Supporting information for:

Catching the First Oligomerization event in the Catalytic Formation of Polyaminoboranes: $H_3B{\cdot}NMeHBH_2{\cdot}NMeH_2$ Bound to Iridium.

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General experimental procedures

All manipulations, unless otherwise stated, were performed under an argon atmosphere using standard Schlenk and glove-box techniques. Glassware was oven dried at 130 °C overnight and flamed under vacuum prior to use. Pentane, hexane, toluene, THF, CH_2Cl_2 and MeCN were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles.[1] C_6H_5F and 1,2-$C_6H_4F_2$ were dried over CaH_2, vacuum distilled and stored over 3 Å molecular sieves. CD_2Cl_2 was dried over CaH_2, distilled and stored in a glovebox. $H_3B{\cdot}NMe_3$ was purchased from Aldrich and sublimed prior to use (5 x 10^{-2} Torr, 298 K). $BH_3{\cdot}$THF was purchased from Aldrich and vacuum distilled prior to use. $MeNH_2$ was purchased from SIP Analytical Limited as the 'standard' grade and used as received. Na[$BAr^F{}_4$][2], Na[$BAr^{Cl}{}_4$][3], [$IrHPCy_2(\eta^2$-$C_6H_9)PCy_2(\eta^3$-$C_6H_8)$][$BAr^F{}_4$][4] and $H_3B{\cdot}NMeH_2$[5] were prepared by literature methods. NMR spectra were recorded on a Unity Plus 500 MHz spectrometer at room temperature, unless otherwise stated. In the case of free **2** in CD_2Cl_2, NMR spectra were recorded using a JEOL JNM-LA300. In C_6H_5F and 1,2-$C_6H_4F_2$, ^{1}H NMR spectra were referenced to the centre of the downfield solvent multiplet, δ = 7.11 and 7.07 respectively. ^{31}P and ^{11}B NMR spectra were referenced against 85% H_3PO_4 (external) and $BF_3{\cdot}OEt_2$ (external) respectively. The spectrometer was pre-locked to CD_2Cl_2. Chemical shifts (δ) are quoted in ppm and coupling constants (J) in Hz. ESI-MS were recorded on a Bruker MicrOTOF-Q instrument interfaced with a glove-box.[6] Microanalyses were performed by Elemental Microanalysis Ltd for all compounds, except **2** for which elemental analysis was performed with a Eurovector EA 3000 Elemental Analyser by Des Davis of the University of Bristol Microanalysis Laboratory.

Synthesis of new complexes

[$IrHPCy_2(\eta^2$-$C_6H_9)PCy_2(\eta^3$-$C_6H_8)$][$BAr^{Cl}{}_4$]

[$IrHPCy_2(\eta^2$-$C_6H_9)PCy_2(\eta^3$-$C_6H_8)$][$BAr^{Cl}{}_4$] was prepared using the literature method for [$IrHPCy_2(\eta^2$-$C_6H_9)PCy_2(\eta^3$-$C_6H_8)$][$BAr^F{}_4$] but by replacing Na[$BAr^F{}_4$] with Na[$BAr^{Cl}{}_4$]. Yield: 65 %.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 7.56 (m, 8H, [$BAr^{Cl}{}_4$]$^-$), 5.00 (br, 1H, alkenyl), 4.90 (br, 1H, alkenyl), 4.82 (br, 1H, alkenyl), 4.75 (br, 1H, alkenyl), 3.93 (br, 1H, alkenyl), 3.15 to 1.05 (m, 56H, Cy), -12.99 (dd, $^2J_{PH}$ = 10, $^2J_{PH}$ = 17, 1H, IrH). Other [$BAr^{Cl}{}_4$]$^-$ peak is obscured by the solvent.

^{31}P {^{1}H} NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 57.87 (d, $^2J_{PP}$ = 287, 1P), 8.13 (d, $^2J_{PP}$ = 287, 1P)

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ -6.4 (s, [$BAr^{Cl}{}_4$]$^-$)

$H_3B{\cdot}NMeHBH_2{\cdot}NH_2Me$ (2)

A 1 M solution of $BH_3{\cdot}$THF (50 mL, 50 mmol) was added to solid **1** (1.48 g, 32.8 mmol) and the mixture heated to 60 °C for 70 hours. The resulting solution was vacuum transferred to remove a small amount of unreacted **1**, producing a ~1 M solution of B_2H_5MeNH in THF (^{11}B {^{1}H} NMR: -23.2, becoming a broad poorly resolved multiplet on proton coupling). A 2 M THF solution of $MeNH_2$ (16.4 mL, 32.8 mmol) was added at -78 °C, and the mixture immediately warmed to RT before stirring overnight. The solvent was removed *in vacuo* to yield a crystalline white solid. Crystals suitable for X-ray diffraction were obtained by recrystallisation from CH_2Cl_2/hexane at -40 °C. Yield: 2.075 g (72 %)

^{1}H NMR (301 MHz, CD_2Cl_2): δ 4.27 (br s, 2H, N<u>H</u>$_2$), 2.49 (t, $^3J_{HH}$ = 6.2, 3H, NH$_2$<u>Me</u>), 2.26 (br s, 3H, NH<u>Me</u>), 1.31 (br q, $^1J_{BH}$ = 92.8, 3H, BH_3),

