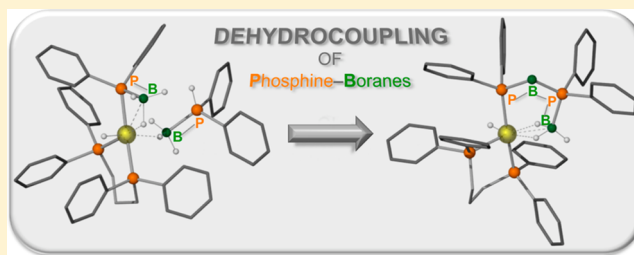


Effect of the Phosphine Steric and Electronic Profile on the Rh-Promoted Dehydrocoupling of Phosphine–Boranes

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Supporting Information

ABSTRACT: The electronic and steric effects in the stoichiometric dehydrocoupling of secondary and primary phosphine–boranes $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$ [$\text{R} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$; $p\text{-(CF}_3)_2\text{C}_6\text{H}_4$; $p\text{-(OMe)C}_6\text{H}_4$; adamantyl, Ad] and $\text{H}_3\text{B}\cdot\text{PCyH}_2$ to form the metal-bound linear diboraphosphines $\text{H}_3\text{B}\cdot\text{PR}_2\text{BH}_2\cdot\text{PR}_2\text{H}$ and $\text{H}_3\text{B}\cdot\text{PRH}_2\text{BH}_2\cdot\text{PRH}_2$, respectively, are reported. Reaction of $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BAR}^{\text{F}}_4]$ [$\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$, $\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$] with 2 equiv of $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$ affords $[\text{Rh}(\text{L})(\text{H})(\sigma,\eta\text{-PR}_2\text{BH}_3)(\eta^1\text{-H}_3\text{B}\cdot\text{PR}_2\text{H})][\text{BAR}^{\text{F}}_4]$. These complexes undergo dehydrocoupling to give the diboraphosphine complexes $[\text{Rh}(\text{L})(\text{H})(\sigma,\eta^2\text{-PR}_2\text{BH}_2\text{PR}_2\text{BH}_3)][\text{BAR}^{\text{F}}_4]$. With electron-withdrawing groups on the phosphine–borane there is the parallel formation of the products of B–P cleavage, $[\text{Rh}(\text{L})(\text{PR}_2\text{H})_2][\text{BAR}^{\text{F}}_4]$, while with electron-donating groups no parallel product is formed. For the bulky, electron rich, $\text{H}_3\text{B}\cdot\text{P}(\text{Ad})_2\text{H}$ no dehydrocoupling is observed, but an intermediate Rh(I) σ phosphine–borane complex is formed, $[\text{Rh}(\text{L})\{\eta^2\text{-H}_3\text{B}\cdot\text{P}(\text{Ad})_2\text{H}\}][\text{BAR}^{\text{F}}_4]$, that undergoes B–P bond cleavage to give $[\text{Rh}(\text{L})\{\eta^1\text{-H}_3\text{B}\cdot\text{P}(\text{Ad})_2\text{H}\}\{\text{P}(\text{Ad})_2\text{H}\}][\text{BAR}^{\text{F}}_4]$. The relative rates of dehydrocoupling of $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$ ($\text{R} = \text{aryl}$) show that increasingly electron-withdrawing substituents result in faster dehydrocoupling, but also suffer from the formation of the parallel product resulting from P–B bond cleavage. $\text{H}_3\text{B}\cdot\text{PCyH}_2$ undergoes a similar dehydrocoupling process, and gives a mixture of stereoisomers of the resulting metal-bound diboraphosphine that arise from activation of the prochiral P–H bonds, with one stereoisomer favored. This diastereomeric mixture may also be biased by use of a chiral phosphine ligand. The selectivity and efficiencies of resulting catalytic dehydrocoupling processes are also briefly discussed.



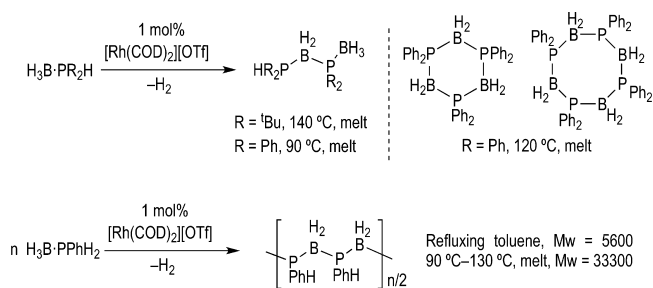
INTRODUCTION

The development of efficient catalytic methods for the formation of bonds between main group elements is of considerable interest for the continued development of main group chemistry. Such processes enable new discoveries to be made in the promising application areas that main group species are now occupying, such as high performance polymers, emissive materials, etch resists for lithography, and precursors to ceramic thin films or devices.^{1–6} However, the development of this field lags substantially behind the advances made in catalytic C–C and C–X bond formation, for which there are now a myriad of efficient ways to promote such unions that are important for the construction of new molecules. Catalytic dehydrocoupling^{5,7,8} of amine– and phosphine–boranes is one method that has emerged for the formation of B–N and B–P bonds, and development in the area has been spurred on by the potential for ammonia–borane to act as a hydrogen carrying vector.^{9–11} In addition, polymeric materials that can arise from dehydropolymerization of primary analogues are also of significant interest as they are valence isoelectronic with technologically ubiquitous polyolefins. Although the metal catalyzed formation of polyaminoboranes has attracted recent attention,^{12–18} catalytic routes to polyphosphinoboranes have

also been known since 1999.¹⁹ Perhaps the best example is that of the $[\text{Rh}(\text{COD})_2][\text{OTf}]$ catalyzed dehydrocoupling of secondary, $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$, and primary, $\text{H}_3\text{B}\cdot\text{PRH}_2$, phosphine–boranes to give oligomeric and polymeric materials (Scheme 1).^{19–21}

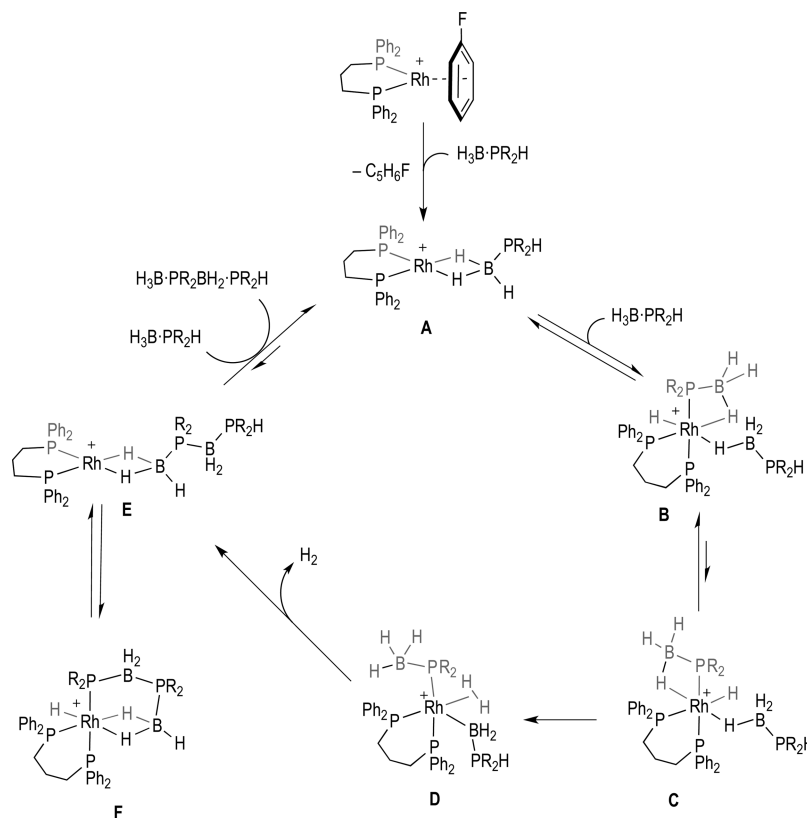
In contrast to amine–borane dehydrocoupling,^{8,10,15,22–24} the mechanism of catalytic dehydrocoupling of phosphine–

Scheme 1. Phosphine–Borane Dehydrocoupling



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Scheme 2. Proposed Catalytic Cycle for the Dehydrocoupling of $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$ To Give $\text{H}_3\text{B}\cdot\text{PR}_2\text{BH}_2\cdot\text{PR}_2\text{H}^a$ 

^a[BARF_4]⁻ anions are not shown.

boranes has received less attention. Although initial reports demonstrated that catalysis using $[\text{Rh}(\text{COD})_2][\text{OTf}]$ was a homogeneous process (i.e., not colloidal),²⁵ there has been only sporadic further work on elucidating the mechanistic details.^{26–29} Progress has no doubt been slowed due to the fact that the reaction conditions reported for phosphine–borane dehydrocoupling often require melt conditions, thus making interrogation of the catalytic cycle problematic. Recently, we have reported that the Rh(I) complexes $[\text{Rh}(\text{P}^t\text{Bu}_2\text{H})_2(\eta^6\text{-FC}_6\text{H}_5)][\text{BARF}_4]$,³⁰ and $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BARF}_4]$,³¹ [$\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$] are particularly well-suited to the study of the dehydrocoupling mechanism of secondary phosphine–boranes in solvents such as fluorobenzene; and on the basis of the observation of intermediates, kinetic studies, and H/D exchange experiments we have proposed a catalytic cycle for the dehydrocoupling of $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$ ($\text{R} = \text{Ph}, ^t\text{Bu}$; Scheme 2). For this cycle, intermediate species were isolated, but their structures could not be confirmed by X-ray crystallography. In particular for $\text{R} = \text{Ph}$, a β -B-agostic σ complex **B**, and the product of dehydrocoupling **F**, that is proposed to sit off cycle, could be isolated and spectroscopically characterized. Under stoichiometric conditions the observation that **B** transforms into **F** on gentle heating allowed for kinetic parameters to be determined that suggested that the rate-determining step(s) for dehydrocoupling were located within the transformations **B** to **D**. In solution phase the turnover limiting step for catalysis is proposed to be the displacement of the linear diboraphosphine product (i.e., **F** to **A**), although under the melt conditions used for efficient catalysis this may well be different. Further insight comes from the observations that for $\text{R} = ^t\text{Bu}$ the barrier to dehydrocoupling is higher (70 °C versus 25 °C for reaction),

P–H activation appears also to be a higher energy process, different intermediates (**A** and **E**) are observed, and the turnover limiting process in catalysis is now suggested to be the P–H activation/dehydrocoupling steps. Prior work has demonstrated a similar difference in relative rates of dehydrocoupling of secondary $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$ [$\text{R} = p\text{-(CF}_3\text{)}_2\text{C}_6\text{H}_4, \text{Ph}, ^t\text{Bu}, ^i\text{Bu}$] and primary $\text{H}_3\text{B}\cdot\text{PRH}_2$ [$\text{R} = \text{Ph}, ^t\text{Bu}, ^i\text{Bu}$] phosphine–boranes using the $[\text{Rh}(\text{COD})_2][\text{OTf}]$ catalyst, and this was suggested to be due to a combination of steric and electronic (relative P–H bond strengths) factors,^{21,32,33} although the mechanism of dehydrocoupling of phosphine–boranes using this catalyst is currently not known.^{20,25,30} Interestingly, the related dehydrogenation of aryl amine–boranes shows that the activity of the N–H bond is such that spontaneous dehydrocoupling occurs in the absence of catalyst, with electron-withdrawing aryl groups [$p\text{-(CF}_3\text{)}_2\text{C}_6\text{H}_4$] undergoing faster reaction than electron-donating [$p\text{-(OMe)}\text{C}_6\text{H}_4$].³⁴ Very recent work has shown that paramagnetic Ti(III) centers might also be involved in dehydrocoupling of phosphine– and amine–boranes when using Cp_2Ti -based catalysts,³⁵ while oligomerization of base-stabilized phosphino–boranes at Cp_2Ti centers has been described.²⁹ Likely decomposition routes in Rh-systems for phosphine–borane dehydrocoupling to form bis(phosphine)boronium salts have also recently been discussed.³⁶

In this Article, we report an extension of our investigations into the mechanism of phosphine–borane dehydrocoupling using the $\{\text{Rh}(\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2)\}^+$ fragment, by varying the electronic and steric profile of the secondary phosphine–boranes $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$ [$\text{R} = 3,5\text{-(CF}_3\text{)}_2\text{C}_6\text{H}_3, p\text{-(CF}_3\text{)}_2\text{C}_6\text{H}_4, p\text{-(OMe)}\text{C}_6\text{H}_4, \text{adamantyl}$], as well as investigations with the

primary phosphine–borane $\text{H}_3\text{B}\cdot\text{PCyH}_2$. Dehydrocoupling forms the corresponding metal–bound linear diboraphosphines $\text{H}_3\text{B}\cdot\text{PR}_2\text{BH}_2\cdot\text{PR}_2\text{H}$ and $\text{H}_3\text{B}\cdot\text{PRHBH}_2\cdot\text{PRH}_2$, respectively. These studies provide insight into the determining role of the electronics and sterics of the phosphine–borane in the dehydrocoupling process, as well as providing as yet unreported examples of the solid-state structures of the intermediates related to the catalytic cycle. We also report for the first time the partial control of diastereoselectivity in dehydrocoupling of primary phosphine–boranes, that can additionally be biased by use of a chiral chelating phosphine on the rhodium center.

