Supporting Information

P–C-Activated Bimetallic Rhodium Xantphos Complexes: Formation and Catalytic Dehydrocoupling of Amine–Boranes**

Heather C. Johnson* and Andrew S. Weller*

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Experimental

Synthesis of new complexes

Reaction between complex 5 and H₃B·NMe₂H (4 eq.)

Addition of MeCN to complex 4

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Experimental

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, CH₂Cl₂ and MeCN were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze-pump-thaw cycles. C₆H₅F, 1,2-C₆H₄F₂ (pretreated with alumina) and CD₂Cl₂ were dried over CaH₂, vacuum distilled and stored over 3 Å molecular sieves. H₃B·NMe₃ and H₃B·NMe₂H were purchased from Aldrich and sublimed prior to use (5 x 10⁻² Torr, 298 K). H₃B·NMMeH₂ was formed by a modification of the literature method. [Rh(κ²P,P-Xantphos)(nbd)][BArF₄] (nbd = norbornadiene), [Rh(κ³P,P-Xantphos)(η²-H₂B(CH₂CH₂Bu·NMe3)][BArF₄] (1), [Rh(k³P,O,P-Xantphos)(PCy3)][BArF₄], [Rh(k³P,O,P-Xantphos)(H)₂(NCMe)][BArF₄], D₃B·NMe₂H, H₃B·NMe₂D and Na[H₃B·NMe₂·BH₃] were prepared by literature methods. NMR spectra were recorded on a Bruker AVIII-500 spectrometer at room temperature, unless otherwise stated. 1,2-Bis(diphenylphosphino)ethane (dppe) was purchased from Aldrich. In 1,2-C₆H₄F₂, ¹H NMR spectra were pre-locked to a sample of C₆D₆ (25%) and 1,2-C₆H₄F₂ (75%) and referenced to the centre of the downfield solvent multiplet, δ = 7.07. ³¹P and ¹¹B NMR spectra were referenced against 85% H₃PO₄ (external) and BF₃·OEt₂ (external) respectively. Chemical shifts (δ) are quoted in ppm and coupling constants (J) in Hz. ESI-MS were recorded on a Bruker MicrOTOF instrument interfaced with a glove-box. GC-MS was performed on a Waters GCT ToF mass spectrometer. Microanalyses were performed by Elemental Microanalysis Ltd. Gel permeation chromatography (GPC) was performed on a Viscotek Rlmax chromatograph, equipped with an automatic sampler, a pump, an injector and inline degasser. Fractionation was achieved with two T5000 columns that were contained within an oven at 35 °C. THF containing 0.1% w/w [¹Bu₄N]Br was used as the eluent at a flow rate of 1.0 mL min⁻¹. Samples were dissolved in the eluent (2 mg mL⁻¹, unless otherwise stated), stirred for 1 h at room temperature and filtered with a Ministart SRP 15 filter (polytetrafluoroethylene membrane of 0.45 μm pore size) before analysis. The calibration was conducted using a series of monodisperse polystyrene standards obtained from Aldrich.
Synthesis of new complexes

$$[\text{Rh}_2(\kappa^2_{P,P}-\text{Xantphos'})_2(\mu-\eta^2:\eta^2-\text{H}_3\text{B}\cdot\text{NMe}_2\cdot\text{BH}_3)][\text{BArF}_4] \quad (4)$$

![Complex 4](image)

**Figure S-1** Complex 4. [BArF₄]⁻ anion not shown.

In a Young’s crystallisation flask containing 1 (20 mg, 0.012 mmol) dissolved in 0.5 mL 1,2-C₆H₄F₂, H₃B-NMe₂H (13.8 mg, 0.234 mmol) dissolved in 0.6 mL 1,2-C₆H₄F₂ was added. Bubbling was observed immediately upon addition and the flask was sealed. After 12 hours, ¹H, ³¹P{¹H} and ¹¹B NMR spectroscopies indicated that 4 was the major metal-containing product, and complete consumption of H₃B-NMe₂H had occurred to yield [H₂BNMe₂]₂ as the major product of dehydrocoupling. The total volume of solution was reduced to ~ 0.5 mL *in vacuo* and pentane (5 mL) was added with stirring, resulting in a cloudy brown solution. On cooling to -78 °C, a brown solid precipitated. The yellow supernatant solution was decanted and the solid washed twice with pentane (2 x 3 mL), each time with sonication. The solid was recrystallised from 1,2-C₆H₄F₂ and pentane at 5 °C, from which orange crystals suitable for X-ray diffraction had grown, alongside brown oil. The oil showed NMR spectra suggestive of a mixture of 4 and decomposition products. Some crystals could be manually separated from the oil, yield: 5 mg (40%). These were nevertheless coated finely with oil and so were unsuitable for microanalysis. Similarly, oil-coated crystals of 4 can be formed in an analogous route using 5 (30 mg, *vide infra*) and 20 eq. H₃B-NMe₂H (yield: 8 mg, 38%). Alternatively, addition of Na[H₃B-NMe₂-BH₃] to 5 forms 4 and Na[BArF₄] within 24 h, although 4 co-crystallised with Na[BArF₄] so material suitable for microanalysis was not obtained.