^{1}H {^{11}B} NMR (301 MHz, CD_2Cl_2): δ 4.27 (br s, 2H, NH_2), 2.49 (t, $^{3}J_{HH}$ = 6.2, 3H, NH_2Me), 2.26 (br s, 3H, NHMe), 2.05 (s, 1H, BH_2), 1.76 (s, 1H, BH_2), 1.31 (s, 3H, BH_3),

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 4.35 (br s, 1H, NH_2), 4.25 (br s,1H, NH_2), 2.47 (br s, 3H, NHMe), 2.45 (t, $^{3}J_{HH}$ = 6.2, 3H, NH_2Me), 1.99 (br q, $^{1}J_{BH}$ = 92.8, 3H, BH_3)

The NHMe peak is not seen in either solvent, presumably as too broad.

^{11}B NMR (96 MHz, CD_2Cl_2): δ -6.2 (t, $^{1}J_{BH}$ = 106.1, 1B, BH_2), -19.3 (q, $^{1}J_{BH}$ = 91.9, 1B, BH_3)

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ -4.8 (t, $^{1}J_{BH}$ = 112.0 Hz, 1B, BH_2), -17.7 (q, $^{1}J_{BH}$ = 93.5, 1B, BH_3)

^{13}C NMR (76 MHz, CD_2Cl_2): δ 40.9 (1C, NHMe), 31.6 (1C, NH_2Me).

Elemental Microanalysis: Calc. $C_2H_{14}B_2N_2$ (88.13 gmol^{-1}): C, 27.23; H, 16.01; N, 31.78. Found: C, 27.66; H, 15.96; N, 31.54.

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeH_2)][BAr^F{}_4]$ (4)

3 was formed *in situ* by the hydrogenation of $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F{}_4]$ (50 mg, 0.031 mmol) at 4 atm in 1,2-$C_6H_4F_2$. After 30 minutes, the colourless solution was opened under argon and rapidly transferred to a Young's flask containing solid **1** (1.4 mg, 0.031 mmol) and stirred for 1 hour. The solution was then transferred into a Schlenk and pentane (50 mL) was added, and the colourless mixture was cooled to -18 °C for 10 days, after which an off-white solid had formed. The solid was washed with pentane (2 x 5 mL) and dried *in vacuo*. Yield: 25 mg (48 %). Crystals suitable for X-ray diffraction were obtained by recrystallisation from C_6H_5F/pentane at 5 °C.

^{1}H NMR (500 MHz, C_6H_5F): δ 8.36 (br, 8H, $[BAr^F{}_4]^-$), 7.66 (s, 4H, $[BAr^F{}_4]^-$), 3.65 (br, 2H, NH_2), 2.39 (t, $^{3}J_{HH}$ = 6, 3H, NMe), 2.20 to 1.10 (m, 66H, Cy), -6.01 (br, 2H, σ-bound BH_2), -20.29 (overlapping dd, $^{2}J_{HP}$ ~ 15, $^{2}J_{HP}$ ~ 17, 2H, IrH_2). The remaining BH signal is not observed, presumably as too broad.

^{1}H NMR (500 MHz, C_6H_5F, 250 K): δ 8.36 (br, 8H, $[BAr^F{}_4]^-$), 7.66 (s, 4H, $[BAr^F{}_4]^-$), 6.09 (br, 1H, BH not σ-bound), 3.64 (br, 2H, NH_2), 2.40 (t, $^{3}J_{HH}$ = 6, 3H, NMe), 2.20 to 1.10 (m, 66H, Cy), -6.01 (br, 2H, σ-bound BH_2), -20.11 (m, 2H, IrH_2)

^{31}P {^{1}H} NMR (202 MHz, C_6H_5F): δ 39.67 (br d, 1P), 32.82 (br d, 1P)

^{31}P {^{1}H} NMR (202 MHz, C_6H_5F, 250 K): δ 39.35 (d, $^{2}J_{PP}$ = 283, 1P), 32.66 (d, $^{2}J_{PP}$ = 283, 1P)

^{11}B NMR (160 MHz, C_6H_5F): δ 13 (br, bound BH_3), -6.0 (s, $[BAr^F{}_4]^-$)

ESI-MS (1,2-$C_6H_4F_2$, 60 °C, 4.5 kV): m/z 800.5285 $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeH_2)]^+$ (calc. 800.5178)

Elemental Microanalysis: Calc. $C_{69}H_{88}B_2F_{24}IrNP_2$ (1663.19 gmol^{-1}): C, 49.83; H, 5.33; N, 0.84. Found: C, 50.06; H, 5.46; N, 0.81.