RESULTS AND DISCUSSION

Phosphine–Borane and Diboraphosphine Starting Materials. A range of secondary phosphine–boranes with differing electronic and steric properties have been used in this study (1, 2, 3, and 4, Figure 1), which also provide comparison

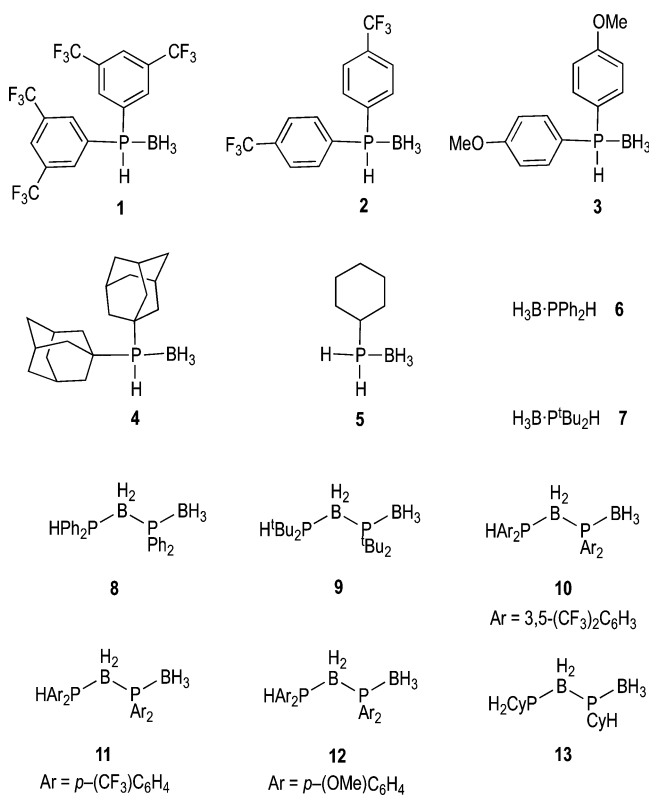


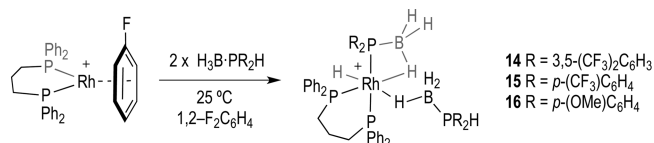
Figure 1. Phosphine–boranes 1–7 and diboraphosphines 8–13.

with the previously reported Ph, 6, and ^tBu, 7, analogues.³¹ The primary phosphine–borane 5 has also been used.³⁷ Compounds 2³³ and 3³⁸ are known adducts and offer electron-withdrawing and donating aryl groups, respectively. Bis-CF₃-substituted 1 is a new complex and offers an alternative to 2. The synthesis of adamantyl-substituted phosphine, 4, an analogue of 7, has been reported in the patent literature.³⁹ Compared with the ^tButyl group, adamantyl has a greater steric bulk due to its larger volume and rigid structure.^{40,41} The new linear diboraphosphines, 10–13, have also been synthesized to aid in the identification of final dehydrocoupling products. Complexes 10–12 are synthesized by a Rh-catalyzed process from the corresponding phosphine–boranes, while primary phosphine containing 13 has been synthesized in good isolated

yield (85%) by addition of $[\text{NBu}_4][\text{BH}_4]$ to the bis(phosphine)boronium $[(\text{CyH}_2\text{P})_2\text{BH}_2]\text{Br}$.³⁶

Stoichiometric Dehydrocoupling of Secondary Phosphine–Boranes. Addition of 2 equiv of 1 to $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BAr}^{\text{F}}_4]$ [$\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2$] in 1,2-F₂C₆H₄ solution at 25 °C rapidly (on time of mixing) resulted in the formation of $[\text{Rh}(\text{L})(\text{H})(\sigma,\eta\text{-PR}_2\text{BH}_3)(\eta^1\text{-H}_3\text{B}\cdot\text{PR}_2\text{H})][\text{BAr}^{\text{F}}_4]$, 14 [$\text{R} = 3,5\text{-}(\text{CF}_3)_2\text{C}_6\text{H}_3$], Scheme 3], which was

Scheme 3. Synthesis of Complexes 14, 15, and 16^a



^a $[\text{BAr}^{\text{F}}_4]^-$ anions are not shown.

characterized by NMR spectroscopy, ESI-MS (electrospray ionization mass spectrometry), and single crystal X-ray diffraction. Likewise, the use of 2 equiv of phosphine–borane 2 or 3 results in the formation of the analogous complexes 15 [$\text{R} = p\text{-}(\text{CF}_3)\text{C}_6\text{H}_4$] and 16 [$\text{R} = p\text{-}(\text{OMe})\text{C}_6\text{H}_4$], respectively, which were fully characterized using solution techniques. All these complexes proceed to dehydrocouple (vide infra), and only for 14 was an analytically pure crystalline solid obtained. Even so, dissolution of crystalline material of 14 resulted in the observation of small amounts (approximately 5–10%) of the associated dehydrocoupling product in the solution NMR spectra after short periods of time. Complexes 15 and 16 could only be isolated as oils, but their characterization by NMR spectroscopy and ESI-MS was fully consistent with their formulation.

The solution NMR spectra for 14, 15, and 16 are very similar to those previously reported for $[\text{Rh}(\text{L})(\text{H})(\sigma,\eta\text{-PPh}_2\text{BH}_3)(\eta^1\text{-H}_3\text{B}\cdot\text{PPh}_2\text{H})][\text{BAr}^{\text{F}}_4]$ (i.e., B, Scheme 2³¹), and data for 14 is discussed in detail. The ³¹P{¹H} NMR spectrum of 14 shows four different phosphorus environments. Two of the resonances are broadened significantly compared to the other two, suggesting these phosphorus atoms are bound to a quadrupolar boron center. One of these shows both a large *trans* PP coupling [$J(\text{PP})$ 244 Hz] and coupling to ¹⁰³Rh [$J(\text{RhP})$ 75 Hz], while the other is a broad singlet. The other two signals are sharper and are assigned to the two ³¹P environments of the Ph₂P(CH₂)₃PPh₂ ligand. One of these sharper resonances [δ 29.5, ddd, $J(\text{RhP})$ 130, $J(\text{PP})$ 35, $J(\text{PP})$ 21 Hz] is assigned to the phosphorus atom *trans* to the weakly bound β -B-agostic interaction on the basis of the larger ¹⁰³Rh coupling constant, while the other signal [δ 11.3, ddd, $J(\text{RhP})$ 103, $J(\text{PP})$ 244, $J(\text{PP})$ 35 Hz] is assigned to the phosphorus atom *trans* to the coordinated phosphido ligand. In the ¹H NMR spectrum of 14 one broad, relative integral 3H, signal is observed at δ –0.78, indicative of a Rh⋯H₃B σ interaction in which the B–H bonds are undergoing rapid site exchange on the NMR spectroscopic time scale between terminal and bridging sites.⁴² A broad, relative integral 1H, resonance at δ –6.12 is assigned to a static β -B-agostic B–H interaction. Cooling of the solution to 0 °C led to the resolution of this signal as doublet [$J(\text{PH})$ = 65 Hz], fully consistent with its *trans* disposition to a phosphine. The remaining BH(terminal) signals are not observed, and it is likely they are coincident with the {CH₂}₃ signals. A sharper signal at δ –16.21, relative integral 1H, is assigned to a metal–hydride resonance, in which the coupling to both ¹⁰³Rh and ³¹P

is clearly small and unresolved. The PH group is observed at δ 5.81 that collapses into a singlet in the $^1\text{H}\{^{31}\text{P}\}$ NMR spectrum. The ^{11}B NMR spectrum shows a broad signal centered at δ -39.8, which is not shifted significantly from that of free phosphine–borane **1** (δ -42.0). This is assigned to a coincidence of the η^1 β -B–H...Rh agostic and σ Rh...H₃B signals, as has been noted previously.^{31,43} Complexes **15** and **16** have similar ^1H , ^{11}B , and ^{31}P NMR spectra, and thus we assign very similar structures.

Crystals of complex **14** of suitable quality for analysis by X-ray diffraction were obtained by layering of a 1,2- $\text{F}_2\text{C}_6\text{H}_4$ solution with pentane at -26 °C. The structure of **14** in the solid-state (Figure 2) is fully consistent with the structure

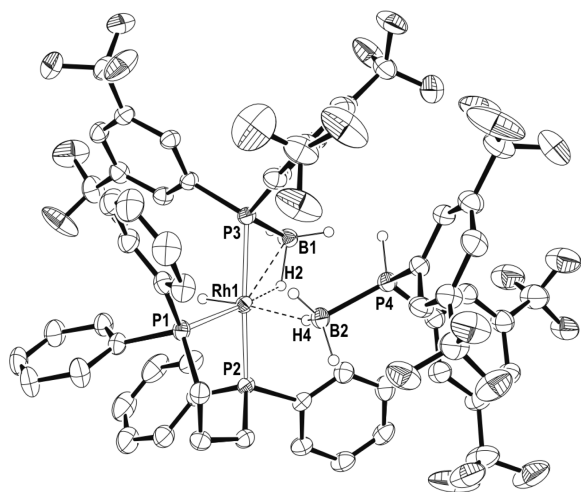


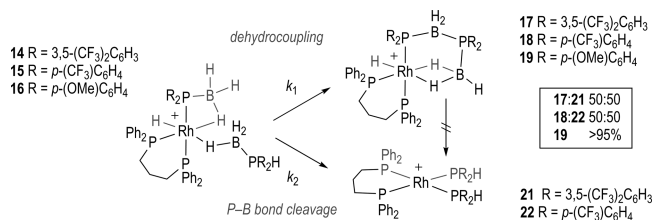
Figure 2. Molecular structure of the cation of **14**. Displacement ellipsoids are drawn at 50% probability level. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1–P1, 2.778(10); Rh1–P2, 2.3163(9); Rh1–P3, 2.3045(10); P3–B1, 1.913(4); P4–B2, 1.918(4); Rh1...B1, 2.515(4); Rh1...B2, 2.740(4); Rh1–P3–B1, 72.54(14); Rh1–B2–P4, 121.3(2).

deduced from the solution NMR spectroscopic data. The formally Rh(III) center adopts a pseudo-octahedral geometry, with the chelating phosphine ligand and the hydride located on one of the faces of the octahedron. Two of the three remaining coordination sites are occupied by a phosphine–borane unit that has undergone P–H activation, and is bound to the metal *via* a phosphido bond [Rh1–P3, 2.3045(10) Å] and a β -B–agostic bond [Rh1–B1, 2.515(4) Å]. The other phosphine–borane unit occupies the last coordination site *via* a σ η^1 -Rh...H–B interaction.⁴² All the hydrides (B–H and Rh–H) were located in the final difference map. The structure is in full accord with the solution NMR spectroscopic data, confirming the spectroscopic assignments that have been made previously.³¹ β -B–agostic interactions are known,^{35,44,45} and we have recently reported [Rh(κ^1 , η -PPh₂BH₂·PPh₃)(PPh₃)₂][BAR^F₄] in which a base-stabilized phosphine–borane adopts a β -B–agostic interaction with the Rh-center.³⁶ σ phosphine–boranes are also known,^{42,46,47} and bimetallic complexes showing both B–agostic and σ borane coordination modes have been reported.⁴⁸ Compared to a Rh(I) complex that shows a bidentate η^2 -coordination mode for the σ borane, [Rh(P^tBu₂H)₂(η^2 -H₃B·P^tBu₂H)][BAR^F₄],³⁰ the Rh...B distance for the η^1 -interaction in **14** is considerably longer [2.188(3) Å versus 2.740(4) Å, respectively], consistent with this different binding motif. Similar changes in M...B distance have been

noted on moving between η^1 and η^2 coordination modes in chelating phosphine–boranes.⁴³

Complexes **14–16** undergo spontaneous dehydrocoupling (25 °C) to form products of the general formula [Rh(L)H-(σ , η^2 -PR₂·BH₂PR₂·BH₃)] [BAR^F₄]: **17**, R = 3,5-(CF₃)₂C₆H₃; **18**, R = *p*-(CF₃)C₆H₄; **19**, R = *p*-(OMe)C₆H₄ (Scheme 4). This

Scheme 4. Dehydrocoupling of Complexes **14–16**^a

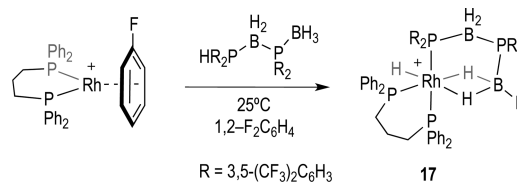


^a[BAR^F₄]⁻ anions are not shown. Time = 6 h **17/21**, **18/22** (25 °C); 8 h **16/19** (35 °C).

process also results in the liberation of H₂ (observed, ^1H NMR spectroscopy). For **17** and **18** there are additional products formed, assigned as [Rh(L)(PR₂H)₂][BAR^F₄], **21** and **22**, respectively, on the basis of NMR spectroscopic data. These complexes are formed in parallel to **17** and **18**, as preformed **17** (*vide infra*) does not proceed to form **21**. Complex **21** has been independently prepared by addition of two equivalents of HP((CF₃)₂C₆H₃)₂ to [Rh(L)(η^6 -FC₆H₅)] [BAR^F₄].

This mixture of products observed for the electron-withdrawing phosphine substituents (i.e., **1** and **2**) contrasts with that found for when R = Ph³¹ and *p*-(OMe)C₆H₄, which yield the dehydrocoupled (e.g., **19** and **F**, Scheme 2) product in essentially quantitative form (~95% by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy). Complex **17** has been synthesized cleanly from direct addition of the preformed dehydrocoupled diboraphosphine product, **10**, to [Rh(L)(η^6 -FC₆H₅)] [BAR^F₄], Scheme 5. It was from this reaction that material of **17** suitable for single crystal X-ray diffraction was obtained.

Scheme 5. Synthesis of **17** by Direct Addition of the Linear Diboraphosphine **10**^a



^a[BAR^F₄]⁻ anions are not shown.

