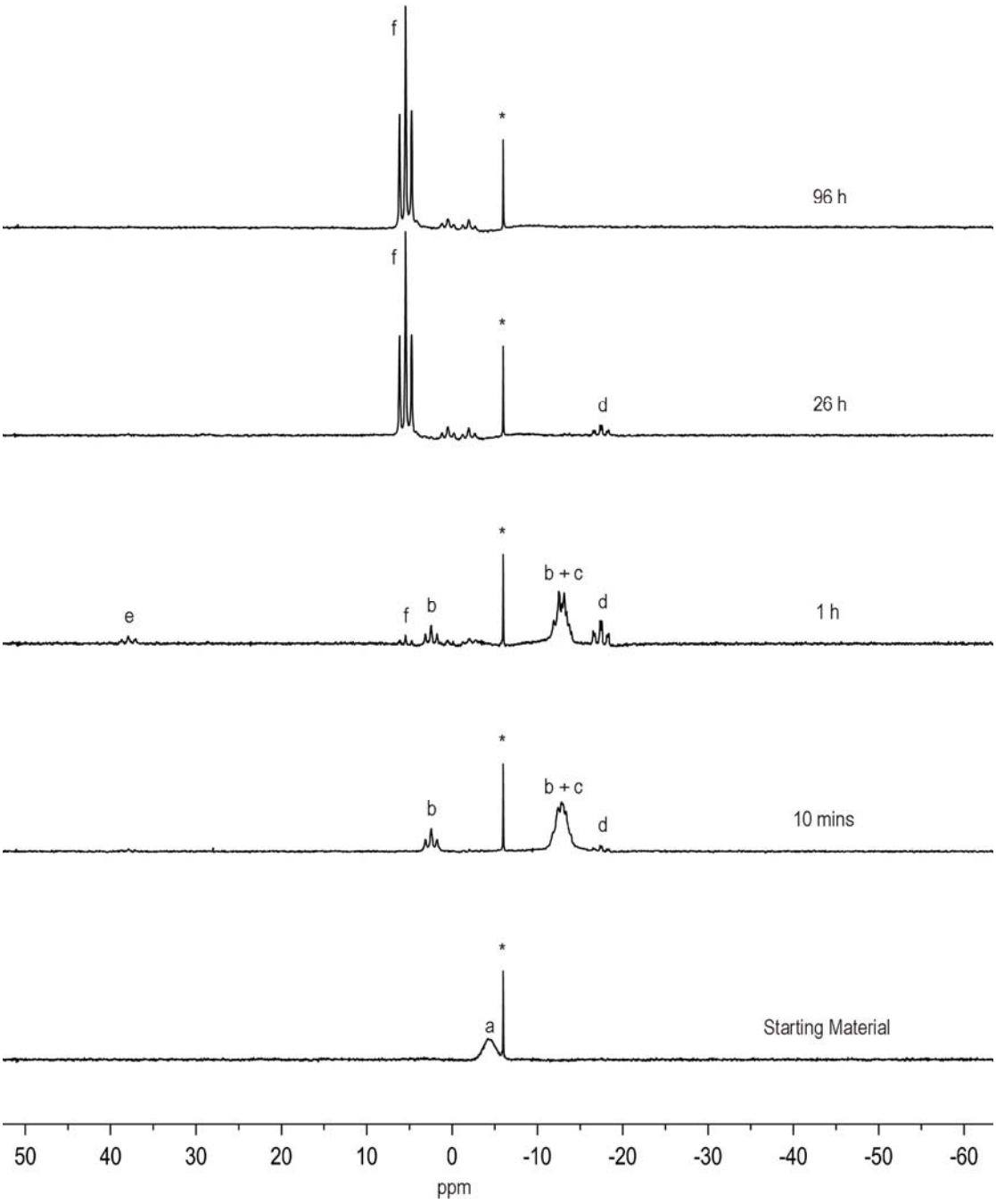

Figure S5: ^{11}B NMR spectra of the catalytic dehydrocoupling of $H_3B{\cdot}NMe_2H$ with **3a[BAr$^F_4$]** (20 mol %, 1,2-$C_6H_4F_2$). a = **3a**, b = $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$, c = $H_3B{\cdot}NMe_2H$, d = $(\mu\text{-}NMe_2)B_2H_5$, e = H_2BNMe_2, f = $[H_2BNMe_2]_2$, * = $[BAr^F_4]^-$.