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeHBH_2{\cdot}NMeH_2)][BAr^{Cl}{}_4]$ (5)

3 was formed *in situ* by the hydrogenation of $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^{Cl}{}_4]$ (50 mg, 0.037 mmol) at 4 atm in 1,2-$C_6H_4F_2$. After 30 minutes, the colourless solution was opened under argon and rapidly transferred to a

Young's flask containing solid **1** (4 mg, 0.09 mmol) and stirred for 4 hours. The solution was then filtered into a Schlenk and pentane (30 mL) was added, and the colourless mixture was cooled to -18 °C overnight, yielding colourless crystals, which were washed with pentane (2 x 5 mL) and dried *in vacuo*. Yield: 23 mg (43 %). Crystals suitable for X-ray diffraction were obtained by recrystallisation from 1,2-$C_6H_4F_2$/pentane at 5 °C. The preparation of **5** with the $BAr^F{}_4^-$ anion was conducted *in situ* and gave similar NMR spectra to the $BAr^{Cl}{}_4^-$ salt, although crystalline material was could not be isolated.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 7.56 (m, 8H, $[BAr^{Cl}{}_4]^-$), 6.42 (br, 1H, BH not σ-bound), 4.13 (br, 1H, NMe$\underline{H}_2$), 4.02 (br, 1H, NMe$\underline{H}_2$), 2.99 (br, 1H, NMe$\underline{H}$), 2.76 (overlapping dd, $^3J_{HH}$ = 6.3 and 6.0, 3H, N$\underline{Me}H_2$), 2.67 (d, $^3J_{HH}$ = 5.8, 3H, N$\underline{Me}$H), 2.43 (br, 2H, BH_2), 2.2 to 1.1 (m, 66H, Cy), -6.15 (br, 1H, σ-bound BH_2), -6.32 (br, 1H, σ-bound BH_2), -19.78 (m, 2H, IrH_2). Other $[BAr^{Cl}{}_4]^-$ peak is obscured by the solvent.

^{1}H {^{11}B} NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 7.57 (m, 6H, $[BAr^{Cl}{}_4]^-$), 6.45 (br, 1H, BH not σ-bound), 4.13 (br, 1H, NMe$\underline{H}_2$), 4.02 (br, 1H, NMe$\underline{H}_2$), 2.99 (br, 1H, NMe$\underline{H}$), 2.76 (overlapping dd, $^3J_{HH}$ = 6.3 and 6.0, 3H, N$\underline{Me}H_2$), 2.69 (d, $^3J_{HH}$ = 5.8, 3H, N$\underline{Me}$H), 2.48 (s, 1H, BH_2), 2.37 (s, 1H, BH_2), 2.2 to 1.1 (m, 66H, Cy), -6.11 (s, 1H, σ-bound BH_2), -6.32 (s, 1H, σ-bound BH_2), -19.78 (m, 2H, IrH_2)

^{31}P {^{1}H} NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 37.91 (d, $^2J_{PP}$ = 285, 1P), 33.01 (d, $^2J_{PP}$ = 285, 1P)

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ 17.1 (br, bound BH_3), -5.8 (br, BH_2), -6.5 (s, $[BAr^{Cl}{}_4]^-$)

ESI-MS (1,2-$C_6H_4F_2$, 60 °C, 4.5 kV): m/z 843.5789 $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeHBH_2{\cdot}NMeH_2)]^+$ (calc. 843.5777)

Elemental Microanalysis: Calc. $C_{62}H_{94}B_3Cl_8IrN_2P_2$ (1437.64 gmol^{-1}): C, 51.80; H, 6.59; N, 1.95. Found: C, 52.39; H, 6.67; N, 1.91.

$H_3B{\cdot}NMeD_2$

$H_3B{\cdot}NMeH_2$ (100 mg, 2.22 mmol) was dissolved in degassed D_2O (0.8 mL, 44.4 mmol) and stirred at 40 °C for 24 h. The solution was then extracted with CH_2Cl_2 (3 x 1 mL), the organic layer was dried with $MgSO_4$ and filtered, and the volatiles were removed under vacuum. The resulting white solid was recrystallised twice with Et_2O. Yield: 56 mg (54 %).

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 2.54 (br s, 3H, NMe), 2.19 (q, $^1J_{BH}$ = 97, 3H, BH_3)

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ -17.0 (q, $^1J_{BH}$ = 97, BH_3)

^{2}H NMR (77 MHz, 1,2-$C_6H_4F_2$): δ 3.31 (s, ND_2)

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeD_2)][BAr^F{}_4]$

3 was formed *in situ* by the hydrogenation of $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F{}_4]$ (24 mg, 0.015 mmol) at 4 atm in 1,2-$C_6H_4F_2$ in a high pressure NMR tube. After 30 minutes, the colourless solution was opened under argon and rapidly transferred to a second high pressure tube containing solid $H_3B{\cdot}NMeD_2$ (0.7 mg, 0.015 mmol). *In situ* NMR spectroscopy indicated that $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeD_2)][BAr^F{}_4]$ had been formed quantitatively.

^{1}H NMR (500 MHz, 1,2-$C_6H_4F_2$): δ 8.32 (br, 8H, $[BAr^F{}_4]^-$), 7.68 (s, 4H, $[BAr^F{}_4]^-$), 2.94 (br s, 3H, NMe), 2.20 to 1.10 (m, 66H, Cy), -5.76 (br, 2H, σ-bound BH_2), -20.14 (overlapping dd, $^2J_{HP}$ ~ 15, $^2J_{HP}$ ~ 17, 2H, IrH_2). The remaining BH signal is not observed, presumably as too broad.