Figure 3 shows the solid-state structure of **17**, in which the diboraphosphine acts as a chelate to the Rh(III) center, *via* a phosphido group and two B–agostic interactions: [Rh(L)H-(σ , η^2 -PR₂·BH₂PR₂·BH₃)] [BAR^F₄] [R = 3,5-(CF₃)₂C₆H₃]. All the hydride ligands (B–H and Rh–H) were located in the final difference map. The Rh(III) center has pseudo-octahedral geometry, in which the oligomeric phosphine–borane is bound tridentate to the metal through η^2 -BH₂...Rh [B2–Rh1, 2.280(5) Å] and phosphido [P3–Rh1, 2.3925(10) Å] interactions. The hydride ligand is positioned *trans* to one of the B–H...Rh interactions. The Rh...B distance is considerably shorter than those observed in **14**, consistent with the η^2 -bidentate binding mode of the borane. This distance is similar

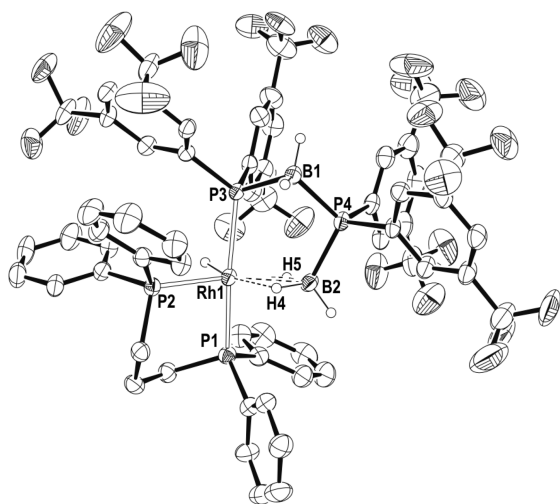


Figure 3. Molecular structure of the cation of **17**. Displacement ellipsoids are drawn at 50% probability level. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh1–P1, 2.3241(11); Rh1–P2, 2.2650(11); Rh1–P3, 2.3925(10); Rh1···B2, 2.280(5); Rh1–P3–B1, 110.88(15); B1–P4–B2, 107.5(2).

to others reported for chelating phosphine–borane complexes with Rh.^{49–52}

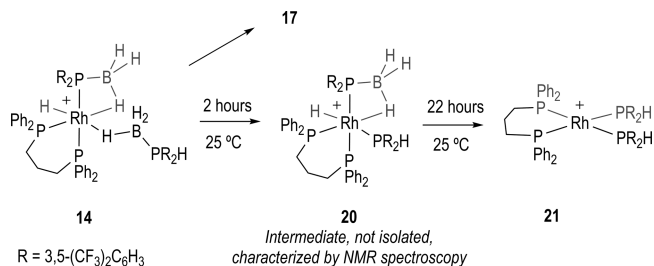
The NMR spectroscopic data for **17** are fully consistent with the solid-state structure being retained in solution and are also very similar to that reported for the analogous complex formed from the dehydrocoupling of **6** (R = Ph).³¹ The ³¹P{¹H} NMR spectrum shows four different phosphorus environments. Two of these signals are well-resolved and show coupling to ¹⁰³Rh, δ 46.6 [$J(\text{RhP})$ 111 Hz] and δ 12.8 [$J(\text{RhP})$ 91 Hz], and are attributed to the chelating phosphine ligand. One of these signals (δ 12.8) also shows large ³¹P–³¹P coupling [$J(\text{PP})$ 260 Hz] suggesting a *trans* position relative to the phosphido center. The other two environments are broad, typical of those observed when coupling to a quadrupolar boron center. For one of these *trans* $J(\text{PP})$ coupling is also observed. The ¹H NMR spectrum shows three different broad, relative integral 1H, environments assigned to the BH₃ moiety [δ –4.54, –1.20, and 4.37]. This indicates that the BH₃ unit is not undergoing exchange on the NMR spectroscopic time scale, as noted previously for similar $\eta^2\text{-M}\cdots\text{H}_3\text{B}$ systems.^{31,43,50,52} The Rh–H signal is observed at δ –13.98 as a sharper signal, although this also shows unresolved coupling. The ¹¹B NMR spectrum shows two different environments [δ –27.1 and 0.21] for the two boron atoms present in the diboraphosphine, with the latter assigned to the $\eta^2\text{-H}_3\text{B}$ unit on the basis of the large downfield shift from free ligand ($\Delta\delta = +36.8$).⁴³ Spectroscopic data for complexes **18** and **19**, that are produced by the direct dehydrocoupling route are similar, although for **18** this is also formed as a mixture with **22**.

The dehydrocoupling reaction (i.e., **14** to **17**) shows a dependence on the substituents on the phosphine. For electron-withdrawing aryl groups (e.g., *p*-CF₃), it is faster when compared with electron rich groups (i.e., *p*-OMe). Following these processes *in situ* using NMR spectroscopy demonstrated that these dehydrocoupling reactions follow a first order rate profile for the consumption of the starting material over at least three half-lives (see Supporting Information): **1** 3 h (25 °C); **2** 3 h (25 °C); **6** 14 h (25 °C);³¹ **3** 8 h (35 °C), ~120 h (25 °C). That the parallel

products **21** and **22** are formed in approximately equal ratio to the dehydrocoupled product (**17**, **18**, respectively)) suggests that $k_1 \approx k_2$ (Scheme 4). In addition to this parallel process, direct comparison of the rate constants is further complicated by the fact that **16** → **19** required heating to 35 °C to make the reaction run over a convenient time scale for analysis by NMR spectroscopy. Nevertheless these relative rates reflect previous observations on the rate of catalytic dehydrocoupling when the electronics of a system are changed, in as much as electron-withdrawing groups promote the reaction.²¹ Interestingly, for all the aryl complexes initial P–H activation to form a phosphido hydride complex (i.e., **14**) is very rapid, occurring on time of mixing. This suggests that for aryl-substituted phosphine–boranes it is not initial P–H activation that is rate-determining for the dehydrocoupling event, as we have commented on for R = Ph.³¹ In this study we suggested that B–H activation/reorganization in intermediates such as **B** (Scheme 2) prior to P–B bond formation might be the rate limiting process.³¹ This might well be promoted by a weaker B–H bond, and calculations on analogous H₃B·L (L = Lewis base) systems show that the B–H bond is considerably weaker when there are electron-withdrawing groups on the Lewis base.⁵³ However, we cannot rule out that the relative P–H bond strengths in intermediates such as **14** also might play a role, or that there is a change in the rate determining step on changing the phosphine–borane ligand, as the intimate details of the mechanism leading to P–B formation still remain to be resolved. The observation that for an electron-withdrawing phosphine there is a significant proportion of parallel product formed that results from P–B bond cleavage is consistent with the weakening of the P–B bond with increasingly electron-withdrawing aryl substituents.^{8,54} P–B bond cleavage has been noted previously in σ phosphine–borane complexes to give either simple adducts⁴⁷ or further reaction to yield bis-(phosphine)boronium salts.³⁰

Prior to the formation of the parallel product **21** (R = 3,5-(CF₃)₂C₆H₃) an intermediate is observed that has been characterized by ¹H and ³¹P{¹H} NMR spectroscopy as [Rh(L)H($\sigma,\eta\text{-PR}_2\text{-BH}_3$)(PR₂H)][BAR^F₄][–] **20**, i.e., a complex that sits directly between **14** and **21** by loss of one “BH₃” fragment (Scheme 6). Complex **20** results from P–B bond

Scheme 6. Formation of the Parallel Products **17** and **21** from **14**^a

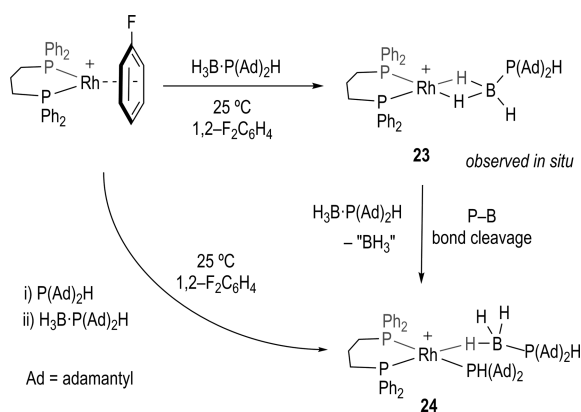


cleavage, formally of the $\sigma\text{-H}_3\text{B}\cdot\text{PR}_2\text{H}$ ligand, to afford a complex with a $\beta\text{-B-agostic}$ interaction from a phosphido borane ligand (as for **14**) and a simple PR₂H ligand *trans* to a hydride. Complex **20** was not isolated in pure form, being observed alongside **14** and the final products **17/21**. However, after 2 h reaction a significant proportion of **20** is present (~20% by ³¹P NMR spectroscopy), allowing for its

identification aided by comparison with the NMR spectroscopic data for **14** (Supporting Information). In particular four environments are observed in the ^{31}P NMR spectrum, with only one of these broadened significantly by coupling to quadrupolar boron. This signal also shows a large, mutual, *trans* $J(\text{PP})$ coupling with another phosphine environment. In the high-field region of the ^1H NMR spectrum a broad doublet is observed at $\delta -7.06$ [$J(\text{HP}) = 76$ Hz] which is assigned to the β -B-agostic interaction, while there is a relatively sharper one at $\delta -9.61$ [$J(\text{HP}) = 165$ Hz] assigned to Rh–H, and again ^{103}Rh coupling is not resolved. These assignments were confirmed by $^1\text{H}\{^{31}\text{P}\}$, $^1\text{H}\{^1\text{B}\}$, and $^1\text{H}/^{31}\text{P}$ correlation experiments.

Addition of 2 equiv of the bulky and electron rich phosphine–borane $\text{H}_3\text{B}\cdot\text{P}(\text{adamantyl})_2\text{H}$, **4**, to $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BAR}^{\text{F}}_4]$ in $1,2\text{-F}_2\text{C}_6\text{H}_4$ solution at 25°C rapidly results in a color change from orange to purple and the formation of the new σ bound Rh(I) phosphine–borane complex $[\text{Rh}(\text{L})(\eta^2\text{-H}_3\text{B}\cdot\text{P}(\text{adamantyl})_2\text{H})][\text{BAR}^{\text{F}}_4]$, **23**, which was characterized *in situ* by NMR spectroscopy. This complex could not be isolated as it undergoes further reaction, by P–B bond cleavage at room temperature, to form **24** (Scheme 7). Addition of 1 equiv of **4** resulted in a final mixture of **24** and $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BAR}^{\text{F}}_4]$.

Scheme 7. Synthesis of Complex **24** by Direct and Indirect Routes^a



^a $[\text{BAR}^{\text{F}}_4]^-$ anions are not shown.

The ^1H NMR spectrum of complex **23** immediately after preparation shows a broad, relative integral 3H, signal at $\delta -1.36$ characteristic of a σ -bound phosphine–borane that is undergoing site exchange between the coordinated and uncoordinated B–H environments.⁴² Two signals are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, in a 2:1 ratio at $\delta 35.1$ [$J(\text{RhP}) 167$ Hz] and $\delta 30.1$ (br). Over time (1 h), complex **23** disappears to be replaced by a new complex that has been characterized by NMR spectroscopy and a solid-state X-ray diffraction experiment as $[\text{Rh}(\text{L})(\text{PHR}_2)(\eta^1\text{-H}_3\text{B}\cdot\text{PHR}_2)]\text{-}[\text{BAR}^{\text{F}}_4]$ (**24**, R = adamantyl). Figure 4 shows the structure of the cation present in **24** in the solid-state. A Rh(I) center is in a pseudo-square-planar geometry with a chelating ligand, and the other two coordination sites are occupied by $\text{P}(\text{adamantyl})_2\text{H}$ and a $\eta^1\text{-H}_3\text{B}\cdot\text{P}(\text{adamantyl})_2\text{H}$ [$\text{Rh}\cdots\text{B}$, 2.457(7) Å] ligands, respectively. The BH and PH hydrogen atoms were located in the final difference map. The solution NMR spectroscopic data for **24** are fully consistent with the solid-state structure, and in particular the *trans* disposition of P1 and P3, and the $\eta^1\text{-H}_3\text{B}\cdot\text{PR}_2\text{H}$ ligand.

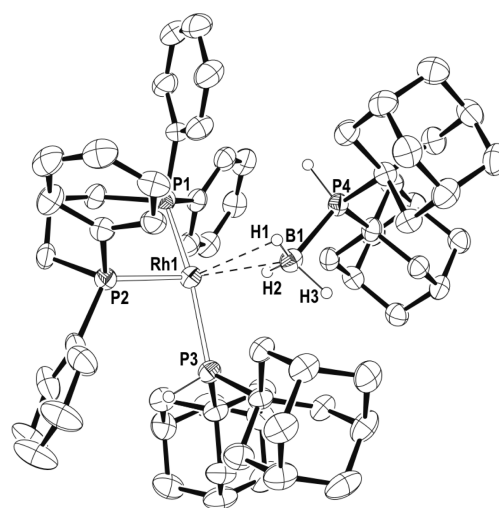


Figure 4. Molecular structure of the cation of **24**. Displacement ellipsoids are drawn at 50% probability level. Some hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Rh1–P1, 2.2262(16); Rh1–P2, 2.2861(16); Rh1–P3, 2.3568(15); Rh1⋯B1, 2.457(7); B1–P4, 1.936(7).

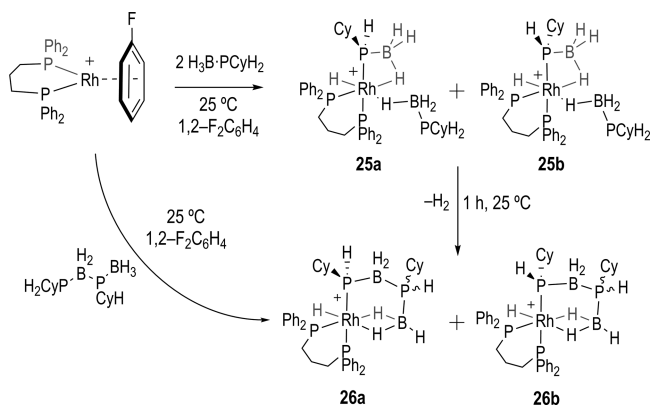
A significant amount of P–B bond cleavage product is thus observed for both electron poor aryl phosphine–boranes (e.g., **14**) and very bulky electron rich phosphine–boranes (e.g., **24**), but *not* the electron rich aryl phosphine **3** or $\text{H}_3\text{B}\cdot\text{PPh}_2\text{H}$ (**6**).³¹ Interestingly we have recently reported that for $\text{H}_3\text{B}\cdot\text{P}^t\text{Bu}_2\text{H}$ P–B bond cleavage is also observed during dehydrocoupling catalysis being accompanied by a further dehydrocoupling step, through which bis(phosphine)boronium salts are ultimately formed.^{30,36} Similar complexes can be prepared on rhodium using $\text{H}_3\text{B}\cdot\text{PPh}_2\text{H}$ and PPh_3 under stoichiometric conditions.³⁶ One suggested mechanism for this process is the reaction of a short-lived phosphino–borane (or its masked equivalent) with coordinated phosphine, not dissimilar to the mechanism suggested for the formation of diamineboranes from amine–boranes and amines catalyzed by alkaline earth catalysts.⁵⁵ Complexes **20** and **24** serve as models for intermediates in this process [Rh(III) and Rh(I), respectively], although we do not observe the formation of corresponding bis(phosphine)boronium salts in this case.