¹H NMR (500 MHz, CD₂Cl₂): δ 7.72 (br, 8H, [BArF₄]⁻), 7.69 – 5.50 (m, 42H, Xantphos’ aryl groups), 7.55 (br, 4H, [BArF₄]⁻), 4.14 (br, 2H, free HB), 2.47 (s, 6H, NMe₂), 1.79 (s, 6H, Xantphos’ CH₃), 1.24 (s, 
6H, Xantphos’ CH₃), –2.68 (br, 2H, coordinated HB), –3.52 (br, 2H, coordinated HB). The signals at δ 4.14, –2.68 and –3.52 sharpen upon ¹¹B decoupling.

³¹P({¹H}) NMR (202 MHz, CD₂Cl₂): δ 108.5 (tt, phosphido groups), 13.3 (ddt, phosphino groups). Estimated coupling constants by gNMR simulations: J₁₃ = 10, J₂₃ = 10, J₁₄ = 10, J₂₄ = 10, J₅₁ = 112, J₅₂ = 112, J₅₃ = 122, J₅₄ = 40, J₆₁ = 112, J₆₂ = 112, J₆₃ = 40, J₆₄ = 122, J₅₆ = 4 (numbering is as in Figure S-1).

¹¹B NMR (160 MHz, CD₂Cl₂): δ 16.6 (br, BH₃), –6.6 (s, [BAR⁺]:)

ESI-MS (1,2-C₆H₄F₂, 60 °C, 4.5 kV): m/z [⁴]⁺ 1280.23 (calc. 1280.24). Peak displays the expected isotopic pattern.

![Figure S-2 ¹H (upper) and ¹H(¹¹B) (lower) NMR spectra of 4 in CD₂Cl₂. # = unidentified impurity.](image-url)
Figure S-3 Back-linear predicted $^{11}$B NMR spectrum of 4 in CD$_2$Cl$_2$.

Figure S-4 Experimental (upper) and simulated (lower) $^{31}$P{$^{1}$H} NMR spectra for 4 in CD$_2$Cl$_2$. 
To a Young’s flask containing $[\text{Rh}(\kappa^2_2,\eta^1_1-\text{Xantphos})(\eta^1_1-\text{H}_3\text{B}\cdot\text{NMe}_3)][\text{BARF}_4]$ (100 mg, 0.061 mmol) and H$_3$B·NMe$_3$ (85 mg, 1.17 mmol), 1,2-C$_6$H$_4$F$_2$ was added (~ 3 mL). The flask was frozen in liquid N$_2$, the headspace evacuated and replaced with H$_2$ (ca. 4 atm) to form $[\text{Rh}(\kappa^3_3,\eta^1_1-\text{H}_3\text{B}\cdot\text{NMe}_3)][\text{BARF}_4]$ (3) on thawing and shaking. This mixture was degassed with three freeze-pump-thaw cycles, refilled with Ar, the flask sealed and heated to 40 °C. This initially formed a mixture of 2 and 3, and periodic sampling of the reaction mixture for $^{31}$P{¹H} NMR spectroscopy indicated complete conversion to 5 within 5 days, during which a dark red solution was formed. Alternatively, formation of 4 was complete within 48 h at 55 °C, although prolonged heating at this temperature caused decomposition to unidentified products. The volatiles were removed in vacuo, yielding dark red oil, which was washed and sonicated with pentane to form a dark red/orange solid. This was recrystallised from 1,2-C$_6$H$_4$F$_2$/pentane at 5 °C, affording crystals suitable for X-ray diffraction. Yield: 63 mg (67%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.75 – 6.53 (m, 42H, Xantphos’ aryl groups), 7.72 (br, 16H, [BARF$_4$]$^-$), 7.55 (br, 8H, [BARF$_4$]$^-$), 1.96 (s, 6H, Xantphos’ CH$_3$), 1.66 (s, 18H, NMe$_3$), 1.48 (s, 6H, Xantphos’ CH$_3$), –0.39 (br, 6H, H$_3$B). The signal at $\delta$ –0.39 sharpened upon $^{11}$B decoupling.