^{31}P {^{1}H} NMR (202 MHz, 1,2-$C_6H_4F_2$): δ 39.76 (br d, 1P), 32.89 (br d, 1P)

^{11}B NMR (160 MHz, 1,2-$C_6H_4F_2$): δ 13 (br, bound BH_3), -6.0 (s, $[BAr^F{}_4]^-$)

^{2}H NMR (77 MHz, 1,2-$C_6H_4F_2$): δ 4.32 (br s, ND_2Me)

Reaction between 4 and $H_3B{\cdot}NMe_3$

3 was formed *in situ* by the hydrogenation of $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F{}_4]$ (16 mg, 0.01 mmol) at 4 atm in C_6H_5F in a high pressure NMR tube. After 30 minutes, the tube was opened under argon and the solution transferred to another high pressure NMR tube containing solid $H_3B{\cdot}NMeH_2$ (0.4 mg, 0.01 mmol). *In situ* NMR spectroscopy indicated that **4** had been formed quantitatively. The solution was transferred to a high pressure NMR tube containing solid $H_3B{\cdot}NMe_3$ (0.7 mg, 0.01 mmol). After 24 hours, NMR spectra (^{11}B NMR spectrum shown in Figure S-1) revealed the known complex $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMe_3)][BAr^F{}_4]$ and $[HBNMe]_3$ as the major products. An excess of $H_3B{\cdot}NMe_3$ was also apparent. ESI-MS was consistent with $[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMe_3)][BAr^F{}_4]$ being only charged product after 48 hours.

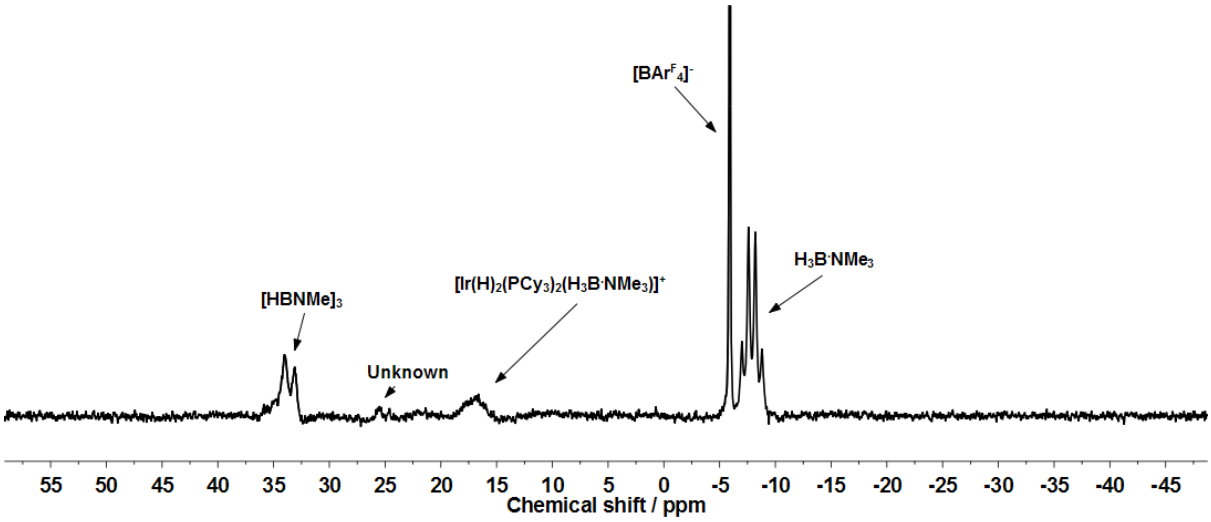

Figure S-1 ^{11}B NMR spectrum of **4** and $H_3B{\cdot}NMe_3$ after 24 hours.

Catalytic reaction between 1 and 3 (10 mol%)

3 was formed *in situ* by the hydrogenation of $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F{}_4]$ (16 mg, 0.01 mmol) at 4 atm in C_6H_5F (0.4 mL) in a high pressure NMR tube. After 30 minutes, the solution was opened under argon and transferred to another high pressure NMR tube containing solid $H_3B{\cdot}NMeH_2$ (4.5 mg, 0.1 mmol). Catalysis was followed by a combination of ^{1}H, ^{31}P{^{1}H} and ^{11}B NMR spectroscopy. The ^{11}B NMR spectrum upon completion of catalysis is shown in Figure S-2.