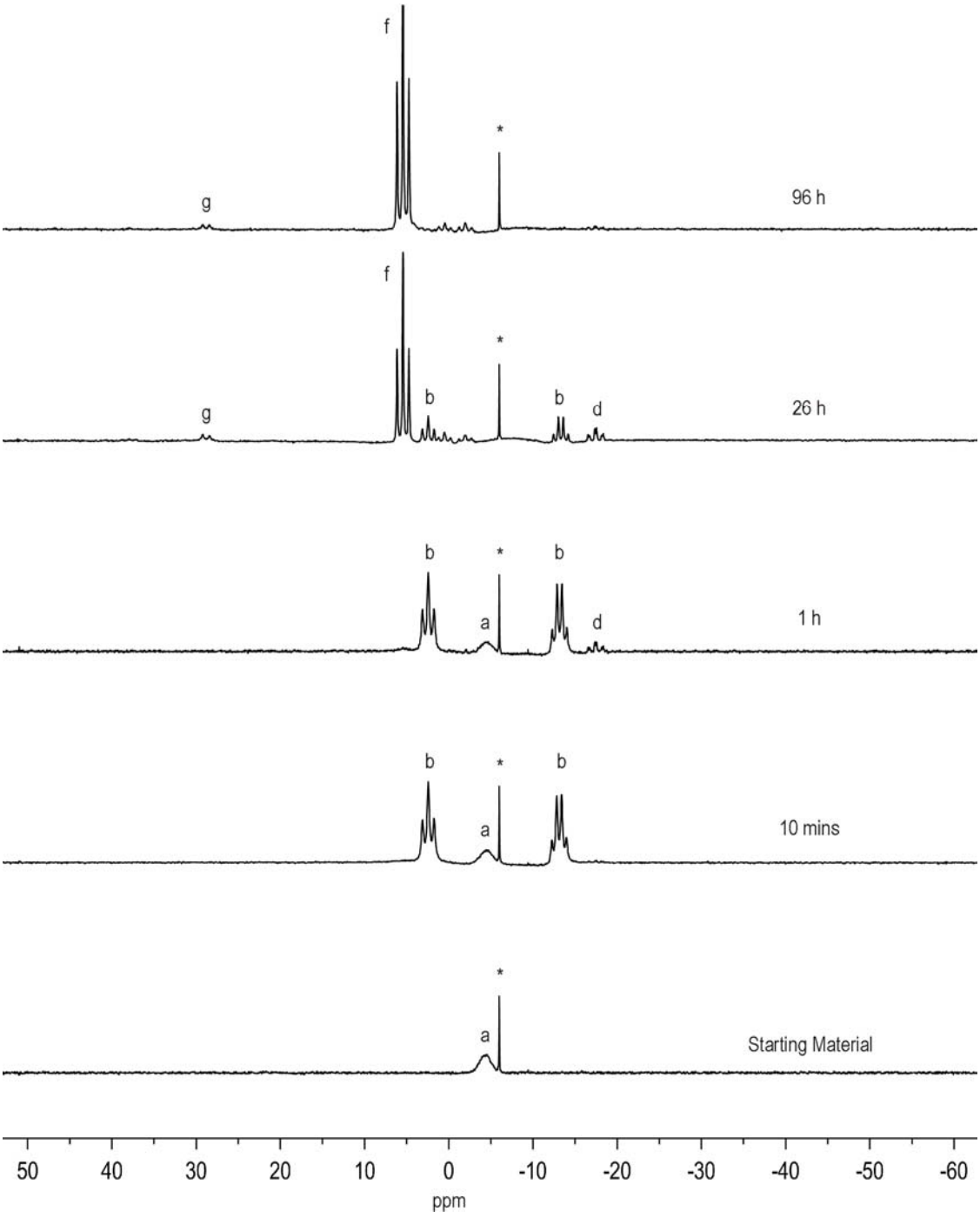

Figure S6: ^{11}B NMR spectra of the catalytic dehydrocoupling of $H_3B{\cdot}NMe_2BH_2{\cdot}NMe_2H$ with **3a[BAr$^F_4$]** (20 mol % relative to $H_3B{\cdot}NMe_2H$, 1,2-$C_6H_4F_2$). a = **3a**, b = $H_3BNMe_2BH_2NMe_2H$, d = (μ-NMe_2)B_2H_5, f = $[H_2BNMe_2]_2$, g = $(NMe_2)_2BH$, * = $[BAr^F_4]^-$.