$^{31}$P{¹H} NMR (202 MHz, CD$_2$Cl$_2$): $\delta$ 135.1 (tt, phosphido groups), 19.2 (ddt, phosphino groups). Estimated coupling constants by gNMR simulations: $J_{13} = 10$, $J_{23} = 10$, $J_{14} = 10$, $J_{24} = 10$, $J_{51} = 125$, $J_{52} = 125$, $J_{53} = 112$, $J_{54} = 56$, $J_{61} = 125$, $J_{62} = 125$, $J_{63} = 56$, $J_{64} = 112$, $J_{65} = 4$ (numbering is as shown in Figure S-5).

$^{11}$B NMR (160 MHz, CD$_2$Cl$_2$): $\delta$ –6.6 (s, [BARF$_4$]$^-$), –7.8 (br, BH$_3$).

ESI-MS was attempted but decomposition to unidentified species resulted.

Elemental Microanalysis: Calc. Rh$_2$P$_3$O$_3$N$_5$B$_4$F$_{48}$C$_{13}$H$_{102}$ (3081.19 g mol$^{-1}$): C, 53.02; H, 3.34; N, 0.91. Found: C, 52.91; H, 3.44; N, 1.00.

S-6
Figure S-6 $^1$H (upper) and $^1$H($^{11}$B} (lower) NMR spectra of 5 in CD$_2$Cl$_2$.

Figure S-7 Experimental (upper) and simulated (lower) $^{31}$P($^1$H} NMR spectrum of 5 in CD$_2$Cl$_2$. 
[Rh(κ^3_P,O,P-Xantphos'){(NCMe)}_2][BArF_4]_2 (6)

Figure S-8 Complex 6. [BArF_4]^− anions not shown.

Addition of MeCN to 5 in 1,2-C_6H_4F_2 or CD_2Cl_2 formed 6 immediately in situ (NMR spectroscopy). Attempts to recrystallize 6 resulted in the formation of orange oil.

^1H NMR (500 MHz, CD_2Cl_2): δ 7.71 (br, 16H, [BArF_4]^−), 7.65 – 6.71 (m, 42H, Xantphos´ aryl groups), 7.54 (br, 8H, [BArF_4]^−), 1.93 (s, 6H, Xantphos´ CH_3), 1.45 (s, 6H, Xantphos´ CH_3), 1.06 (s, 6H, MeCN).

^31P{^1H} NMR (202 MHz, CD_2Cl_2): δ 130.1 (tt, phosphido groups), 20.7 (ddt, phosphino groups). Estimated coupling constants by gNMR simulations: J_{13} = 10, J_{23} = 10, J_{14} = 10, J_{24} = 10, J_{51} = 122, J_{52} = 122, J_{53} = 104, J_{54} = 53, J_{61} = 122, J_{62} = 122, J_{63} = 53, J_{64} = 104, J_{56} = 5 (numbering is as in Figure S-8).

ESI-MS (1,2-C_6H_4F_2, 60 °C, 4.5 kV): Molecular ions observed at m/z 604.06 ([Rh(Xantphos')]_2^{2+}, calc. 604.06, major), 624.57 ([{Rh(Xantphos')]_2{(NCMe)}]^{2+}, calc. 624.57, mid), 645.09 ([6]^{2+}, calc. 645.09, minor).
Figure S-9 Complex 7. [BAR$_4$]$_2^-$ anions not shown.

To a mixture of 5 (15 mg, 0.005 mmol) and dppe (2 mg, 0.005 mmol), 1,2-C$_6$H$_4$F$_2$ was added, forming a red solution. Upon layering the solution with pentane at 5 °C, red crystals of 7 formed. Yield: 10 mg (62%).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): δ 7.79 – 5.83 (m, 62H, Xantphos’ and dppe aryl groups), 7.72 (br, 16H, [BAR$_4$]$_2^-$), 7.55 (br, 8H, [BAR$_4$]$_2^-$), 3.38 (m, 2H, 2 x CH, CH$_2$ chain), 2.19 (m, 2H, 2 x CH, CH$_2$ chain), 1.73 (s, 6H, Xantphos´ CH$_3$), 0.70 (s, 6H, Xantphos´ CH$_3$).