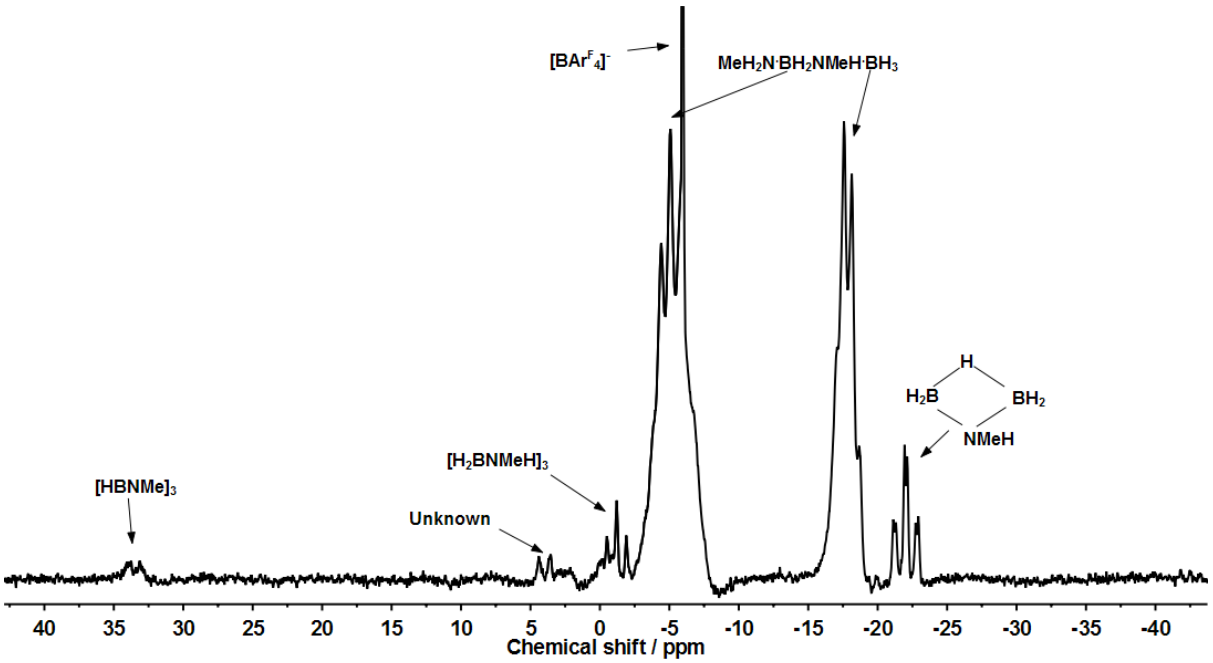

Figure S-2 ^{11}B NMR spectrum of the reaction between **1** and **3** (10 mol%) on completion of catalysis.

Reaction between 5 and 1 (1eq.)

Solid **5** (16.2 mg, 0.01 mmol) was dissolved in 1,2-$C_6H_4F_2$ in a high pressure NMR tube. The solution was then transferred to another tube containing solid $H_3B{\cdot}NMeH_2$ (0.5 mg, 0.01 mmol) and the solution heated to 40 °C. The reaction was followed by a combination of NMR spectroscopy and ESI-MS. No evidence for further oligomeric species was seen by NMR and ESI-MS.

Reaction between 4-*N*-D_2 and 1

$[Ir(H)_2(PCy_3)_2(H_3B{\cdot}NMeD_2)][BAr^F_4]$ (0.015 mmol), formed *in situ* in a high pressure NMR tube in 1,2-$C_6H_4F_2$, was degassed and transferred to another high pressure tube containing solid **1** (0.7 mg, 0.015 mmol). The reaction was followed by a combination of ^{1}H, ^{31}P, ^{11}B and ^{2}H NMR spectroscopy, which indicated that bound oligomer had been formed in quantitative yield. Deuterium was partially incorporated in all NH positions, the BH_2 signal at ~ -6ppm, IrH_2 and the cyclohexyl signals (potentially including the BH_2 signal that is found under the cyclohexyl peaks). In addition, both HD (δ 4.56, t, $^1J_{HD}$ = 43) and H_2 (δ 4.59, s) were observed.

Reaction between 3 and 2

3 was formed *in situ* by the hydrogenation of $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F_4]$ (16 mg, 0.01 mmol) at 4 atm in C_6H_5F (0.4 mL) in a high pressure NMR tube. After 30 minutes, the solution was opened under argon and transferred to another high pressure NMR tube containing solid $H_3B{\cdot}NMeHBH_2.NMeH_2$ (0.9 mg, 0.1 mmol). ^{1}H, ^{31}P and ^{11}B NMR indicated that **5** was formed quantitatively.

Reaction between 4 and D_2

4 (0.01 mmol) was formed *in situ* in a high pressure NMR tube and immediately frozen in liquid N_2 and degassed. The sample was thawed and the headspace was rapidly refilled with D_2 (4 psi). The sample was again frozen before following with ^{1}H, ^{11}B, ^{31}P and ^{2}H NMR spectroscopy for 2 hours. Deuterium was observed in the IrH, BH and PCy_3 CH signals, but no ND signals were observed.

Reaction between 5 and MeCN (10 eq.)

5 (0.01 mmol) was formed *in situ* in a high pressure NMR tube in C_6H_5F. 5 µL (0.1 mmol) of MeCN was added and the solution was immediately frozen. The reaction was monitored by ^{1}H, ^{11}B and ^{31}P NMR, which initially showed free **2** and the complex $[Ir(PCy_3)_2H_2(NCMe)_2][BAr^F_4]$. However, after 30 minutes, **2** was almost completely converted to $[H_2BNMeH]_3$ and $[HBNMe]_3$. After 24 hours, all **2** had been consumed.

Reaction between 5 and 1 (8 eq.)

5 (0.01 mmol) was formed *in situ* in a high pressure NMR tube in C_6H_5F and checked by NMR spectroscopy. The sample was added to another high pressure NMR tube containing **1** (3.6 mg, 0.08 mmol) and the reaction was monitored by ^{1}H, ^{11}B and $^{31}P\{^{1}H\}$ NMR spectroscopy, which showed 5 to be a competent catalyst for the formation of **2**.