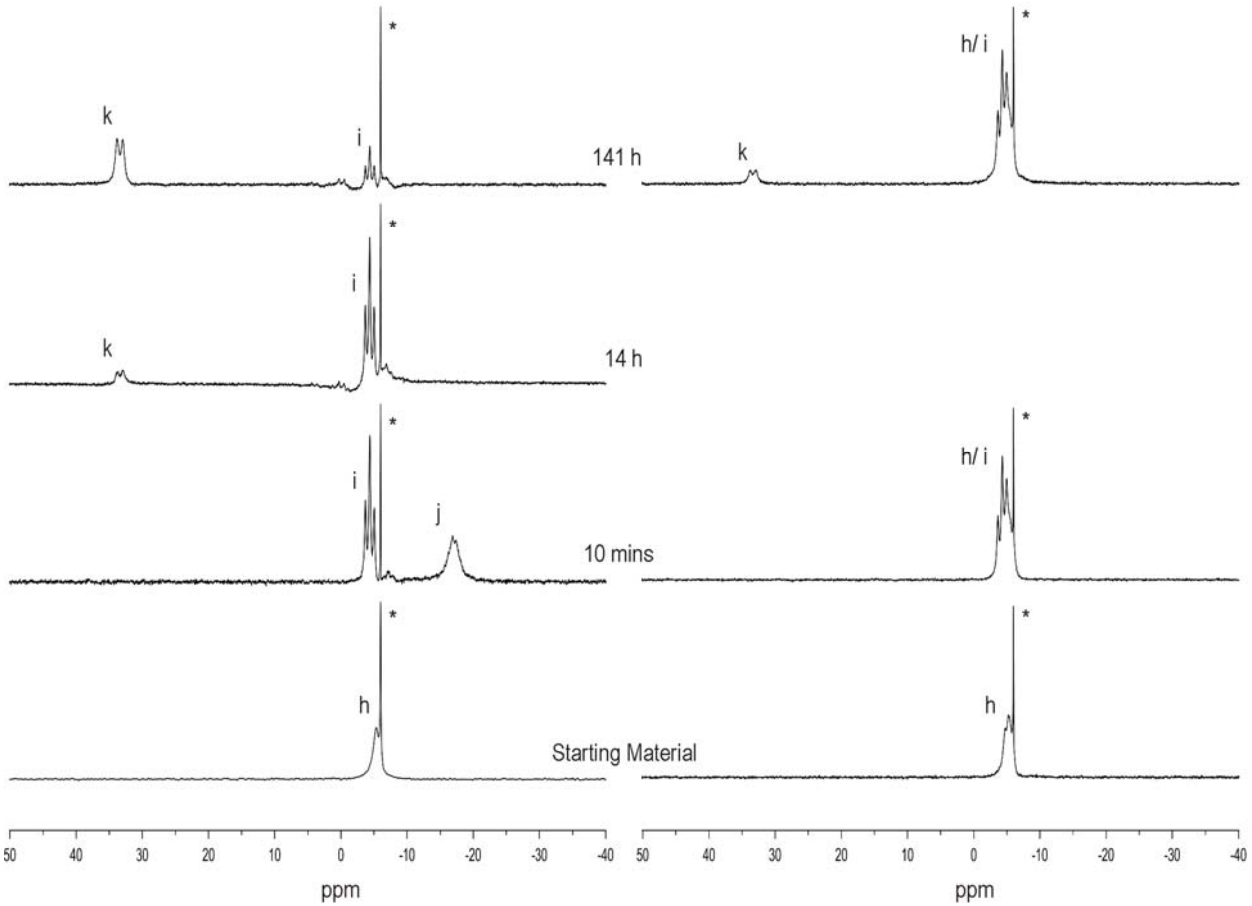

Figure S7: left: ^{11}B NMR spectra of the catalytic dehydrocoupling of $H_3B{\cdot}NMeH_2$ with **4a[BAr$^F_4$]** (20 mol %, 1,2-$C_6H_4F_2$). Right: ^{11}B NMR spectrum of the catalytic dehydrocoupling of $[H_2BNMeH]_3$ with **4a[BAr$^F_4$]** (20 mol % relative to $H_3B{\cdot}NMeH_2$, 1,2-$C_6H_4F_2$). h = **4a**, i = $[H_2BNMeH]_3$, j = $H_3B{\cdot}NMeH_2$, k = $[HBNMe]_3$, * = $[BAr^F_4]^-$. Partial solubility of i and j makes reliable ratios based upon relative intergrals difficult to obtain.