Stoichiometric Dehydrocoupling of Primary Phosphine–Boranes. The dehydrocoupling of primary phosphine–boranes can yield polyphosphinoboranes, rather than the simple oligomers observed with secondary phosphine–boranes (Scheme 1). With an appreciation of the intermediate metal complexes formed with secondary phosphine–boranes from this and previous work,^{30,31,36} it was of interest to explore whether the proposed dehydrocoupling mechanism for secondary phosphine–boranes using $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)]\text{-}[\text{BAR}^{\text{F}}_4]$ could be applied to primary analogues. Such insight into the mechanism of dehydropolymerization of phosphine–boranes is important, as these processes currently remain unresolved due to the melt conditions employed that make following intermediates or kinetics problematic.^{20,28,33}

In situ investigations using stoichiometric quantities of primary phosphine–boranes $\text{H}_3\text{B}\cdot\text{PPh}_2\text{H}$ resulted in immediate reaction when combined with $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)]\text{-}[\text{BAR}^{\text{F}}_4]$, but a number of products were formed which we have not been able to convincingly characterize. This mixture of species observed is in contrast with $\text{H}_3\text{B}\cdot\text{PPh}_2\text{H}$ where single products

are formed analogous to **14**–**16**.³¹ However, reaction of $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BAR}^{\text{F}}_4]$ with a slight excess of $\text{H}_3\text{B}\cdot\text{PCyH}_2$ (**5**) in 1,2- $\text{F}_2\text{C}_6\text{H}_4$ solution at 25 °C led to the instantaneous formation of only two complexes in a 1:1 ratio, **25a** and **25b**, $[\text{Rh}(\text{L})\text{H}(\sigma,\eta\text{-PCyH}\cdot\text{BH}_3)(\eta^1\text{-H}_3\text{B}\cdot\text{PCyH}_2)][\text{BAR}^{\text{F}}_4]$, as a proposed diastereomeric pair (Scheme 8). This stereoisomerism

Scheme 8. Synthesis of **25a**, **25b**, and the Dehydrocoupled Products **26a** and **26b**^a



^a $[\text{BAR}^{\text{F}}_4]^-$ anions are not shown.

comes from P–H activation at the prochiral primary phosphine. These new products are directly analogous to those formed with secondary phosphine–boranes (i.e., **14**), and the NMR spectroscopic data match closely. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum from this reaction shows 8 resonances, in addition to a broad peak at $\delta -35.5$ due to excess phosphine–borane, as each diastereomer contains four distinct phosphorus environments. Signals centered at $\delta 31.7$ and 30.5 are assigned to one of the chelating phosphine ligand ^{31}P environments in each diastereoisomer, and show characteristic $J(\text{RhP})$ coupling constants consistent with a Rh(III) center. Complex overlapping multiplets at $\delta 11.8$ [$2 \times \text{ddd}$] represent the resonances for both diastereomers of the second chelated phosphorus center, which is *trans* to the phosphido position, displaying a large *trans* PP coupling constant [$J(\text{PP}) \sim 200$ Hz] in addition to coupling to ^{103}Rh and *cis*- ^{31}P . The remaining 4 signals are broad indicating the phosphorus centers are bound to a quadrupolar ^{11}B nucleus. Of these, peaks at $\delta -11.0$ and -32.1 are assigned to the phosphido centers of each diastereomer *trans* to the chelating phosphine [$J(\text{PP}) \sim 200$ Hz], and resonances at $\delta -39.8$ and $\delta -44.2$ as assigned to phosphorus centers in the σ -bound phosphine–borane unit. These large differences in chemical shift of the phosphido signal ($\Delta\delta 21.2$) might reflect significant local difference in steric pressure between **25a** and **25b** at this group. Interestingly, a much smaller difference is observed with the dehydrocoupled products (**26a/b**, $\Delta\delta 3.5$) in which the phosphido group is part of a chelate ring. The ^1H NMR spectrum does not have the necessary resolution to separate out the diastereomers in the hydride region, with broad resonances observed at $\delta -2.3$ (3 H, BH_3), $\delta -7.9$ (1 H, Rh–H–B), $\delta -17.5$ (Rh–H).

Complexes **25a/b** cannot be isolated in pure form, and characterization by NMR spectroscopy is best performed on freshly prepared samples, as after 1 h (25 °C) they have undergone dehydrocoupling to give a mixture of two resolvable diastereomers **26a** and **26b**, with one of the diastereomers present in a significantly larger amount $\sim 6:1$ (Scheme 8),

indicating that the dehydrocoupling step occurs with some stereocontrol.⁵⁶ The decomposition product $[\text{Rh}(\text{L})(\text{PH}_2\text{Cy})_2]^+$, analogous to **21/22**, was also observed. NMR spectroscopic and ESI-MS analysis suggests that the dehydrocoupling products formed are direct analogues of **17**. This mixture of diastereomers can also be synthesized cleanly by direct reaction of $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BAR}^{\text{F}}_4]$ with the preformed diaborophosphine $\text{H}_3\text{B}\cdot\text{PCyH}\cdot\text{BH}_2\cdot\text{PCyH}_2$ (**13**) in 1,2- $\text{F}_2\text{C}_6\text{H}_4$ solution at 25 °C (Figure 5 for the solid-state

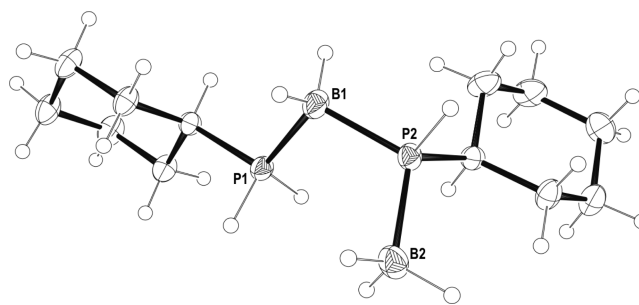


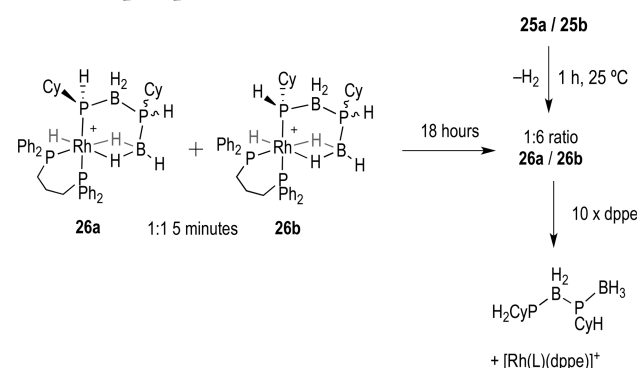
Figure 5. Molecular structure of **13**. Displacement ellipsoids are drawn at 50% probability level. Selected bond lengths (Å) and angles (deg): P1–B1 1.9267(18), B1–P2 1.9381(18), P2–B2 1.926(2); P1–B1–P2 108.34(9), B1–P2–B2 113.32(9).

structure). Immediate measurement of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum after mixing showed clean conversion to complexes **26a** and **26b** in an approximate 1:1 ratio, interestingly different from the 1:6 ratio observed from dehydrocoupling.

Resonances in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **26** can, again, be assigned aided by reference to those of structurally characterized **17**. Peaks centered at $\delta 37.9$ and 34.5 result from the chelated phosphorus *trans* to the B-agostic site, while the signals for the phosphorus *trans* to the phosphido group overlap at $\delta 10.7$, and display characteristic $J(\text{PP})$ *trans* coupling [255 Hz]. The broad resonances of the diborophosphine are observed at $\delta 19.8$ and 16.2 for the phosphido center [$J(\text{PP}) 255$] and $\delta -14.9$ and -16.6 ppm for the remaining site. The high-field region of the ^1H NMR spectrum of **26a/26b** shows a slight downfield shift of the Rh–H hydride resonance to $\delta -16.1$, when compared to **25a/25b**, while the $\eta^2\text{-BH}_2\cdots\text{Rh}$ units are observed as two broadened resonances at $\delta -2.98$ (1H) and $\delta -5.98$ (1H). For these hydride signals the separate signals are not resolved for each diastereoisomer, although each resonance is rather asymmetric suggesting two overlapping environments.

A $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum taken of this mixture after 18 h at 25 °C showed a significant change in the ratios of the diastereomers **26a/26b** (Scheme 9). The peaks for one isomer at [$\delta 34.5, 16.2, 10.7$, and -14.9] have reduced relative area, giving an approximate ratio of 6:1 for the two diastereoisomers. This ratio is similar to that found from direct dehydrocoupling in **25a/25b** after 1 h (*vide supra*), underscoring the stereocontrol occurring in the P–B bond forming process. Leaving this solution for one week resulted in no significant change to this ratio, suggesting equilibrium had been reached. We suggest that the mechanism for equilibration involves reductive elimination of the phosphido and hydride ligands to form a Rh(I) σ phosphine–borane complex,³⁰ similar to **E** in Scheme 2, which then undergoes rapid oxidative addition of the other P–H bond. This must be a reversible process, leading to a thermodynamic ratio of the diastereoisomers and the resulting

Scheme 9. Change in Diastereoisomeric Ratio and Release of the Diboraphosphine^a

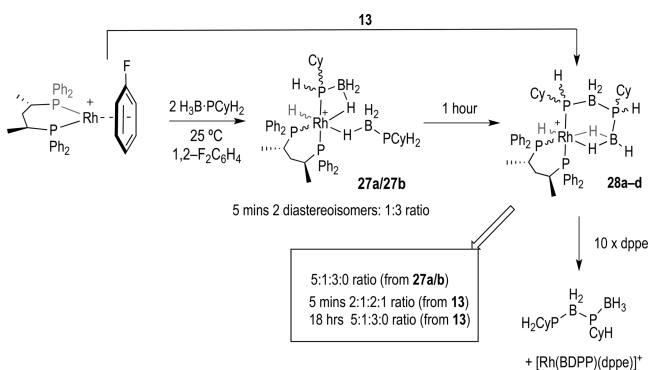


^a[BAR^F₄]⁻ anions are not shown.

selectivity. Unfortunately we were unable to deduce the stereochemistry of the preferred isomer using ROESY experiments or a solid-state structure. However, inspection of models leads us to propose that the thermodynamic product is likely to have the cyclohexyl group pointing away from the chelating phosphine ligand's phenyl groups, i.e., **26b**. That these diastereoisomers are a result of the metal activation of the prochiral terminal P–H bonds in **13** is shown by addition of an excess of dppe to **26a/b**.⁵⁶ This affords [Rh(dppe)(L)]-[BAR^F₄]⁻ with the concomitant formation of free **13** (Scheme 9).

We have briefly explored the use of a chiral metal/ligand fragment in dehydrocoupling, [Rh(BDPP)]⁺ [*S,S*-BDPP = (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane]. This chiral ligand was chosen as electronically and sterically (i.e., bite angle) it is similar to Ph₂P(CH₂)₃PPh₂. Addition of H₃B-PCyH₂, **5**, to [Rh(BDPP)(η⁶-FC₆H₅)] [BAR^F₄]⁻ results in the immediate formation of *two* diastereoisomers of [Rh(BDPP)-H(σ,η²-PCyHBH₃)(η¹-H₃B-PCyH₂)] [BAR^F₄]⁻, **27**, in a 3:1 ratio (Scheme 10). Although we are unable to comment on the

Scheme 10. Use of a Chiral Ligand in Dehydrocoupling^a



^a[BAR^F₄]⁻ anions are not shown.

absolute configuration of these isomers, it is interesting to note that this is biased away from the 1:1 ratio observed in the achiral system. Compounds **27a/b** proceed on to dehydrocouple to form diastereoisomers of [Rh(BDPP)H(σ,η²-PRH-BH₂PRH-BH₃)] [BAR^F₄]⁻, **28**, 1:5:3:0 ratio. The same mixture of diastereoisomers can be formed by direct addition of **13** to [Rh(BDPP)(η⁶-FC₆H₅)] [BAR^F₄]⁻. Initially a 2:1:2:1 ratio of 4 isomers is observed, that changes to a 5:1:3:0 ratio after 18 h.

We are unable to comment in more detail on the conformation of these isomers, although the observation of stereocontrol in the direct dehydrocoupling is similar to that observed for the achiral system. Addition of excess dppe to this mixture forms a product identified by ESI-MS as [Rh(BDPP)(dppe)]⁺ and free **13** (by ³¹P and ¹¹B NMR spectroscopy). We have not explored whether there is enantiocontrol at the central {PCyH unit} arising from this PB coupling event on release from the metal.

For these experiments with H₃B-PCyH₂ it is interesting to note that P–H activation is rapid and reversible with the Rh(I) precursor. This is in contrast to results obtained with secondary phosphine–boranes H₃B-P^tBu₂H and H₃B-P^tBu₂BH₂.P^tBu₂H, which on addition to [Rh(L)(η⁶-FC₆H₅)] [BAR^F₄]⁻ gave the corresponding Rh(I) σ-phosphine–borane complexes with no P–H activation.³¹ Such selectivity for primary over secondary phosphines in P–H activation at a metal center has been described previously for both phosphine⁵⁷ and phosphine–borane ligands.²⁷ In particular it has been shown that addition of H₃B-PPh₂ to Pt(PET₃)₂H(PPh₂·BH₃) results in exchange of the metal bound phosphide complex to give the primary phosphido–borane complex.²⁶ Here it was suggested that the greater thermodynamic driving force for formation of the primary phosphido–borane complex comes from steric effects, as M–P bonds to smaller primary phosphido ligands are likely to be stronger.