Reaction between 3 and $[H_2BNMeH]_3$

3 was formed *in situ* by the hydrogenation of $[IrHPCy_2(\eta^2\text{-}C_6H_9)PCy_2(\eta^3\text{-}C_6H_8)][BAr^F_4]$ (16 mg, 0.01 mmol) at 4 atm in C_6H_5F (0.4 mL) in a high pressure NMR tube. After 30 minutes, the solution was opened under argon and transferred to another high pressure NMR tube containing solid $[H_2BNMeH]_3$ (1.2 mg, 0.01 mmol). After 1 hour, ^{11}B NMR spectroscopy indicated complete conversion to $[HBNMe]_3$ (Figure S-3). ^{1}H and $^{31}P\{^{1}H\}$ NMR spectroscopy showed that **3** remained intact.

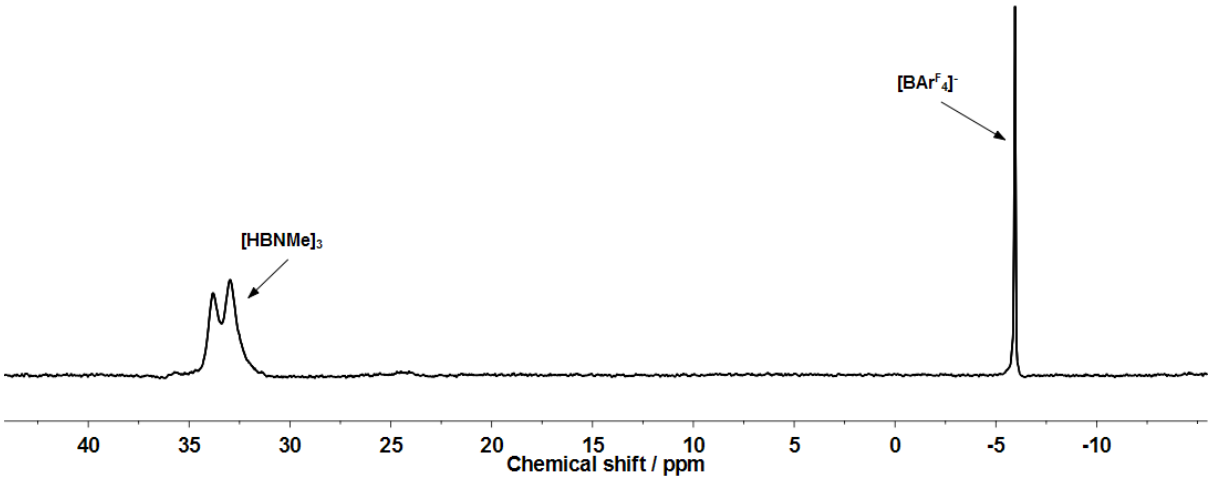

Figure S-3 ^{11}B NMR spectrum of **3** and $[H_2BNMeH]_3$ after 1 hour.