Crystallography

Data was acquired on a Nonius Kappa CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and a low-temperature device (150 K);[7] data was collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK.[8] Structures were solved by direct methods using SIR2004[9] and refined full-matrix least squares on F^2 using SHELXL-97.[8] All non-hydrogen atoms were refined anisotropically. The alkene and B-H hydrogen atoms were located on the difference map; their isotropic displacement parameters were fixed to ride on the parent atoms. The B-H hydrogen atoms were freely refined; restraints were applied to the alkene C-H distances. All other hydrogen atoms were placed in calculated positions using the riding model. Disorder of the fluorobenzene ligand in [Rh{P^{i}Pr$_2$(η^2-C$_5$H$_7$)}(η^6-C$_6$H$_5$F)][BAr$^F{}_4$] was treated by modelling the fluorine atom over two sites and restraining the 1,2 and 1,3-C-F distances. Disorder in the phosphine ligands (present in all structures) was treated by modelling the appropriate phosphine substituents over two sites and restraining their geometry. Disorder of the pentane solvent model in **4b[BAr$^F{}_4$]** was treated by modelling it over two sites and restraining its geometry (the central atom lies on a special position). Problematic solvent disorder in **3b[BAr$^F{}_4$]** was treated using the SQUEEZE algorithm.[10] Rotational disorder of the anion CF_3 groups was treated by modelling the fluorine atoms or the entire CF_3 group over two sites and restraining their geometry. Restraints to thermal parameters were applied where necessary in order to maintain sensible values. Graphical representations were made with ORTEP3.[11]

Table 1: Crystallographic data.

	[Rh{P^{i}Pr$_2$(η^2-C$_5$H$_7$)}(η^6-C$_6$H$_5$F)][BAr$^F_4$]	3a[BAr$^F_4$]	4a[BAr$^F_4$]
Formula	$C_{49}H_{38}BF_{25}PRh$	$C_{47}H_{51}B_3F_{24}N_2PRh$	$C_{46}H_{51}B_4F_{24}N_3PRh\cdot\frac{1}{2}(C_5H_{12})$
M	1246.48	1266.21	1315.09
cryst syst	Orthorhombic	Triclinic	Monoclinic
space group	$P2_12_12_1$	P-1	$P2_1/c$
a [Å]	12.51030(10)	13.11340(10)	13.22060(10)
b [Å]	19.3211(2)	15.09320(10)	18.33470(10)
c [Å]	20.3470(3)	15.6507(2)	24.0722(2)
α [deg]		84.6142(4)	
β [deg]		78.4318(4)	98.7365(4)
γ [deg]		86.9282(4)	
V [Å^3]	4918.13(10)	3019.40(5)	5767.30(7)
Z	4	2	4
density [gcm^{-3}]	1.683	1.393	1.515
μ (mm^{-1})	0.511	0.415	0.438
θ range [deg]	$5.10 \leq \theta \leq 26.37$	$5.10 \leq \theta \leq 26.37$	$5.14 \leq \theta \leq 26.37$
Reflns collected	9979 [R_{int} = 0.078]	23676 [R_{int} = 0.0154]	22949 [R_{int} = 0.0231]
Completeness	99.0 %	99.2 %	99.2 %
no. of data/restr/param	9979 / 409 / 805	12244 / 982 / 962	11699 / 590 / 930
*R*1 [$I > 2\sigma(I)$]	0.0406	0.0466	0.0415
*wR*2 [all data]	0.0986	0.1364	0.1143
GoF	1.023	1.082	1.041
Flack *x*	-0.03(2)		
Largest diff. pk and hole [eÅ^{-3}]	0.683, -0.503	0.744, -0.855	0.699, -0.619