Catalytic Dehydrocoupling of Secondary Phosphine–Boranes. Under the standard catalytic melt conditions (90 °C, 5 mol %),²⁰ [Rh(L)(η⁶-FC₆H₅)] [BAR^F₄]⁻ will dehydrocouple the secondary aryl phosphine–boranes used in this study to form the corresponding linear diboraphosphines **10–12**, although we have not explored in detail the temporal evolution of these systems due to the problems associated with directly interrogating the melt. However, trends can be observed. For electron-withdrawing groups (**1** and **2**), complete consumption of starting material occurs in 4 h (Table 1). The reaction at this

Table 1. Conversion of H₃B-PR₂H with Time^a

H ₃ B-PR ₂ H	time/h	H ₃ B-PR ₂ H/%	H ₃ B-PR ₂ BH ₂ PR ₂ H/%	(BH ₂ PR ₂) _n /%
1	1	10	55	<5
	4	<5	45	10
	8	<5	35	50
2	1	10	70	10
	4	<5	70	15
	8	<5	70	15
3	1	50	30	<5
	4	30	45	5
	8	20	60	5

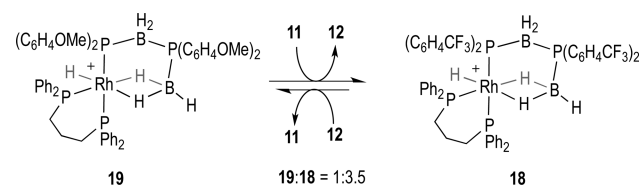
^aR = aryl, see Figure 1. [Cat.] = [Rh(L)(η⁶-FC₆H₅)] [BAR^F₄]⁻, L = Ph₂P(CH₂)₃PPh₂. Conversions calculated from ³¹P{¹H} NMR spectra. Conditions: [Rh(L)(η⁶-FC₆H₅)] [BAR^F₄]⁻, 5 mol %, 90 °C, melt.

temperature is not selective, and although the main product is the linear diboraphosphine, there are products that we tentatively identify as the cyclic oligomers (BH₂PR₂)_n (n = 3, 4).^{20,33} Our results are broadly in line with the previously reported catalyzed dehydrocoupling of **2** using [Rh(COD)Cl]₂, which, at a slightly lower temperature (60 °C, 16 h, melt), affords the linear diboraphosphine product in 69% isolated yield, while at 100 °C only the cyclic oligomers are isolated. The mechanism of formation of the higher cyclic oligomers, (BH₂PR₂)_n, remains to be resolved.²⁰ For electron-donating **3** the reaction is slower using the [Rh(L)(η⁶-FC₆H₅)] [BAR^F₄]⁻

catalyst (8 h) but overall is more selective. For R = Ph we have previously shown that $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BAR}^{\text{F}}_4]$ catalyzes dehydrocoupling to give the corresponding linear diboraphosphine in greater than 95% conversion after 4 h.³¹ For secondary phosphine–boranes, $\text{H}_3\text{B}\cdot\text{PPh}_2\text{H}$ thus offers balance between overall rate and selectivity.

Given the product distributions and likely decomposition pathways in the melt it is inappropriate to comment in detail on the nature of the rate-determining steps during catalysis under these conditions. However, on the basis of the solution studies, P–B bond formation, (dehydrocoupling) is faster with electron-withdrawing groups. The temporal differences in observed product conversion in the melt could reflect a difference in the rate of the P–B bond forming event, or alternatively, they could reflect the ease at which the bound product is substituted on the metal center, i.e., a turnover limiting step. To probe this latter scenario, reaction between **19** (aryl-OMe) and diboraphosphine **11** (aryl- CF_3) to form **18** and free **12** demonstrates that an equilibrium is established slightly in favor of **18** (Scheme 11). This suggests that there is not a

Scheme 11. Competition Experiments between Linear Diboraphosphines^a



^a $[\text{BAR}^{\text{F}}_4]^-$ anions are not shown.

strong inherent difference in binding strengths between the two products, with the implication being that the observed rate differences in the melt arise from the dehydrocoupling step. Although this is different from what is observed in solution at room temperature, in which release of the product is likely the turnover limiting step, it is consistent with the high local concentration of $\text{H}_3\text{B}\cdot\text{PR}_2\text{H}$ that being under melt conditions (90 °C) would promote such a substitution.

Catalytic Dehydrocoupling of Primary Phosphine–Boranes. $[\text{Rh}(\text{L})(\eta^6\text{-FC}_6\text{H}_5)][\text{BAR}^{\text{F}}_4]$ also acts as a catalyst for the dehydrocoupling of primary phosphine–boranes. Under melt conditions (90 °C, 5 mol %, 4 h) $\text{H}_3\text{B}\cdot\text{PPhH}_2$ is dehydrocoupled to give a major product which is identified by ³¹P NMR spectroscopy as being polymeric $(\text{BH}_2\text{PPhH})_n$ by comparison with previously reported^{19,20} data for purified material coming from the $[\text{Rh}(\text{COD})_2][\text{OTf}]$ catalyzed process [δ –49.3, d, $J(\text{PH}) \sim 350$ Hz, 1,2- $\text{F}_2\text{C}_6\text{H}_4$; lit.: δ –48.9, δ , $J(\text{PH})$ 360 Hz, CDCl_3]. There were also other species observed $\sim \delta$ –55, which could be reduced in relative concentration (to $\sim 10\%$) by precipitation into hexanes. Such species have been previously suggested to be short-chain oligomers.²⁰ Interestingly, these proposed shorter chain oligomers are present in a greater proportion at shorter reaction times, which might suggest that polycondensation is occurring to give higher molecular weight polymer. Under non-melt conditions²⁰ (toluene heated to reflux, 0.5 mol %, 16 h) these shorter oligomers are by far the dominant species (Supporting Information). It thus appears that a high local concentration of phosphine–borane is necessary for productive dehydrocoupling. Positive mode ESI-MS (electrospray mass

spectrometry) of the melt reaction product demonstrated polymerization, showing repeat units of $[\text{H}-(\text{PPhHBH}_2)_n\text{PPhH}_2]^+$ up to $n = 10$ (Supporting Information). Similar analyses have been reported for amine–borane dehydrocoupling.^{12,14,58} That these polymers are terminated by $\{\text{PPhH}_2\}$ groups rather than $\{\text{BH}_3\}$ is confirmed by inspection of the corresponding isotopomer patterns. This formulation also argues against cyclic oligomers being observed by ESI-MS, and presumably the additional phosphine arises from P–B bond cleavage. Use of $\text{H}_3\text{B}\cdot\text{PCyH}_2$ under these conditions afforded significantly more complex mixtures that we were unable to resolve.

CONCLUSIONS

The solid-state structures of the intermediates in the dehydrocoupling of secondary phosphine–boranes using the $\{\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\}^+$ fragment have been determined. This demonstrates that the complex that precedes dehydrocoupling to form a linear diboraphosphine has σ bound and P–H activated phosphine–borane ligands, while the product has a linear diboraphosphine bound to the metal center. For aryl phosphine–boranes, electron-withdrawing groups (CF_3) promote stoichiometric dehydrocoupling faster than for more electron-donating (OMe) groups. This increase in rate is accompanied by a significant degree of parallel and competitive P–B bond cleavage to afford metal complexes with two monodentate phosphine ligands, which we suggest is due to a weakening of the P–B bond with electron-withdrawing aryl groups. These systems also turnover catalytically under melt conditions, with the overall rate of conversion broadly following the relative dehydrocoupling rates observed in the stoichiometric studies, suggesting that the dehydrocoupling step under melt conditions might also be the turnover limiting step. P–B bond cleavage also occurs for very bulky electron rich adamantyl phosphine–boranes, to such an extent that stoichiometric dehydrocoupling is not observed. For this phosphine–borane we suggest that sterics play a role in this process.

A significant observation is that, for primary phosphine–boranes, which are precursors to polyphosphinoboranes, use of the $\{\text{Rh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{CH}_2\text{PPh}_2)\}^+$ fragment results in some apparent diastereoselectivity in the dehydrocoupling step, at least in the stoichiometric reactions that produce metal-bound diboraphosphines. Such selectivity could well have implications in the control of the stereochemistry of polymer that would result from further insertion events. A significant future challenge is to harness any inherent bias in each dehydrocoupling insertion step productively while also developing the necessary spectroscopic and physical characterization markers to interrogate the oligomer and polymer stereochemistry.

EXPERIMENTAL SECTION

All manipulations, unless otherwise stated, were performed under an atmosphere of argon, using standard Schlenk and glovebox techniques. Glassware was oven-dried at 130 °C overnight and flamed under vacuum prior to use. Hexane and pentane were dried using a Grubbs type solvent purification system (MBraun SPS-800) and degassed by successive freeze–pump–thaw cycles.⁵⁹ CD_2Cl_2 , $\text{C}_6\text{H}_5\text{F}$, and 1,2- $\text{F}_2\text{C}_6\text{H}_4$ were distilled under vacuum from CaH_2 and stored over 3 Å molecular sieves, 1,2- $\text{F}_2\text{C}_6\text{H}_4$ was stirred over alumina for 2 h prior to drying. Bis-1,3-(diphenylphosphino)propane (dpp3) and (2*S*,4*S*)-2,4-bis(diphenylphosphino)pentane (BDPP) were purchased from Aldrich. $[\text{Rh}(\text{nbd})\text{Cl}]_2$ ⁶⁰ and $[\text{Rh}(\text{nbd})(\text{dpp3})][\text{BAR}^{\text{F}}_4]$ ¹⁶ were prepared as previously described. (4-Methoxyphenyl)₂HP·BH₃ (**3**),

(adamantyl)₂HP·BH₃ (4), and CyH₂P·BH₃ (5) were prepared by the same method as Me₃P·BH₃⁶¹ but with the phosphine changed. (4-Trifluoromethylphenyl)₂PH·BH₃ (2) and (3,5-bis(trifluoromethyl)phenyl)₂PH·BH₃ (1) were prepared according to literature procedures reported by Clark et al.³³ NMR spectra were recorded on a Bruker AVD 500 MHz spectrometer at room temperature unless otherwise stated. In 1,2-C₆H₄F₂, ¹H NMR spectra were referenced to the center of the downfield solvent multiplet (δ 7.07), and ³¹P and ¹¹B NMR spectra were referenced against 85% H₃PO₄ (external) and BF₃·OEt₂ (external), respectively. The spectrometer was prelocked and preshimmed using a C₆D₆ (0.1 mL) and 1,2-C₆H₄F₂ (0.3 mL) sample. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker micrOTOF instrument.⁶² In all ESI-MS spectra there was a good fit to both the principal molecular ion and the overall isotopic distribution. Signals in the ³¹P{¹H} NMR spectra were integrated relative to those in similar environments (i.e., Rh–P or B–P) to obtain the relative ratios of products, and data was acquired with a pulse repetition time of 1 s. This avoids potential problems with different relaxation times for different phosphorus environments. Nevertheless, the quoted relative ratios based upon this data should be treated as qualitative rather than quantitative.

Synthesis and Characterization of New Complexes. *Synthesis of H₃B·PR₂H [R = 3,5-Bis(trifluoromethyl)phenyl] (1).* A solution of (3,5-bis(trifluoromethyl)phenyl)₂PCL (1.48 g, 3.0 mmol) in diethyl ether (5 mL) was added dropwise to a diethyl ether (20 mL) suspension of LiBH₄ (0.070 g, 3.21 mmol) cooled to 5 °C with an ice bath. The mixture became cloudy immediately and was allowed to stir for 30 min. The diethyl ether was removed *in vacuo*, and the residue was dissolved in hexanes (30 mL) and filtered through Celite. The hexanes were reduced *in vacuo* to ~10 mL, and the solution was placed in the freezer (–20 °C) overnight yielding colorless crystals. Excess hexanes were decanted, and crystals were dried to afford a fine white powder which was subsequently washed with 2 × 3 mL of cold hexanes. Removal of all volatiles under reduced pressure yielded 630 mg of fine white powder (1).

¹H NMR (300 MHz, CDCl₃): δ 8.14 (br s, 1 H, *p*-Ar-H), 8.09 (br s, 2 H, *o*-Ar-H), 6.58 (dm, ¹J_{HP} = 388 Hz, 1 H, PH), 0.3–2.0 (br m, 3 H, BH). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 4.7 (br s, PH). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ –41.7 (br s, BH₃). ¹⁹F NMR (282 MHz, CDCl₃): δ –62.9 (s, CF₃). EI-MS (70 eV) *m/z* (%): 458 (62) [M⁺ – BH₃]. Anal. Found: C 40.71%, H 2.02%. Calcd for C₁₆H₁₀BF₁₂P: C 40.68%, H 2.14%.

Synthesis of (Adamantyl)₂PH·BH₃ (4). (Adamantyl)₂PH·BH₃ was prepared under the same conditions as Me₃P·BH₃⁶¹ but with (adamantyl)₂PH instead of PMe₃.

¹H NMR (300 MHz, CDCl₃): δ 3.61 (dm, 1 H, ¹J_{HP} = 379 Hz, PH), 2.11 to 1.83 (30 H, adamantyl-H), 0.41 to –0.15 (br m, 3 H, BH). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ 40.1 (br m, PH). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ –44.8 (br d, BH₃). Anal. Found: C 75.78%, H 10.71%. Calcd for C₂₀H₃₄BP: C 75.89%, H 10.84%.

Synthesis of H₃B·PR₂BH₂·PR₂H [R = 3,5-Bis(trifluoromethyl)phenyl] (10); 4-Trifluoromethylphenyl (11); 4-Methoxyphenyl (12)]. A Youngs flask charged with 0.25 mmol of R₂PH·BH₃ (118 mg of 1, 84 mg of 2, 65 mg of 3) and 5 mol % of [Rh(dpp3)(C₆H₅F)] [BAr^F]₄ (18.4 mg, 0.0125 mmol) was heated to 90 °C for 4 h (10 and 11) or 8 h (12) in melt conditions. The resulting solids were washed with *n*-hexane and recrystallized from a mixture of diethyl ether and hexane at –18 °C (10 30 mg, 25%; 11 22 mg, 26%; 12 32 mg, 49%).

Details follow for 10. ¹H NMR (300 MHz, CDCl₃): δ 8.09 to 7.89 (12 H, Ar–H), 7.32 (dm, ¹J_{HP} = 412 Hz, 1 H, PH), 2.45 (br m, 2 H, BH₂), 1.11 (br m, 3 H, BH₃). ³¹P{¹H} NMR (121 MHz, CDCl₃): δ –1.7 (br s, PHR₂), –14.0 (br s, PR₂). ¹¹B{¹H} NMR (160 MHz, CDCl₃): δ –33.2 (br s, BH₂), –37.7 (br s, BH₃). Anal. Found: C 40.90%, H 1.83%. Calcd for C₃₂H₁₈B₂F₂₄P₂: C 40.76%, H 1.93%.