ESI-MS and NMR spectra of 5

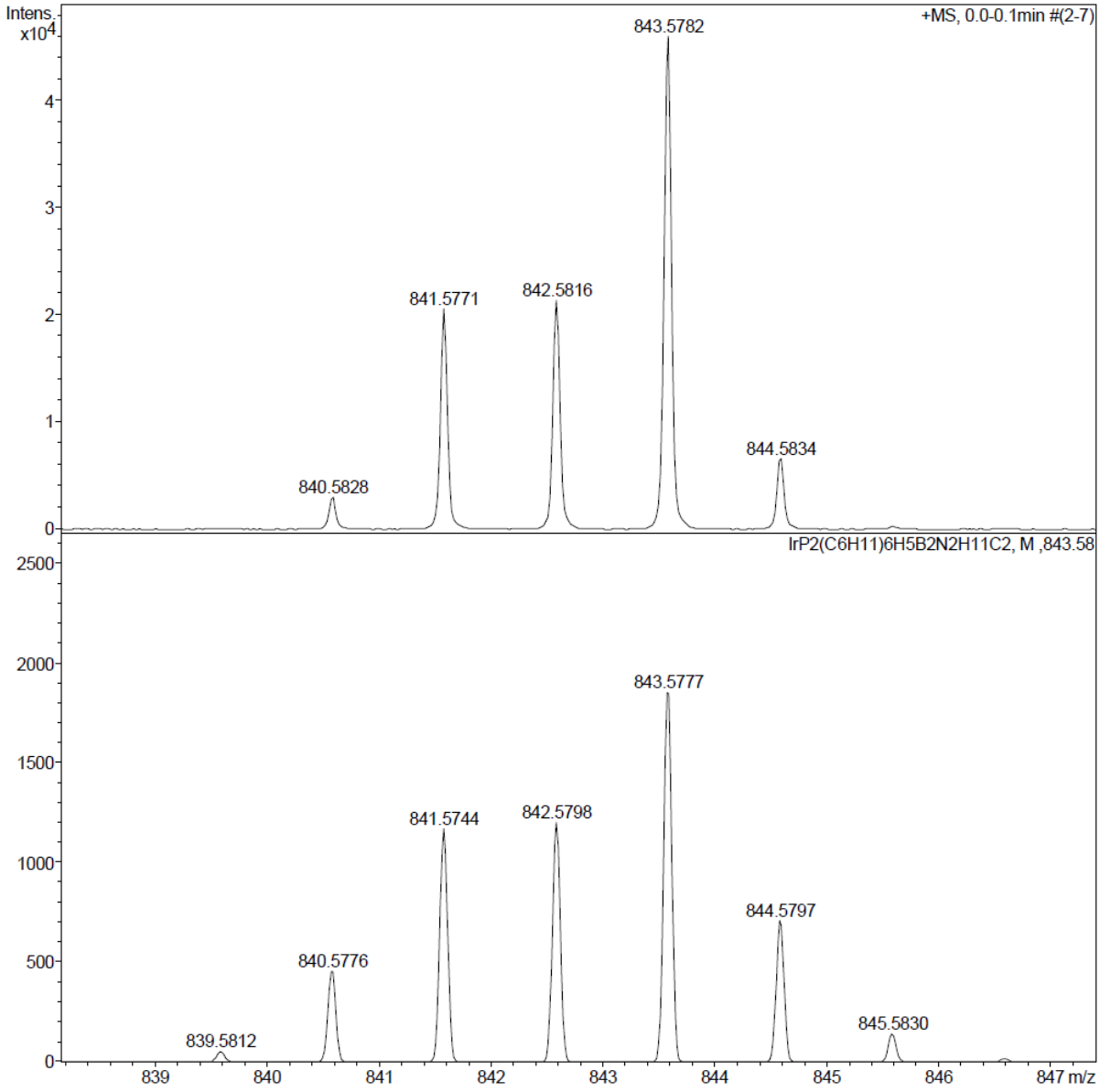

Figure S-4 ESI-MS of **5** (top) and simulated spectrum (bottom).

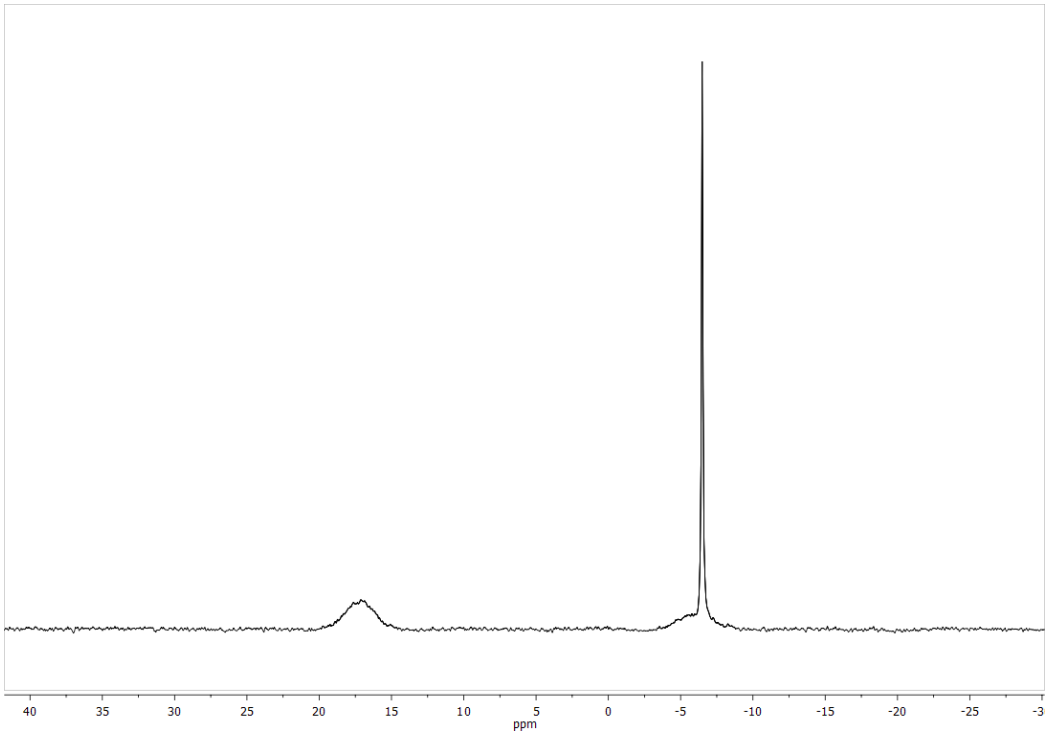

Figure S-5 ^{11}B NMR spectrum of **5**.