Upon $^{31}$P decoupling, the signals at δ 3.38 and 2.19 collapsed to doublets ($^2$J$_{PH}$ = 12).

$^{31}$P($^1$H) NMR (202 MHz, CD$_2$Cl$_2$): δ 134.1 (m, P1 and P2), 19.2 (m, P3 and P4), 3.9 (m, P5 and P6).

Unfortunately, we were unable to simulate these signals satisfactorily. The peak at δ 134.1 was assigned on the basis of chemical shift as corresponding to bridging phosphido groups. A $^1$H-$^{31}$P HMBC experiment showed a correlation between the signal at δ 3.9 and the dppe chain protons, assigning this signal as P5/P6.

ESI-MS (1,2-C$_6$H$_4$F$_2$, 60 °C, 4.5 kV): m/z [7]$^{2+}$ 803.63 (calc. 803.63). Peak displays the expected isotopic pattern.

Elemental Microanalysis: Calc. Rh$_2$P$_6$O$_2$B$_2$F$_4$C$_{156}$H$_{102}$ (3333.73 g mol$^{-1}$): C, 56.20; H, 3.08. Found: C, 56.07; H, 3.16.
**Figure S-10** $^{31}$P-$^1$H NMR spectrum of 7 (the range ca. δ 130 – 22 ppm has been omitted for clarity).

**Figure S-11** $^{31}$P-$^{31}$P COSY NMR spectrum of 7. Circles are drawn to highlight the weaker cross peaks.
Reaction between complex 5 and H₃B·NMe₂H (4 eq.)

5 (10 mg, 0.003 mmol) and H₃B·NMe₂H (0.7 mg, 0.012 mmol) were each dissolved in 0.2 mL 1,2-C₆H₄F₂ and the two solutions were mixed in a high pressure NMR tube. The reaction was followed by ¹H, ³¹P{¹H} and ¹¹B NMR spectroscopies. The major organometallic complex observed within 10 minutes was a complex consistent with the formulation [Rh(Xantphos')(η¹-H₃B·NMe₂H)]₂[BAR₄]₂; in particular, two ³¹P environments were observed in the ³¹P{¹H} NMR spectrum at δ 135.0 and δ 18.6, and a broad signal in the ¹H NMR spectrum at δ ~0.45 that sharpens upon ¹¹B decoupling was observed. These chemical shifts are very similar to those for 5 in 1,2-C₆H₄F₂ (³¹P{¹H} NMR: δ 135.3 and δ 19.1; ¹H NMR: δ ~0.04), supporting this tentative assignment. After 2 hours (~ 30% consumption of H₃B·NMe₂H), a mixture of this new complex and 5 were the major organometallic species observed by NMR spectroscopy. After 20 hours, the H₃B·NMe₂H had been fully consumed to form [H₂BNMe₂]₂, and a ca. 50:50 mixture of 4 and 5 had formed.

Addition of MeCN to complex 4

Excess MeCN (20 eq.) was added to in situ formed 4 (via dehydrocoupling of H₃B·NMe₂H by 5) in a high pressure NMR tube. An intractable mixture of species was observed by ¹H and ³¹P{¹H} NMR spectroscopies. No evidence for 6 was observed.
General procedures for amine-borane dehydrocoupling catalysis

Open system
In a typical experiment (e.g. 0.072 M H₃B·NMe₂H, 0.1 mol% 5), H₃B·NMe₂H (21.2 mg, 0.36 mmol) in 4.75 mL 1,2-C₆H₄F₂ was added to a 3-necked Schlenk flask with a magnetic stirrer bar. Under a flow of argon, an external mineral oil bubbler was connected and the argon flow adjusted to bubble at a rate of approximately 1.5 bubbles per second. In a separate flask, 5 (4.4 mg, 0.0014 mmol) was dissolved in 1 mL of 1,2-C₆H₄F₂. 0.25 mL of this precatalyst solution was injected via syringe into the 3-necked Schlenk flask. Catalysis was monitored by analysing regular aliquots of the reaction solution (0.1 mL samples, diluted with 0.25 mL 1,2-C₆H₄F₂ under argon, frozen in liquid N₂) by ¹¹B NMR spectroscopy. The reactions were performed at 298 K.