Details follow for 11. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.77 to 7.52 (16 H, Ar–H), 7.04 (dt, ¹J_{HP} = 426 Hz, ³J_{H_{HH}} = 7.8 Hz, 1 H, PH), 2.37 (br m, 2 H, BH₂), 1.02 (br m, 3 H, BH₃). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ –3.5 (br s, PHR₂), –15.4 (br s, PR₂). ¹¹B{¹H} NMR (160 MHz, CD₂Cl₂): δ –33.7 (br s, BH₂), –37.6 (br s, BH₃).

Details follow for 12. ¹H NMR (500 MHz, CD₂Cl₂): δ 7.64 to 6.77 (16 H, Ar–H), 6.69 (dt, ¹J_{HP} = 415 Hz, ³J_{H_{HH}} = 6.6 Hz, 1 H, PH), 3.84 (s, 6 H, CH₃), 3.80 (s, 6 H, CH₃), 2.14 (br m, 2 H, BH₂), 0.96 (br m, 3 H, BH₃). ³¹P{¹H} NMR (202 MHz, CD₂Cl₂): δ –7.6 (br s, PHR₂), –22.1 (br s, PR₂). ¹¹B{¹H} NMR (160 MHz, CD₂Cl₂): δ –33.3 (br s, BH₂), –37.1 (br s, BH₃).

Synthesis of [Rh(dpp3)H(PR₂·BH₃)(H₃B·PHR₂)] [BAr^F]₄ [R = 3,5-Bis(trifluoromethyl)phenyl (14); 4-Trifluoromethylphenyl (15); 4-Methoxyphenyl (16)]. To a Youngs flask charged with [Rh(dpp3)(C₆H₅F)] [BAr^F]₄ (50 mg, 0.034 mmol) and 2 equiv of H₃B·PR₂H (32 mg of 1, 23 mg of 2, 18 mg of 3 0.068 mmol) was added 1,2-F₂C₆H₄ (5 mL). The solution was stirred at room temperature 10 min, and a change in color from pale orange to bright yellow was observed. Complexes 15 and 16 were isolated as yellow oils, and characterized *in situ* by NMR spectroscopy and ESI-MS. Complex 14 could be crystallized at –24 °C in the freezer inside the glovebox (yield 29.6 mg, 37%). Complexes 15 and 16 could not be isolated cleanly, and attempts to do so led to intractable mixtures of 15 and 16 with 18 and 19, respectively.

Details follow for 14. Slow diffusion of pentane (10 mL) over a solution of 14 in 1,2-F₂C₆H₄ at –24 °C afforded yellow crystals (one of which was employed for an X-ray diffraction study).

¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAr^F), 7.69 (s, 4 H, BAr^F), 5.81 (d, ¹J_{HP} = 435 Hz, 1 H, PH), 3.12–0.81 (8 H, 3CH₂dpp3 + BH₂), –0.78 (br, 3 H, BH₃), –6.12 (br, 1 H, BH–Rh), –16.21 (s, 1 H, Rh–H). Signals from the aromatics were not observed due to being overlapped by signals from 1,2-F₂C₆H₄.

¹H NMR (500 MHz, 1,2-F₂C₆H₄, selected data at 0 °C): δ –6.12 (d, ¹J_{HP} = 65 Hz, 1 H, BH–Rh). ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 29.5 (ddd, ¹J_{PRh} = 130 Hz, ¹J_{PP(cis)} = 35 Hz, ¹J_{PP(trans)} = 21 Hz, Ph₂P(CH₂)₃PPh₂), 11.3 (ddd, ¹J_{PP(trans)} = 244 Hz, ¹J_{PRh} = 103 Hz, ¹J_{PP(cis)} = 35 Hz, Ph₂P(CH₂)₃PPh₂), –0.7 (dd, ¹J_{PP(trans)} = 248 Hz, ¹J_{PRh} = 75 Hz, Rh–PR₂BH₃), –2.62 (br s, PHR₂BH₃). ¹¹B{¹H} NMR (160 MHz, 1,2-F₂C₆H₄): δ –6.2 (BAr^F), –39.8 (br, 2 × BH₃). ESI-MS (1,2-F₂C₆H₄, 60 °C) positive ion: *m/z* = 1431.07 (calcd 1431.07, M⁺ – 2BH₃). Anal. Found: C 46.82%, H 2.39%. Calcd for C₉₁H₅₈B₃F₄₈P₄Rh: C 47.02%, H 2.52%.

Details follow for 15. ¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAr^F), 7.69 (s, 4 H, BAr^F), 4.90 (d, ¹J_{HP} = 414 Hz, PH), 3.01–1.10 (8 H, 3CH₂dpp3 + BH₂), –1.18 (br, 3H, BH₃), –6.95 (d, ¹J_{HP} = 78 Hz, 1 H, BH–Rh), –16.51 (s, 1 H, Rh–H). Signals from the aromatics were not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 27.3 (ddd, ¹J_{PRh} = 127 Hz, ¹J_{PP(cis)} = 37 Hz, ¹J_{PP(trans)} = 16 Hz, Ph₂P(CH₂)₃PPh₂), 11.8 (ddd, ¹J_{PP(trans)} = 231 Hz, ¹J_{PRh} = 100 Hz, ¹J_{PP(cis)} = 37 Hz, Ph₂P(CH₂)₃PPh₂), –0.3 (dd, ¹J_{PP(trans)} = 231 Hz, ¹J_{PRh} = 70 Hz, Rh–PR₂BH₃), –5.96 (br s, PHR₂BH₃). ¹¹B{¹H} NMR (160 MHz, 1,2-F₂C₆H₄): δ –6.2 (BAr^F), –39.9 (br, 2 × BH₃). ESI-MS (1,2-F₂C₆H₄, 60 °C) positive ion: *m/z* = 1159.13 (calcd 1159.13, M⁺ – 2BH₃).

Details follow for 16. ¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAr^F), 7.69 (s, 4 H, BAr^F), 4.93 (d, ¹J_{HP} = 409 Hz, 1 H, PH), 3.77 (s, 6 H, –OCH₃), 3.69 (s, 6 H, –OCH₃), 3.16–0.58 (8 H, 3CH₂dpp3 + BH₂), –1.11 (br, 3 H, BH₃), –6.53 (d, ¹J_{HP} = 73 Hz, 1 H, BH–Rh), –16.49 (s, 1 H, Rh–H). Signals from the aromatics were not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 27.3 (ddd, ¹J_{PRh} = 132 Hz, ¹J_{PP(cis)} = 37 Hz, ¹J_{PP(trans)} = 12 Hz, Ph₂P(CH₂)₃PPh₂), 9.5 (ddd, ¹J_{PP(trans)} = 227 Hz, ¹J_{PRh} = 98 Hz, ¹J_{PP(cis)} = 37 Hz, Ph₂P(CH₂)₃PPh₂), 0.7 (br dd, ¹J_{PP(trans)} = 227 Hz, ¹J_{PRh} = 65 Hz, Rh–PR₂BH₃), –11.2 (br s, PHR₂BH₃). ¹¹B{¹H} NMR (160 MHz, 1,2-F₂C₆H₄): δ –6.2 (BAr^F), –38.7 to –49.8 (br, 2 × BH₃). ESI-MS (1,2-F₂C₆H₄, 60 °C) positive ion: *m/z* = 1021.25 (calcd 1021.25, M⁺ – BH₃), 914.19 (calcd 914.20, M⁺ – BH₃ – C₆H₄OMe), 900.17 (calcd 900.17, M⁺ – 2BH₃ – C₆H₄OMe), 775.17 (calcd 775.17, M⁺ – (MeOC₆H₄)₂HP·BH₃).

Synthesis of [Rh(dpp3)H(PR₂·BH₂·PR₂·BH₃)] [BAr^F]₄ [R = 3,5-Bis(trifluoromethyl)phenyl (17); 4-Trifluoromethylphenyl (18); 4-Methoxyphenyl (19)]. Method A follows. To a Youngs flask charged with [Rh(dpp3)(C₆H₅F)] [BAr^F]₄ (50 mg, 0.034 mmol) and 2 equiv of H₃B·PR₂H (32 mg of 1, 23 mg of 2, 18 mg of 3 0.068 mmol) was added 1,2-F₂C₆H₄ (5 mL). The solution was stirred at room

temperature for 24 h. The formation of H₂ gas is also observed. Complex **19** was isolated as yellow oil (37 mg, 61%). Complexes **17** and **18** could not be isolated cleanly; they were observed with **22** and **23**, respectively.

Method B follows. To a Youngs flask charged with [Rh(dpp3)-(C₆H₅F)](BAR^F₄) (50 mg, 0.034 mmol) and 1 equiv of **10** (32 mg, 0.068 mmol) was added 1,2-F₂C₆H₄ (4 mL). Complex **17** was isolated as yellow solid (65 mg, 82%).

Details follow for **17**. Slow diffusion of pentane (10 mL) over a solution of **17** in 1,2-F₂C₆H₄ at -24 °C afforded yellow crystals (one of which was employed for an X-ray diffraction study).

¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8H, BAR^F₄), 7.69 (s, 4H, BAR^F₄), 4.40 (vbr, 1H, BH), 3.10–2.12 (8H, 3CH₂ dpp3 + BH₂), -1.20 (vbr, 1H, BH), -4.54 (vbr, 1H, BH), -13.98 (s, 1H, Rh–H). Signals from aromatics not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 46.6 (dd, J_{Rh–P} = 111, J_{P–P}(cis) = 36, Ph₂P(CH₂)₃PPh₂), 29.5 (m, J_{P–P}(trans) = 260, Rh-PR₂BH₃PR₂HBH₃), 12.8 (ddd, J_{P–P}(trans) = 260, J_{Rh–P} = 91, J_{P–P}(cis) = 33, Ph₂P(CH₂)₃PPh₂), -2.7 (s, Rh-PR₂BH₃PR₂HBH₃). ¹¹B{¹H} NMR (160 MHz, 1,2-F₂C₆H₄): δ 0.21 (br), -6.2 (s, BAR^F₄), -27.1 (br). ESI-MS (1,2-F₂C₆H₄, 60 °C) positive ion: m/z = 1457.09 (calcd 1457.12, M⁺). Anal. Found: C 47.15%, H 2.34%. Calcd for C₉₁H₅₆B₃F₄₈P₄Rh: C 47.07%, H 2.43%.

Details follow for **18**. ¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAR^F₄), 7.69 (s, 4 H, BAR^F₄), 4.24 (v br, 1 H, BH), 2.61–1.72 (8 H, 3CH₂ dpp3 + BH₂), -1.29 (v br, 1 H, BH), -4.65 (v br, 1 H, BH), -14.90 (s, 1 H, Rh–H). Signals from aromatics not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 42.5 (dd, J_{PRh} = 106 Hz, J_{PP}(cis) = 34 Hz, Ph₂P(CH₂)₃PPh₂), 28.6 (m, J_{PP}(trans) = 272 Hz, Rh-PR₂BH₃PR₂HBH₃), 15.3 (ddd, J_{PP}(trans) = 272 Hz, J_{PRh} = 101 Hz, J_{PP}(cis) = 33 Hz, Ph₂P(CH₂)₃PPh₂), -6.4 (s, Rh-PR₂BH₃PR₂HBH₃). ¹¹B{¹H} NMR (160 MHz, 1,2-F₂C₆H₄): δ 0.4 (br), -6.2 (s, BAR^F₄), -25.9 (br). ESI-MS (1,2-F₂C₆H₄) positive ion: m/z = 1185.17 (calcd 1185.18, M⁺).

Details follow for **19**. ¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAR^F₄), 7.69 (s, 4 H, BAR^F₄), 3.77 (s, 3 H, -OCH₃), 3.76 (s, 3 H, -OCH₃), 3.69 (s, 6 H, -OCH₃), 2.85–1.72 (8 H, 3CH₂ dpp3 + BH₂), -1.03 (v br, 1 H, BH), -4.00 (v br, 1 H, BH), -14.55 (s, 1 H, Rh–H). Signals from aromatics not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 42.7 (ddd, J_{PRh} = 109 Hz, J_{PP}(cis) = 35 Hz, J_{PP}(cis) = 12 Hz, Ph₂P(CH₂)₃PPh₂), 28.1 (br m, J_{PP}(trans) = 279 Hz, Rh-PR₂BH₃PR₂HBH₃), 12.5 (ddd, J_{PP}(trans) = 279 Hz, J_{PRh} = 88 Hz, J_{PP}(cis) = 12 Hz, Ph₂P(CH₂)₃PPh₂), -11.7 (br s, Rh-PR₂BH₃PR₂HBH₃). ¹¹B{¹H} NMR (160 MHz, C₆H₄F₂): δ 3.42 (br), -6.2 (s, BAR^F₄), -27.7 (br). ESI-MS (1,2-F₂C₆H₄) positive ion: m/z = 1033.27 (calcd 1033.27, M⁺).

Synthesis of [Rh(dpp3)(PHR₂)₂][BAR^F₄] [R = 3,5-Bis(trifluoromethyl)phenyl] (21**).** Method A follows. To a Youngs flask charged with [Rh(dpp3)(C₆H₅F)](BAR^F₄) (50 mg, 0.034 mmol) and 2 equiv of H₃B-PR₂H (32 mg of **1**) was added 1,2-F₂C₆H₄ (5 mL). The solution was stirred at room temperature for 24 h. The formation of H₂ (gas) is also observed. Complex **21** could not be isolated cleanly as **17** was also observed.

Method B follows. To a Youngs flask charged with [Rh(dpp3)-(C₆H₅F)](BAR^F₄) (20 mg, 0.034 mmol) and 2 equiv of PHR₂ (31 mg, 0.068 mmol, R = 3,5-bis(trifluoromethyl)phenyl) was added 1,2-F₂C₆H₄ (1 mL). After stirring for 10 min the solution was evaporated to dryness and the solid washed with pentane (2 mL). Complex **21** was isolated as yellow solid (yield 17.8 mg, 57%).

¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.33 (s, 8 H, BAR^F₄), 7.69 (s, 4 H, BAR^F₄), 6.41 (dm, J_{HP} = 375 Hz, 2 H, PH), 2.62 (br, 4 H, 2 CH₂ dpp3), 2.17 (m, 2 H CH₂, dpp3). Signals from aromatics not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 9.6 (m, 2P, AA'BB'M), 5.5 (m, 2P, AA'BB'M). ESI-MS (1,2-F₂C₆H₄) positive ion: m/z = 1431.04 (calcd 1431.07, M⁺). Anal. Found: C 47.71%, H 2.21%. Calcd for C₉₁H₅₂BF₄₈P₄Rh: C 47.60%, H 2.28%.