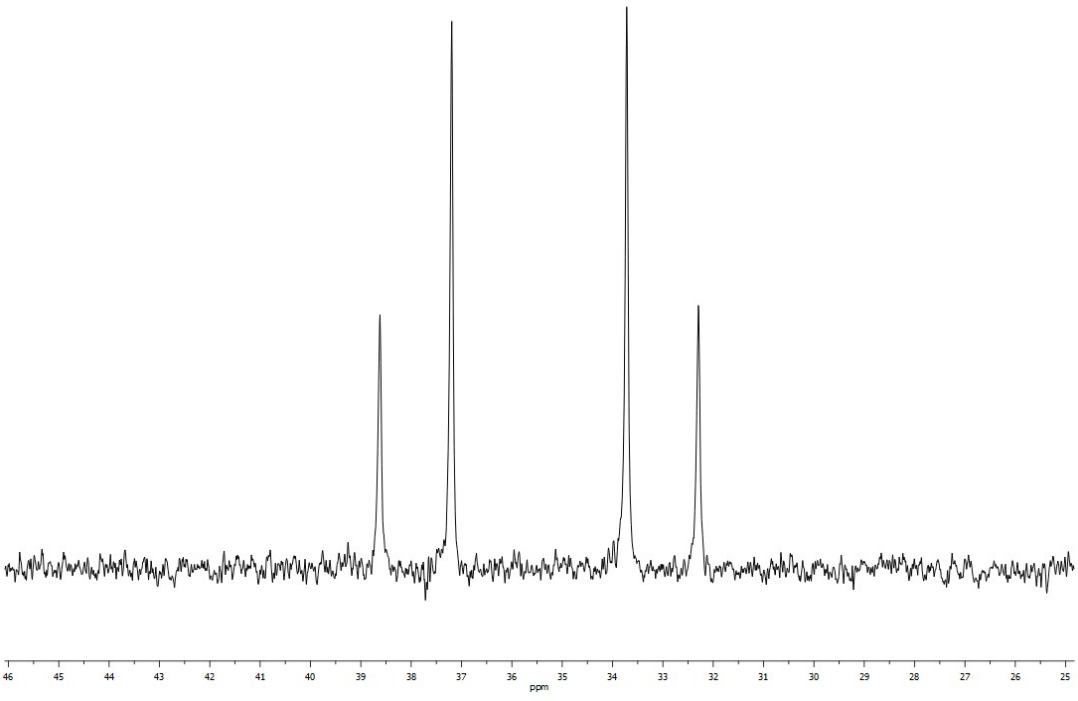

Figure S-6 $^{31}P\{^{1}H\}$ NMR spectrum of **5**

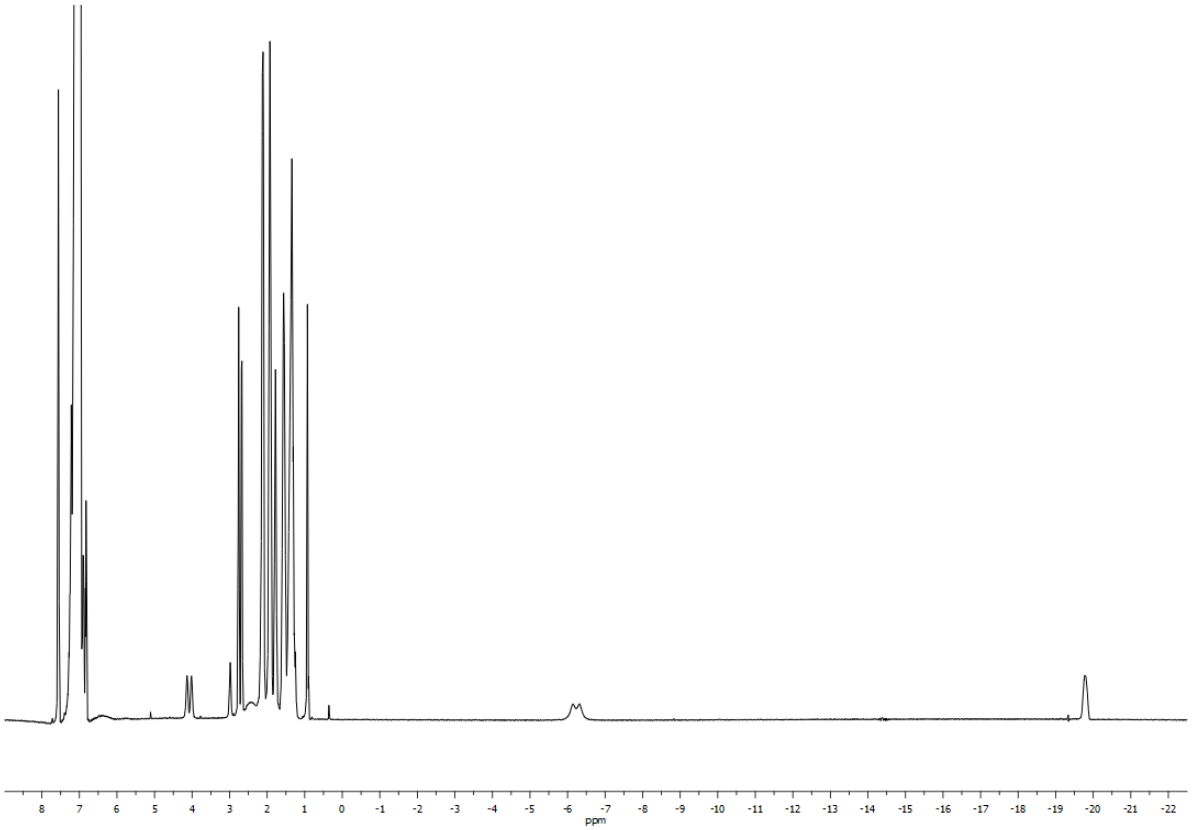

Figure S-7 ^{1}H NMR spectrum of **5**

References

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