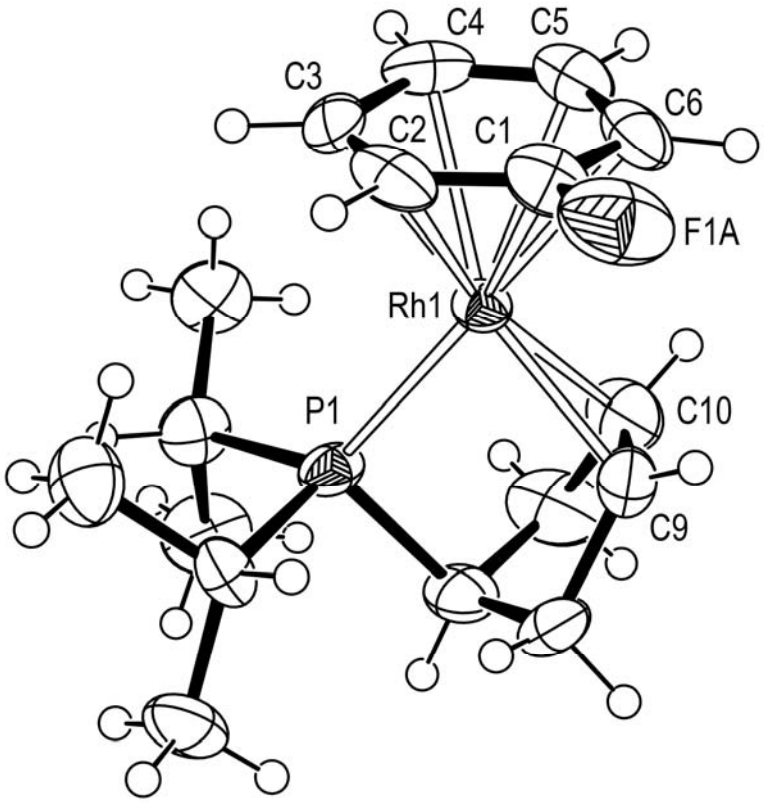

Figure S8: Solid-state structure of [Rh{P^{i}Pr$_2$(η^2-C$_5$H$_7$)}(η^6-C$_6$H$_5$F)][BAr$^F{}_4$]; ellipsoids are depicted at the 50% probability level. Anion and minor disordered components omitted for clarity. Selected bond lengths (Å): Rh1-P1, 2.2507(11); Rh1-C$_{arene}$, 2.259(4)-2.324(4); Rh1-C9, 2.127(5); Rh1-C10, 2.131(5).