Closed system
To H₃B·NMe₂H (5.6 mg, 0.095 mmol), 1 mL of 1,2-C₆H₄F₂ was added. 0.3 mL was sampled and added to a high pressure NMR tube. To 5 (1.0 mg, 0.0003 mmol), 1 mL 1,2-C₆H₄F₂ was added. 0.1 mL was sampled and added to the high pressure NMR tube, resulting in a 0.072 M H₃B·NMe₂H solution with 0.1 mol% 5. The reaction was followed in situ by ¹¹B NMR spectroscopy at 298 K.

Dehydropolymerisation of H₃B·NMeH₂
To a Schlenk flask containing H₃B·NMeH₂ (100 mg, 2.22 mmol) and a stirrer bar, 4.5 mL C₆H₅F was added. To a Young’s NMR tube containing 5 (6.9 mg, 0.0022 mmol), 0.5 mL C₆H₅F was added, 5 was fully dissolved and transferred by cannula to the stirring solution of H₃B·NMeH₂. The mixture was stirred under argon, open to a mercury bubbler, for the allotted time period, before quenching via syringe with 35 mL of hexanes. Following addition of hexanes, the [H₂BNMeH]ₙ/H₃B·NMeH₂ mixture precipitated as an off-white solid at −78 °C. The yellow supernatant solution was filtered off, and the solid was dried for 2 minutes in vacuo to remove residual C₆H₅F. THF (2.5 mL) was added, dissolving the [H₂BNMeH]ₙ/H₃B·NMeH₂ mixture, and this was filtered into a new Schlenk flask. Hexanes (40 mL) were added to the solution and cooled immediately to −78 °C, allowing the product to precipitate. The supernatant solution was removed by filtration, and the resulting solid was dried in vacuo for at least 12 hours before GPC analysis. Yield: 52 mg solid (containing ~15% unreacted H₂BN·MeH₂, measured by ¹¹B NMR spectroscopy).
Kinetic plots

Effect of [H₃B·NMe₂H] upon rate of 5-catalysed dehydrocoupling – open systems

Typical dehydrocoupling plots in open systems are shown in Figure S-12 ([H₃B·NMe₂H]₀ = 0.288 M), Figure S-13 ([H₃B·NMe₂H]₀ = 0.144 M), Figure S-14 ([H₃B·NMe₂H]₀ = 0.072 M) and Figure S-15 ([H₃B·NMe₂H]₀ = 0.018 M). The rates between the points in the graphs ranging from [H₃B·NMe₂H]₀ = 0.288 M – 0.018 M (and duplicate runs, induction period excluded) were plotted vs [H₃B·NMe₂H] to yield the saturation curve shown in Figure S-16. Addition of excess mercury to the reaction mixture after the induction period ([H₃B·NMe₂H]₀ = 0.072 M) did not halt catalysis as has been observed in other systems,¹⁰ suggesting homogeneous catalysis, although the total consumption of H₃B·NMe₂H was reduced to ca. 85%, and we suggest decomposition due to other factors.

Figure S-12 Plot of concentration vs time (by ¹¹B NMR spectroscopy) of the dehydrocoupling of H₃B·NMe₂H by 5. [H₃B·NMe₂H]₀ = 0.288 M; [5] = 7.2 x 10⁻⁵ M; 1,2-C₆H₄F₂ solvent; open conditions. ◆ = H₃B·NMe₂H; ■ = H₂B=NMe₂; ○ = HB(NMe₂)₂; ▲ = [H₂BNMe₂]₂.
**Figure S-13** Plot of concentration vs time (by $^{11}$B NMR spectroscopy) of the dehydrocoupling of H$_3$B-NMe$_2$H by 5. [H$_3$B-NMe$_2$H]$_0$ = 0.144 M; [5] = 7.2 x $10^{-5}$ M; 1,2-C$_6$H$_4$F$_2$ solvent; open conditions.

◆ = H$_3$B-NMe$_2$H; ■ = H$_2$B=NMe$_2$; ○ = HB(NMe$_2$)$_2$; ▲ = [H$_2$BNMe$_2$]$_2$.