[Rh(dpp3)(PHR₂)₂][BAR^F₄] [R = 4-Trifluoromethylphenyl] (22**).**

Complex **22** was characterized by *in situ* NMR spectroscopy. ¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.33 (s, 8 H, BAR^F₄), 7.69 (s, 4 H, BAR^F₄), 5.91 (dm, J_{HP} = 359 Hz, 2 H, PH), 2.57 (br, 4 H, 2 × CH₂ dpp3), 2.06 (m, 2 H × CH₂, dpp3). Signals from aromatics not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 12.2 (m, 2P, AA'BB'M), 5.2 (m, 2P, AA'BB'M).

Synthesis of [Rh(dpp3)(η²-H₃B-PR₂H)][BAR^F₄] [R = Adamantyl] (23**).** To a Youngs flask charged with [Rh(dpp3)(C₆H₅F)](BAR^F₄) (50 mg, 0.034 mmol) and H₃B-PR₂H (**4**) (11 mg, 0.034 mmol) was added 1,2-F₂C₆H₄ (5 mL). The solution was stirred at room temperature for 1 min, and a change in color from pale orange to purple was observed. Complex **23** could not be isolated because further reaction to form **24** occurred.

¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAR^F₄), 7.68 (s, 4 H, BAR^F₄), 3.45 (d, 1 H, J_{HP} = 380 Hz, B-PH), 2.52–1.12 (36 H, adamantyl-H + dpp3 CH₂), -1.36 (br, 3 H, BH₃). Signals from aromatics not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 35.1 (d, J_{PRh} = 167 Hz, dpp3), 30.5 (br, B–P). ¹¹B NMR (160 MHz, 1,2-F₂C₆H₄): δ -0.8 (br), -6.0 (s, BAR^F₄). ESI-MS (1,2-F₂C₆H₄) positive ion: m/z = 629.09 (calcd 629.08, [Rh(dpp3)(C₆H₄F₂)⁺]). The weakly bound σ-complex could not be observed.

Synthesis of [Rh(dpp3)(PR₂H)(H₃B-PR₂H)][BAR^F₄] [R = Adamantyl] (24**).** Method A follows. To a Youngs flask charged with [Rh(dpp3)(C₆H₅F)](BAR^F₄) (50 mg, 0.034 mmol) and 2 equiv of H₃B-PR₂H (**4**) (22 mg, 0.068 mmol) was added 1,2-F₂C₆H₄ (5 mL). The solution was stirred at room temperature for 24 h. Complex **24** was isolated as orange solid.

Method B follows. To a Youngs flask charged with [Rh(dpp3)-(C₆H₅F)](BAR^F₄) (50 mg, 0.034 mmol) and 1 equiv of PHR₂ (10 mg, 0.034 mmol) was added 1,2-F₂C₆H₄ (5 mL). The solution was stirred for 5 min, and then 1 equiv of H₃B-PR₂H (**4**) (11 mg, 0.034 mmol) was added. The solution was stirred for 5 min, and complex **24** was isolated as orange solid (yield 48 mg, 71%). Slow diffusion of pentane (10 mL) into a solution of **24** in 1,2-F₂C₆H₄ at -24 °C afforded yellow crystals (one of which was employed for X-ray diffraction studies).

¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.33 (s, 8 H, BAR^F₄), 7.69 (s, 4 H, BAR^F₄), 3.30 (d, J_{HP} = 362 Hz, 1 H, B-PH), 2.87 (d, J_{HP} = 412 Hz, 1 H, PH), 2.45–1.56 (66 H, dpp3 CH₂ and adamantyl-H), -0.24 (br, 3 H, BH₃). ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 60.4 (ddd, J_{PP}(trans) = 266 Hz, J_{PRh} = 142 Hz, J_{PP}(cis) = 30 Hz, Ph₂P(CH₂)₃PPh₂), 30.5 (s, PHR₂BH₃), 22.8 (dd, J_{PRh} = 163 Hz, J_{PP}(cis) = 30 Hz, PPh₂(CH₂)₃PPh₂), 6.6 (ddd, J_{PP}(trans) = 270 Hz, J_{PRh} = 144 Hz, J_{PP}(cis) = 30 Hz, Rh-PR₂BH₃). ¹¹B{¹H} NMR (160 MHz, 1,2-F₂C₆H₄): δ -6.0 (s, BAR^F₄), -42.2 (br, BH₃). ESI-MS (1,2-F₂C₆H₄) positive ion: m/z = 956.30 (unidentified fragment). Anal. Found: C 59.38%, H 4.99%. Calcd for C₉₉H₁₀₃B₂F₂₄P₄Rh: C 59.50%, H 5.20%.

Synthesis of [Rh(dpp3)H(PCyH-BH₃)(H₃B-PCyH₂)](BAR^F₄) (25a** and **25b**).** To a Youngs flask charged with [Rh(dpp3)(C₆H₅F)](BAR^F₄) (50 mg, 0.034 mmol) was added 1,2-F₂C₆H₄ (5 mL). A 2 equiv portion of H₃B-PH₂Cy (**5**) (0.68 mL, 0.1 M solution in 1,2-F₂C₆H₄, 0.068 mmol) was then added. The solution was stirred at room temperature for 1 min, and a change in color from orange to pale yellow was observed. Complexes **25a** and **25b** were observed as an approximate 1:1 ratio of isomers and were characterized *in situ* by NMR spectroscopy. Complexes **25a** and **25b** could not be isolated as they reacted quickly to form complexes **26a** and **26b**. The ³¹P{¹H} NMR spectrum of this reaction mixture indicates that 2 diastereomers are present; while we were able to identify the 2 sets of 4 resonances each (labeled † and §, based on coupling constants and approximate integrations) it was not possible to determine which set of signals belonged to which diastereomer. See Figure S4, Supporting Information, for more detail.

¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAR^F₄), 7.69 (s, 4 H, BAR^F₄), 2.73–0.32 (32 H, 3 CH₂ dpp3 + BH₂, CyH, PH), -2.29 (v br, 3 H, BH), -7.92 (br d, 1 H, BH-Rh), -17.51 (s, 1 H, Rh–H). Signals from aromatics not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ

31.7 (dm, $J_{\text{PRh}} = 134$ Hz, $\text{Ph}_2\text{P}^{11}(\text{CH}_2)_3\text{PPh}_2$), 30.5 (dm, $J_{\text{PRh}} = 129$ Hz, $\text{Ph}_2\text{P}^{18}(\text{CH}_2)_3\text{PPh}_2$), 11.8 (overlapping ddd, $J_{\text{PP(trans)}} =$ approximately 200 Hz, $J_{\text{PRh}} =$ approximately 104 Hz, $J_{\text{PP(cis)}} =$ approximately 25 Hz, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}^{27}(\text{Ph}_2)$), -11.0 (br d, $J_{\text{PP(trans)}} =$ approximately 200 Hz, Rh- $\text{P}^{38}\text{HCy-B}$), -32.1 (br d, $J_{\text{PP(trans)}} =$ approximately 200 Hz, Rh- $\text{P}^{37}\text{HCy-B}$), -39.8 (br s, Rh- $\text{H}_3\text{BP}^{48}\text{H}_2\text{Cy}$), -44.2 (br s, Rh- $\text{H}_3\text{BP}^{48}\text{H}_2\text{Cy}$). ESI-MS ($1,2\text{-F}_2\text{C}_6\text{H}_4$, 60 °C) positive ion: $m/z = 747.20$ (calcd 747.21, $\text{M}^+ - 2\text{BH}_3$).

Synthesis of [(CyH₂P)₂BH₂]Br. To a stirred solution of PCyH₂ (3.40 mL, 10% wt in hexane, 2.0 mmol) in dichloromethane (20 mL) was added BrH₂B-SMe₂ (1.0 mL, 1.0 M in CH₂Cl₂, 1.0 mmol) and the solution stirred at room temperature for 2 h. The resulting colorless solution was concentrated *in vacuo* to approximately 3 mL, and diethyl ether (30 mL) was added to precipitate a white solid. The solvent was decanted off and the solid washed with a further 10 mL of diethyl ether. The solid was redissolved in dichloromethane, filtered, and recrystallized from a mixture of dichloromethane and diethyl ether at -18 °C to yield white crystals (first crop 0.190 g, second crop 0.041 g, overall yield 71%). At room temperature in CD₂Cl₂ [(CyH₂P)₂BH₂]Br undergoes a degenerate exchange reaction; [(CyH₂P)₂BH₂]Br is in equilibrium with CyH₂PBH₂Br + PH₂Cy. This exchange process does not occur at -60 °C on the NMR time scale, and each of these species can be observed. In the solid-state the complex exists as [(CyH₂P)₂BH₂]Br.

¹H NMR (500 MHz, -60 °C, CD₂Cl₂): δ 5.46 (dm, ¹J_{HP} = 429 Hz, [(CyH₂P)₂BH₂]⁺), 4.75 (dm, ¹J_{HP} = 388 Hz, CyH₂PBH₂Br), 2.52 (dm, ¹J_{HP} = 196 Hz, CyH₂P), 2.37–1.16 (CyH and BH). ³¹P{¹H} NMR (202 MHz, -60 °C, CD₂Cl₂): δ -35.5 (br s, [(CyH₂P)₂BH₂]⁺), -38.2 (br s, CyH₂PBH₂Br), -107.5 (s, CyH₂P). Anal. Found: C 44.35%, H 8.74%. Calcd for C₁₂H₂₈BBP₂: C 44.30%, H 8.68%.}}}

Synthesis of CyH₂P-BH₂PCyH-BH₃ (13). [(CyH₂P)₂BH₂]Br (0.150 g, 0.461 mmol) (prepared as above) and [NⁿBu₄][BH₄] (0.119 g, 0.461 mmol) were added to a Schlenk tube. Dichloromethane (10 mL) was added, and effervescence was observed; the solution was stirred at room temperature for 1 h. The solvent was removed *in vacuo*, and *n*-hexane (20 mL) was added to the white solid. The solution was filtered to remove [NⁿBu₄]⁺Br and concentrated to approximately 2 mL. Storage of this solution for 16 h at -18 °C yielded colorless crystals of **13** (0.102 g, 86%).

¹H NMR (500 MHz, 25 °C, CD₂Cl₂): δ 4.68 (dm, ¹J_{HP} = 386 Hz, CyH₂P-BH₂PHCy-BH₃), 3.50 (dm, ¹J_{HP} = 326 Hz, CyH₂P-BH₂PHCy-BH₃), 2.17–0.02 (CyH and BH). ³¹P{¹H} NMR (202 MHz, 25 °C, CD₂Cl₂): δ -36.6 (br, CyH₂P-BH₂PHCy-BH₃), -45.1 (br, CyH₂P-BH₂PHCy-BH₃). Anal. Found: C 55.79%, H 11.82%. Calcd for C₁₂H₃₀B₂P₂: C 55.77%, H 11.71%.}}

Synthesis of [Rh(dpp3)H(PCyH-BH₂PHCy-BH₃)] [BAR^F₄] (26a and 26b). Method A follows. To a Youngs flask charged with [Rh(dpp3)(C₆H₅F)] [BAR^F₄] (50 mg, 0.034 mmol) was added 1,2-F₂C₆H₄ (5 mL) followed by 2 equiv of H₃B-PCyH₂ (5) (0.68 mL, 0.1 M solution in 1,2-F₂C₆H₄, 0.068 mmol). The solution was stirred at room temperature for 12 h. The formation of H₂ is also observed. Complexes **26a** and **26b** were characterized as a mixture in solution by NMR spectroscopy and ESI-MS. The ³¹P{¹H} NMR spectrum of this reaction mixture indicates that 2 diastereomers are present; we were able to identify the 2 sets of 4 resonances each (labeled **26a** and **26b**, based on coupling constants and approximate integrations) and tentatively assigned the individual diastereomers (Scheme S5, Supporting Information) by inspection of a model.

Method B follows. To a Youngs flask charged with [Rh(dpp3)(C₆H₅F)] [BAR^F₄] (50 mg, 0.034 mmol) and 1 equiv of CyH₂P-BH₂PCyH-BH₃ (**13**) (8.8 mg, 0.034 mmol) was added 1,2-F₂C₆H₄ (4 mL). Complexes **26a** and **26b** were characterized as a mixture in solution by NMR spectroscopy and ESI-MS.

¹H NMR (500 MHz, 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAR^F₄), 7.69 (s, 4 H, BAR^F₄), 4.35–3.01 (PH and BH), 2.92–0.92 (30 H, 3CH₂ dpp3, BH₂, CyH), -2.98 (br, 1 H, BH-Rh), -5.98 (br, 1 H, BH-Rh), -16.08 (s, 1 H, Rh-H). Signals from aromatics not observed due to being overlapped by signals from 1,2-F₂C₆H₄. ³¹P{¹H} NMR (202 MHz, 1,2-F₂C₆H₄): δ 37.9 (dm, $J_{\text{PRh}} = 102$ Hz, $\text{Ph}_2\text{P}^{1b}(\text{CH}_2)_3\text{PPh}_2$), 34.5 (dm, $J_{\text{PRh}} = 102$ Hz, $\text{Ph}_2\text{P}^{1a}(\text{CH}_2)_3\text{PPh}_2$), 19.8 (br d, $J_{\text{PP(trans)}} =$

approximately 255 Hz, Rh- P^{3b}HCyB), 16.2 (br d, $J_{\text{PP(trans)}} =$ approximately 255 Hz, Rh- P^{3a}HCyB), 10.7 (overlapping dm, $J_{\text{PP(trans)}} = 255$ Hz, $J_{\text{PRh}} = 88$ Hz, $J_{\text{PP(cis)}} =$ approximately 25 Hz, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}^{2ab}(\text{Ph}_2)$), -14.9 (br s, Rh-PHCyBH₂P^{4a}HCyBH₃), -16.6 (br s, Rh-PHCyBH₂P^{4b}HCyBH₃). ESI-MS ($1,2\text{-F}_2\text{C}_6\text{H}_4$, 60 °C) positive ion: $m/z = 773.26$ (calcd 773.24, M^+).