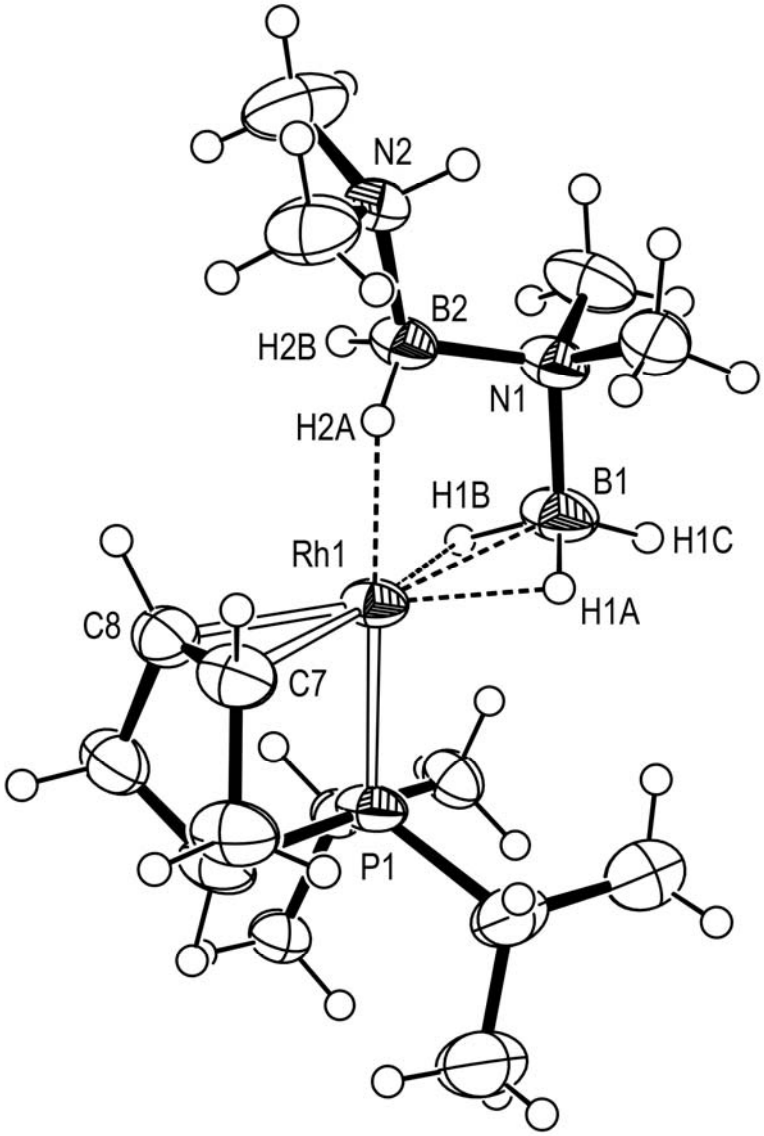

Figure S9: Solid-state structure of **3b[BAr$^F_4$]**; ellipsoids are depicted at the 50% probability level. Anion and minor disordered components omitted for clarity. Selected bond lengths (Å) and angles (º): Rh1-P1, 2.2058(9), Rh1-B1, 2.242(5); Rh1-B2, 2.626(4); Rh1-H1A, 1.85(5), Rh1-H1B, 1.84(5), Rh1-H2A, 1.96(4); Rh1-C7, 2.107(4); Rh1-C8, 2.121(4); B1-H1A, 1.23(5); B1-H1B, 1.22(5); B1-H1C, 1.13(5); B2-H2A, 1.13(4); B2-H2B, 1.12(4); B1-N1-B2, 103.3(3); N1-B2-N2, 112.7(3); Rh1-H2A-B2, 113(3).

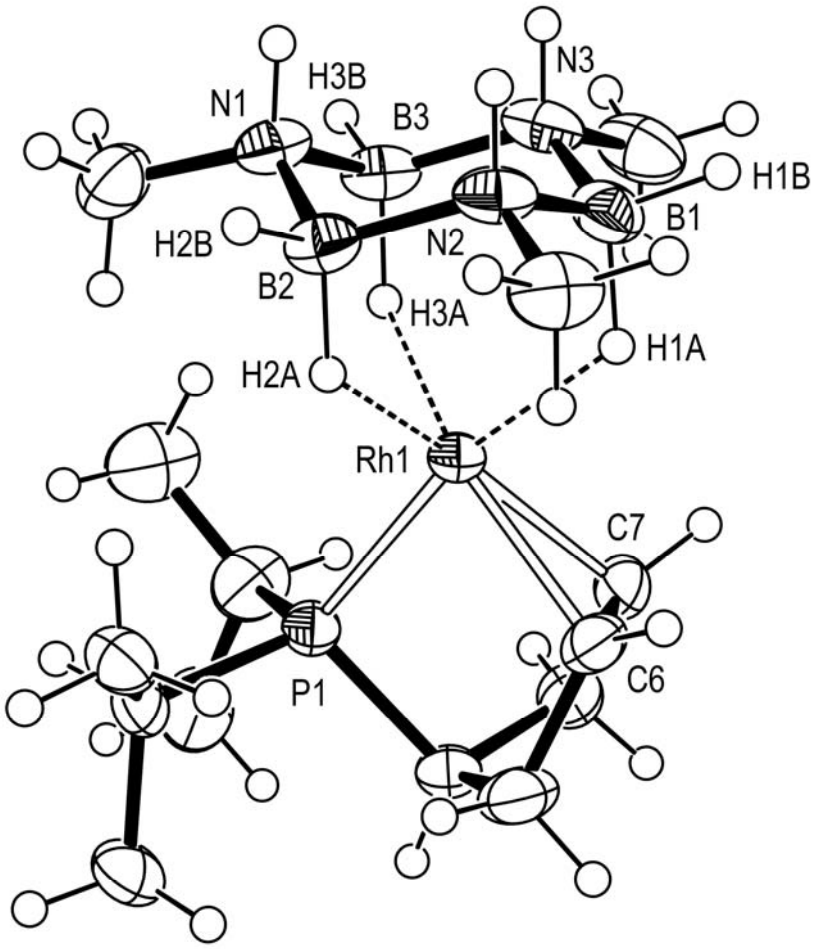

Figure S10: Solid-state structure of **4b[BAr$^F_4$]**; ellipsoids are depicted at the 50% probability level. Anion and minor disordered components omitted for clarity. Selected bond lengths (Å) and angles (º): Rh1-P1, 2.2354(8); Rh1-B1, 2.693(4); Rh1-B2, 2.808(4); Rh1-B3, 2.761(4); Rh1-H1A, 1.84(4); Rh1-H2A, 1.94(4); Rh1-H3A, 1.86(4); Rh1-C6, 2.096(3); Rh1-C7, 2.094(3); B1-H1A, 1.20(4); B1-H1B, 1.06(4); B2-H2A, 1.17(4); B2-H2B, 1.10(4), B3-H3A, 1.20(4); B3-H3B, 1.12(4); B1-N2-B2, 112.9(3); B2-N1-B3, 111.7(3); B3-N3-B1, 112.6(3); Rh1-H1A-B1, 123(3); Rh1-H2A-B2, 128(3); Rh1-H3A-B3, 128(3).

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