**Figure S-14** Plot of concentration vs time (by $^{11}$B NMR spectroscopy) of the dehydrocoupling of H$_3$B-NMe$_2$H by 5. [H$_3$B-NMe$_2$H]$_0$ = 0.072 M; [5] = 7.2 x $10^{-5}$ M; 1,2-C$_6$H$_4$F$_2$ solvent; open conditions.

◆ = H$_3$B-NMe$_2$H; ■ = H$_2$B=NMe$_2$; ○ = HB(NMe$_2$)$_2$; ▲ = [H$_2$BNMe$_2$]$_2$.
Figure S-15 Plot of concentration vs time (by $^{11}$B NMR spectroscopy) of the dehydrocoupling of H$_3$B-NMe$_2$H by 5. [H$_3$B-NMe$_2$H]$_0$ = 0.018 M; [5] = 7.2 x 10$^{-5}$ M; 1,2-C$_6$H$_4$F$_2$ solvent; open conditions.

◆ = H$_3$B·NMe$_2$H; ■ = H$_2$B=NMe$_2$; ○ = HB(NMe$_2$)$_2$; △ = [H$_2$BNMe$_2$].
Figure S-16 Plot of [H₃B·NMe₂H] vs rate of H₃B·NMe₂H consumption over the concentration range 0 to 0.27 M. Catalyst = 5, 298 K, open system. Trendline is for illustration only. Rates measured by taking gradients between successive data points of ¹¹B concentration as measured by periodic sampling of the reaction. The scatter in the plot is a result of the measurements being taken over multiple separate runs.
Closed system

Figure S-17 (a) Plot of concentration vs time (by $^{11}$B NMR spectroscopy) during the catalytic dehydrocoupling of H$_3$B·NMe$_2$H (initial concentration 0.072 M) with [5] = 7.2 x 10$^{-5}$ M. ◆ = H$_3$B·NMe$_2$H; ■ = H$_2$B=NMe$_2$; ○ = HB(NMe$_2$)$_2$; ▲ = [H$_2$BNMe$_2$]$_2$. Sealed conditions. (b) Plot of ln[H$_3$B·NMe$_2$H] vs time during productive catalysis. Linear fit depicted by trendline. From trendline, $k = (4.37 \pm 0.07) \times 10^{-4}$ s$^{-1}$. $R^2 = 0.99656$. 
**Kinetic isotope effects**

Kinetic isotope effects were obtained from the zero order regions of the dehydrocoupling of H₃B·NMe₂H, D₃B·NMe₂H and H₃B·NMe₂D (initial concentrations of 0.288 M, [5] = 7.2 x 10⁻⁵ M, open conditions). A representative plot is shown in Figure S-18. Calculated kinetic isotope effects were 1.1 ± 0.2 for B—H/D substitution, and 2.0 ± 0.3 for N—H/D substitution.

![Plot of concentrations vs time](image)

**Figure S-18** Plot of concentrations vs time (by ¹¹B NMR spectroscopy) during separate catalytic dehydrocoupling reactions of H₃B·NMe₂H (■), D₃B·NMe₂H (▲) and H₃B·NMe₂D (◆), each with [5] = 7.2 x 10⁻⁵ M and initial [amine-borane] = 0.288 M. First 6000 s shown.
Order in [Rh]

Figure S-19 shows a first order relationship between catalyst concentration and the rate of dehydrocoupling (zero order region).

**Figure S-19** Plot of rates vs [5] during separate catalytic dehydrocoupling reactions of H$_3$B-NMe$_2$H (initial concentration 0.144 M) upon altering the starting concentration of 5. Rates obtained from the zero order region of the plots. Trendline shows line of best fit.
Dehydrocoupling catalysis using complex 4

Catalysis starting with complex 4 (Figure S-1) showed a longer induction period and a slower turnover frequency than under analogous conditions with complex 5 (Figure S-14), possibly due to the stronger coordination of $[\text{H}_3\text{BNMe}_2\text{BH}_3]^-$ vs $\text{H}_2\text{BNMe}_2$.