Synthesis of [Rh(BDPP)(nbd)] [BAR^F₄]. [Rh(nbd)₂] [BAR^F₄] was synthesized by an adaptation of the preparation of [Rh(cod)₂] [BAR^F₄].⁶³ [Rh(nbd)₂] [BAR^F₄] (0.100 g, 0.0869 mmol) was dissolved in CH₂Cl₂ (10 mL) to produce a deep red solution. (2*S*,4*S*)-2,4-Bis(diphenylphosphino)pentane (BDPP) (0.0383 g, 0.0869 mmol) was added, and a color change to red was observed. The solution was stirred for 1 h at room temperature before the solvent was removed *in vacuo*. *n*-Pentane (20 mL) was added, and the solution was sonicated to produce an orange powder. The solvent was decanted and the solid washed with pentane (2 × 20 mL). The product was dried *in vacuo* and isolated (yield 0.102 g, 78%).

¹H NMR (300 MHz, CD₂Cl₂): δ 7.72 (s, 8 H, BAR^F₄), 7.56 (s, 4 H, BAR^F₄), 7.70–7.36 (m, P-Ph), 4.86 (m, 2 H, =C-H), 4.30 (m, 2 H, =C-H), 3.90 (m, 2 H, nbd C-H), 2.77 (m, 2 H, P-C-H), 1.84 (tt, ³J_{HH} = 6.45 Hz, ³J_{HP} = 19.95 Hz, 2 H, CH₂), 1.58 (m, 2 H, nbd CH₂), 1.13 (m, 6 H, CH₃). ³¹P{¹H} NMR (121.6 MHz, CD₂Cl₂): δ 27.4 (d, $J_{\text{PRh}} = 149$ Hz). Anal. Found: C 54.32%, H 3.18%. Calcd for C₆₈H₅₀BF₂₄P₂Rh: C 54.47%, H 3.36%.}}

Synthesis of [Rh(BDPP)(C₆H₅F)] [BAR^F₄]. [Rh(BDPP)(nbd)] [BAR^F₄] prepared as above (0.020 g, 0.0133 mmol) was added to a high-pressure NMR tube and dissolved in fluorobenzene (0.5 mL). The sample was degassed by the freeze-pump-thaw method and hydrogen gas (4 atm) introduced. The sample was mixed for 30 min and then degassed by the freeze-pump-thaw method and placed under argon.

¹H NMR (500 MHz, C₆H₅F): δ 8.32 (s, 8 H, BAR^F₄), 7.61 (s, 4 H, BAR^F₄), 5.63 (m, 2 H, Ar-H), 5.43 (m, 2 H, Ar-H), 5.10 (m, 1 H, Ar-H), 2.38 (m, 2 H, P-CH), 1.40 (m, 2 H, CH₂), 0.78 (m, 6 H, CH₃). Signals from P-Ph not observed due to being overlapped by signals from C₆H₅F. Signals from norbornane (from hydrogenation of norbornadiene) can also be observed at δ 2.12 (m, 2 H, nba C-H), 1.40 (m, 2 H, nba CH₂, overlapped), 1.11 (m, 2 H, nba CH₂). ³¹P{¹H} NMR (202 MHz, C₆H₅F): δ 39.9 (d, $J_{\text{PRh}} = 194$ Hz). ESI-MS (C₆H₅F, 60 °C) positive ion: $m/z = 639.13$ (calcd 639.12, M^+).

Synthesis of [Rh(BDPP)H(PCyH-BH₂PHCy-BH₃)] [BAR^F₄] (27a and 27b). [Rh(BDPP)(C₆H₅F)] [BAR^F₄] (**26**) was prepared in a high-pressure NMR tube as above. To this was added 2 equiv of H₃B-PH₂Cy (**5**) (0.27 mL, 0.1 M solution in 1,2-F₂C₆H₄, 0.027 mmol) and the solution mixed for 1 min. Complexes **27a** and **27b** were observed as ratio of isomers and were characterized *in situ* by NMR spectroscopy. Complexes **27a** and **27b** could not be isolated as they reacted quickly to form complexes of **28**; signals for **28** can be observed in both ¹H and ³¹P{¹H} NMR spectra of **27a** and **27b** which, along with the presence of H₂, show that the complexes rapidly undergo dehydrocoupling to form complexes of **28**. The ³¹P{¹H} NMR spectrum of this reaction mixture indicates that 2 diastereomers are present; while we were able to identify the 2 sets of 4 resonances (labeled † and §, based on coupling constants and approximate integrations), it was not possible to determine which set of signals belonged to which diastereomer. See Figure S6, Supporting Information.

¹H NMR (500 MHz, C₆H₅F + 1,2-F₂C₆H₄): δ 8.32 (s, 8 H, BAR^F₄), 7.69 (s, 4 H, BAR^F₄), 4.19 to 0.32 (CH₃, CH₂, CH, BDPP, BH₂, CyH, PH), -1.80 to -3.31 (v br, 3 H, BH₃), -7.54 to -8.86 (br d, 1 H, BH-Rh), -17.73 (br s, 1 H, Rh-H). Signals from aromatics not observed due to being overlapped by signals from C₆H₅F and 1,2-F₂C₆H₄. H₂ can be observed in the NMR spectrum as a sharp singlet at δ 4.52 ppm suggesting that some dehydrocoupling to complex **28** has occurred. This is further evidenced by the small Rh-H hydride signal at δ -16.07 ppm which is observed for complex **28**. ³¹P{¹H} NMR (202 MHz, C₆H₅F + 1,2-F₂C₆H₄): δ 42.5 (dm, $J_{\text{PRh}} = 129$ Hz, $\text{Ph}_2\text{P}^{11}(\text{CH}_2)_3\text{PPh}_2$), 32.6 (dm, $J_{\text{PRh}} = 119$ Hz, $\text{Ph}_2\text{P}^{18}(\text{CH}_2)_3\text{PPh}_2$), 28.3 (overlapping ddd, $J_{\text{PP(trans)}} =$ approximately 208 Hz, $J_{\text{PRh}} =$ approximately 98 Hz, $J_{\text{PP(cis)}} =$ approximately 32 Hz, Ph_2P

$(\text{CH}_2)_3\text{P}^{2\ddagger}\text{Ph}_2$), 3.6 (br d, $J_{\text{PP}(\text{trans})}$ = approximately 208 Hz, Rh- $\text{P}^{3\ddagger}\text{HCy-B}$), -12.1 (br d, $J_{\text{PP}(\text{trans})}$ = approximately 208 Hz, Rh- $\text{P}^{3\ddagger}\text{HCy-B}$), -42.1 (br s, Rh- $\text{H}_3\text{BP}^{4\ddagger}\text{H}_2\text{Cy}$), -44.2 (br s, Rh- $\text{H}_3\text{BP}^{4\ddagger}\text{H}_2\text{Cy}$).

Synthesis of $[\text{Rh}(\text{BDPP})(\text{PCyH-BH}_2\text{PCyH-BH}_3)][\text{BAR}^{\text{F}}_4]$ (28a, 28b, 28c, and 28d). Method A follows. $[\text{Rh}(\text{BDPP})(\text{C}_6\text{H}_5\text{F})][\text{BAR}^{\text{F}}_4]$ was prepared on an NMR scale from $[\text{Rh}(\text{BDPP})(\text{nbD})][\text{BAR}^{\text{F}}_4]$ (0.020 g, 0.0133 mmol) as above. This solution was transferred by cannula to an NMR tube containing $\text{CyH}_2\text{P-BH}_2\text{PHCy-BH}_3$ (13) (3.4 mg, 0.0133 mmol), and the solution was mixed briefly to yield a pale yellow solution.

Method B follows. $[\text{Rh}(\text{BDPP})(\text{C}_6\text{H}_5\text{F})][\text{BAR}^{\text{F}}_4]$ was prepared on an NMR scale from $[\text{Rh}(\text{BDPP})(\text{nbD})][\text{BAR}^{\text{F}}_4]$ (0.020 g, 0.0133 mmol) as above. To this was added 2 equiv of $\text{H}_3\text{B-Ph}_2\text{Cy}$ (5) (0.27 mL, 0.1 M solution in 1,2- $\text{C}_6\text{H}_4\text{F}_2$, 0.027 mmol) and the solution mixed for 18 h.

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum arising from method A indicates that 4 diastereomers are present; while we were able to identify some of the signals from the 4 sets of 4 resonances (labeled †, §, \$, and & based on coupling constants and approximate integrations), it was not possible to determine which set of signals belonged to which of the diastereomers. See Figure S7, Supporting Information. Method B affords, essentially, only one diastereoisomer.

^1H NMR (500 MHz, $\text{C}_6\text{H}_5\text{F}$): δ 8.32 (s, 8 H, BAR^{F}_4), 7.69 (s, 4 H, BAR^{F}_4), 5.47–2.46 (PH), 2.11–0.63 (CH, CH_2 , and CH_3 BDPP, BH_2 , CyH), -3.21 (br, 1 H, BHRh), -5.65 to -6.85 (br, 1 H, BHRh), -16.09, -16.20, and -17.04 (s, 1 H, Rh-H). Signals from aromatics not observed due to being overlapped by signals from $\text{C}_6\text{H}_5\text{F}$ and 1,2- $\text{C}_6\text{H}_4\text{F}_2$. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, $\text{C}_6\text{H}_5\text{F}$): δ 58.9 (ddd, $J_{\text{PRh}} = 107$ Hz, $J_{\text{PP}(\text{cis})} = 30$ Hz, $J_{\text{PP}(\text{trans})} = 12$ Hz, $\text{Ph}_2\text{P}^{1\ddagger}(\text{CH}_2)_3\text{PPh}_2$), 58.0 (dm, $J_{\text{PRh}} = 102$ Hz, $\text{Ph}_2\text{P}^{1\ddagger}(\text{CH}_2)_3\text{PPh}_2$), 46.6 (dm, $J_{\text{PRh}} = 100$ Hz, $\text{Ph}_2\text{P}^{1\ddagger}(\text{CH}_2)_3\text{PPh}_2$), 43.6 (dm, $J_{\text{PRh}} = 102$ Hz, $\text{Ph}_2\text{P}^{1\ddagger}(\text{CH}_2)_3\text{PPh}_2$), 28.7 (ddd, $J_{\text{PP}(\text{trans})} = 254$ Hz, $J_{\text{PRh}} = 90$ Hz, $J_{\text{PP}(\text{cis})} = 32$ Hz, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}^{2\ddagger}\text{Ph}_2$), 27.5 (ddd, $J_{\text{PP}(\text{trans})} = 250$ Hz, $J_{\text{PRh}} = 92$ Hz, $J_{\text{PP}(\text{cis})} = 32$ Hz, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}^{2\ddagger}\text{Ph}_2$), 24.8–17.7 (overlapping m, $J_{\text{PP}(\text{trans})} =$ approximately 254 Hz, $J_{\text{PRh}} =$ approximately 87 Hz, $J_{\text{PP}(\text{cis})} =$ approximately 26 Hz, $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{P}^{2\ddagger}\text{Ph}_2$ and Rh- $\text{P}^{3\ddagger}\text{HCy-B}$), -13.5 to -20.6 (br s of 4 isomers, Rh- $\text{PHCyBH}_2\text{P}^4\text{HCyBH}_3$). ESI-MS (1,2- $\text{C}_6\text{H}_4\text{F}_2$, 60 °C) positive ion: $m/z = 801.29$ (calcd 801.29, M^+).

In order to establish that dehydrocoupling had occurred when method B was used to form complexes 28, excess (10 equiv) of 1,2-bis(diphenylphosphino)ethane was added to the reaction mixture to release the dehydrocoupled product, $\text{CyH}_2\text{P-BH}_2\text{PHCy-BH}_3$, from the metal center. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two broad signals at $\delta -37.9$ and -43.9 which are in agreement with those found for compound 13.

Attempted Polymerization of $\text{PhH}_2\text{P-BH}_3$ in Solution. In a procedure similar to that reported by Manners et al.,²⁰ $\text{PhH}_2\text{P-BH}_3$ (0.248 g, 2.0 mmol) was dissolved in toluene (10 mL) either in the presence of $[\text{Rh}(\text{dpp3})(\text{C}_6\text{H}_5\text{F})][\text{BAR}^{\text{F}}_4]$ (14.7 mg, 0.01 mmol) or with no catalyst present. The solution was heated to reflux for 16 h before cooling to room temperature. The solution was concentrated *in vacuo* and added to stirred hexane (100 mL) to produce a white precipitate. The solvent was decanted and the solid washed with hexane (2 × 50 mL). The solid was dried *in vacuo* and isolated in air (yield 0.110 g Rh catalyzed, 0.101 g uncatalyzed). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the isolated solids produced by the different methods are very similar with several very broad peaks from $\delta -45$ to -57 and very broad peaks of lower intensity from $\delta -72$ to -87 . See Figure S8, Supporting Information. This is in agreement with the results obtained by Manners et al. for uncatalyzed polymerization of $\text{PhH}_2\text{P-BH}_3$.²⁰

Melt Polymerization of $\text{PhH}_2\text{P-BH}_3$. A Youngs flask charged with $\text{PhH}_2\text{P-BH}_3$ (31 mg, 0.25 mmol) and 5 mol % of $[\text{Rh}(\text{dpp3})(\text{C}_6\text{H}_5\text{F})][\text{BAR}^{\text{F}}_4]$ (18.4 mg, 0.0125 mmol) was heated to 90 °C for 4 h in melt conditions. The resulting solid was dissolved in 1,2-difluorobenzene and analyzed by NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a peak at $\delta -49.3$ ppm in agreement with that observed by Manners et al.⁷ for polymeric material and a lower intensity resonance at $\delta -55.0$ ppm. See Supporting Information Figure S9. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum the peak at $\delta -49.3$ ppm

split into a broad doublet with a J_{PH} coupling constant of approximately 350 Hz. Analysis by ESI-MS of the reaction mixture showed a repeating pattern corresponding to the polymeric repeat unit $-\text{[PhHP-BH}_2\text{]}_n-$, see Figure S10, Supporting Information.

■ ASSOCIATED CONTENT

📄 Supporting Information

Further experimental and characterization details, including selected NMR data and X-ray crystallographic data (including data in CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center (CCDC) and can be obtained via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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