**Figure S-20** Plot of concentration vs time (by $^{11}$B NMR spectroscopy) of the dehydrocoupling of $\text{H}_3\text{B-NMe}_2\text{H}$ by 4. $[\text{H}_3\text{B-NMe}_2\text{H}]_0 = 0.072$ M; $[4] = 7.2 \times 10^{-5}$ M; 1,2-C$_6$H$_4$F$_2$ solvent; open conditions. ◆ = $\text{H}_3\text{B-NMe}_2\text{H}$; ■ = $\text{H}_2\text{B=NMe}_2$; ○ = $\text{HB(NMe}_2)_2$; ▲ = $[\text{H}_2\text{BNMe}_2]_2$. 
Dehydropolymerisation of $\text{H}_3\text{B} \cdot \text{NMeH}_2$

![Gel permeation chromatogram](image)

**Figure S-21** Gel permeation chromatogram recorded for $[\text{H}_2\text{BNMeH}]_n$ at 2 mg/mL. By $^{11}\text{B}('/\text{H})$ NMR spectroscopy, 80% conversion to $[\text{H}_2\text{BNMeH}]_n$ was achieved after 2 hours of reaction with 5 (0.1 mol%), with the remainder being unreacted $\text{H}_3\text{B} \cdot \text{NMeH}_2$. $M_n = 28,700 \text{ g mol}^{-1}$; $M_w = 47,500 \text{ g mol}^{-1}$.

**X-ray crystallography**

Relevant details about structure refinement are given in Table S-1. Data for 4, 7 and 8 were collected on an Agilent Supernova diffractometer using graphite monochromated Cu Kα radiation ($\lambda = 1.54180$ Å) and a low temperature device; reduction and cell refinement was performed using CrysAlisPro.$^{[11]}$ Data for 5 were collected on a Enraf Nonious Kappa CCD diffractometer using graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) and a low temperature device.$^{[12]}$ data were collected using COLLECT, reduction and cell refinement was performed using DENZO/SCALEPACK.$^{[13]}$ All structures were solved using Sir92$^{[14]}$ or Superflip.$^{[15]}$ All were refined using CRYSALT.$^{[16]}$ Specific refinement details are given below.
Complex 4

The $\text{[BArF}_4^-\text{]}$ anion exhibits considerable disorder, with two of the four aryl rings (and their corresponding CF$_3$ groups) each disordered over two sites. The rings were modelled over the two sites and their occupancies refined. In addition, a molecule of 1,2-C$_6$H$_4$F$_2$ solvent (0.3 occupancy) was located as part of the major component of one disordered ring, overlapping with the minor component. In addition, rotational disorder of one of the CF$_3$ groups in a non-disordered aryl ring was treated by modelling the fluorine atoms over two sites and restraining their geometry. Owing to the extensive disorder, some planarity and bond length restraints were used to give sensible structural parameters. A molecule of disordered pentane was also located, to which restraints were also applied.

All hydrogen atoms were located on the Fourier map, except those on the disordered pentane and 1,2-C$_6$H$_4$F$_2$. The hydrogen atoms on these molecules were placed in calculated positions. The hydrogen atoms were refined before RIDE restraints were added. The atoms H1/H2 and H4/H5 were placed riding upon B1 and B2, respectively.

Complex 5

The Fourier difference map indicated the presence of diffuse electron density believed to be a molecule of the pentane solvent. SQUEEZE was used, leaving a void from which the electron density was removed. Rotational disorder of six of the CF$_3$ groups of the anion was treated by modelling the fluorine atoms over two sites and restraining their geometry. The hydrogen atoms were found on the Fourier map and refined before adding RIDE restraints. The atom H1 was placed riding upon B1.

Complex 7

Rotational disorder of some of the CF$_3$ groups on the $\text{[BArF}_4^-\text{]}$ anions was treated by modelling the fluorine atoms over two sites and restraining their geometry. Hydrogen atoms were found on the Fourier map and refined before RIDE restraints were added.
Figure S-22 Solid state structure of the cationic portion of 4. Displacement ellipsoids are drawn at the 50% probability level. For clarity, carbon-bound H atoms are omitted, and the carbon atoms in the Xantphos’ ligands are depicted as a wireframe. Selected bond lengths (Å) and angles (°): Rh1-Rh2, 2.5928(4); Rh1-P1, 2.2455(12); Rh1-P2, 2.2500(11); Rh1-P3, 2.3427(11); Rh2-P1, 2.2461(11); Rh2-P2, 2.2663(11); Rh2-P4, 2.3325(11); Rh1-B1, 2.234(5); Rh2-B2, 2.229(5); Rh1-O1, 3.393(4); Rh2-O2, 3.412(4); B1-N1, 1.600(7); N1-B2, 1.583(7); P1-Rh2-P4, 114.64(4); P2-Rh1-P3, 110.89(4); B1-N1-B2, 117.5(4).
Figure S-23 Solid state structure of the cationic portion of 5. Displacement ellipsoids are drawn at the 50% probability level. For clarity, H atoms are omitted, and the carbon atoms in Xantphos ligands are depicted as a wireframe. Selected bond lengths (Å) and angles (°): Rh1-Rh1’, 2.7965(5); Rh1-P2’, 2.1940(9); Rh1-P2, 2.2192(8); Rh1-P1, 2.3344(9); Rh1-O1, 2.288(2); Rh1-B1, 2.722(4); N1-B1, 1.594(5); P2-Rh1-P1, 119.72(3); Rh1-P2-Rh1’, 78.64(3); Rh1’-Rh1-P2’, 51.08(2); Rh1’-Rh1-P2, 50.28(2).
Figure S-24 Solid state structure of the cationic portion of 7. Displacement ellipsoids are drawn at the 50% probability level. For clarity, H atoms are omitted, and the carbon atoms in Xantphos’ ligands are depicted as a wireframe. Selected bond lengths (Å) and angles (°): Rh1-Rh2, 2.8362(5); Rh1-P1, 2.2135(12); Rh1-P2, 2.2464(12); Rh1-P3, 2.3360(12); Rh1-P5, 2.4352(12); Rh1-O1, 2.309(3); Rh2-P1, 2.2571(12); Rh2-P2, 2.2194(12); Rh2-P4, 2.3565(12); Rh2-P6, 2.4165(12); Rh2-O2, 2.285(3); P2-Rh1-P3, 114.58(4); P1-Rh2-P4, 111.92(4); P6-Rh2-P4, 106.74(4); P6-Rh2-P1, 137.67(4); P6-Rh2-P2, 97.28(4); P5-Rh1-P3, 106.67(4); P5-Rh1-P1, 99.56(4); P5-Rh1-P2, 135.08(4).
### Table S-1 Crystallographic data for 4, 5, and 7.

|       | 4                     | 5                     | 7                     |
|-------|-----------------------|-----------------------|-----------------------|
| CCDC number | 1062781            | 1062782            | 1062783            |
| Formula | C_{106.8}H_{91.2}B_{3}F_{24.6}NO_{2}P_{5}Rh_{2} | C_{136}H_{102}B_{2}F_{48}O_{2}P_{4}Rh_{2} | C_{156}H_{102}B_{2}F_{48}O_{2}P_{6}Rh_{2} |
| M      | 2250.19              | 3081.17              | 3333.71              |
| Crystal system | Triclinic           | Monoclinic           | Monoclinic           |
| Space group | P -1               | C 2/c                | P 21/n               |
| T [K]  | 150(2)              | 150(2)              | 150(2)              |
| a [Å]  | 13.6309(2)          | 32.5926(3)          | 14.6815(2)          |
| b [Å]  | 16.5228(3)          | 24.6249(3)          | 16.8673(2)          |
| c [Å]  | 22.7975(4)          | 19.6743(2)          | 58.7574(5)          |
| α [°]  | 94.0197(16)         | 90                  | 90                  |
| β [°]  | 95.2079(14)         | 108.2170(5)         | 90.9227(8)          |
| γ [°]  | 91.9282(14)         | 90                  | 90                  |
| V [Å³] | 5096.56(15)         | 14999.0(3)         | 14548.6(3)          |
| Z      | 2                    | 4                   | 4                   |
| Density [g cm⁻³] | 1.466              | 1.364              | 1.522              |
| μ [mm⁻¹] | 4.039               | 0.369              | 3.48               |
| θ range [°] | 3.200 ≤ θ ≤ 76.090 | 5.110 ≤ θ ≤ 27.489 | 3.115 ≤ θ ≤ 76.171 |
| Refns collected | 61481              | 105008             | 167693             |
| R indices | 0.051               | 0.058              | 0.052              |
| Completeness | 98.80%             | 99.20%             | 99.30%             |
| Data/restr/param | 20971/1906/1622     | 17080/1140/1032     | 30115/1140/2085     |
| R₁ [l > 2σ(l)] | 0.0603             | 0.0644             | 0.0596             |
| wR₂ [all data] | 0.1695             | 0.171              | 0.1578             |
| GoF    | 1.0108              | 0.9446             | 1.0967             |
| Largest diff. pk and hole [e Å⁻³] | 2.41, -1.70       | 1.33, -1.13        | 1.17, -1.18        |
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