**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 H₃B-PR₂-H, H₃B-PR₂H₂, and H₃B-PR₃H of amine–boranes 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 elements are now occupying, such as high performance polymers, emissive materials, etch resists for lithography, and precursors to ceramic thin films or devices. 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 of amine–boranes 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 aminoborane to act as a hydrogen carrying vector. In addition, polymeric materials that can arise from dehydrocouplerization 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, catalytic routes to polyboraphosphines have also been known since 1999. Perhaps the best example is that of the [Rh(COD)₂][OTf] catalyzed dehydrocoupling of secondary, H₃B-PR₂H, and primary, H₃B-PR₃H, phosphine–boranes to give oligomeric and polymeric materials (Scheme 1).

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

**Scheme 1. Phosphine–Borane Dehydrocoupling**

| Reaction | Product |
|----------|---------|
| H₃B-PR₂H₂ | H₃B-PR₂H₂ |
| R = Bu, 140°C, melt | H₃B-PR₂H₂ |
| Ph, 90°C, melt | H₃B-PR₂H₂ |

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boranes has received less attention. Although initial reports demonstrated that catalysis using \( [\text{Rh(COD)}_2][\text{OTf}] \) was a homogeneous process (i.e., not colloidal),\(^{25}\) there has been only sporadic further work on elucidating the mechanistic details.\(^{26}\) 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 \( [\text{Rh} (\text{Ph}_2\text{P})(\eta^6-\text{FC}_6\text{H}_5)][\text{BARF}_4] \)\(^{30}\) 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 \( \text{H}_3\text{B}·\text{PR}_2\text{H} \) (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 \( \beta\)-B-agostic \( \sigma \) complex \( \text{B} \), and the product of dehydrocoupling \( \text{F} \), that is proposed to sit off cycle, could be isolated and spectroscopically characterized. Under stoichiometric conditions the observation that \( \text{B} \) transforms into \( \text{F} \) on gentle heating allowed for kinetic parameters to be determined that suggested the rate-determining step(s) for dehydrocoupling were located within the transformations \( \text{B} \) to \( \text{D} \). In solution phase the turnover limiting step for catalysis is proposed to be the displacement of the linear diboraphosphine product (i.e., \( \text{F} \) to \( \text{A} \)), although under the melt conditions used for efficient catalysis this may well be different. Further insight comes from the observations that for \( \text{R} = \text{Bu} \) 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 (\( \text{A} \) and \( \text{E} \)) 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 \( \text{H}_3\text{B}·\text{PR}_2\text{H} \) [\( \text{R} = p-(\text{CF}_3)\text{C}_6\text{H}_4, \text{Ph}, \text{Bu}, \text{Bu}\) ] and primary \( \text{H}_3\text{B}·\text{PR}_2\text{H} [\text{R} = \text{Ph}, \text{Bu}, \text{Bu} \) ] phosphine−boranes using the \( [\text{Rh(COD)}_2][\text{OTf}] \) 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 \( [p-(\text{CF}_3)\text{C}_6\text{H}_4] \) 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 \( \text{Cp}_2\text{Ti}\)-based catalysts,\(^{35}\) while oligomerization of base-stabilized phosphino−boranes at \( \text{Cp}_2\text{Ti} \) 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 \( \text{H}_3\text{B}·\text{PR}_2\text{H} \) [\( \text{R} = 3,5-(\text{CF}_3)\text{C}_6\text{H}_4, p-(\text{CF}_3)\text{C}_6\text{H}_4, p-(\text{OMe})\text{C}_6\text{H}_4, \text{adamantyl} \)] as well as investigations with the

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**Scheme 2. Proposed Catalytic Cycle for the Dehydrocoupling of \( \text{H}_3\text{B}·\text{PR}_2\text{H} \) To Give \( \text{H}_3\text{B}·\text{PR}_2\text{BH}_2·\text{PR}_2\text{H} \)**

\[ [\text{BARF}_4^-] \text{ anions are not shown.} \]
primary phospahne–borane $H_2B·PCyH_2$. Dehydrocoupling forms the corresponding metal–bound linear diboraphosphines $H_2B·PR_3BH·PR·H$ and $H_2B·PRHBH·PRH_2$, respectively. These studies provide insight into the determining role of the electronics and steric 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 phospahne–boranes, that can additionally be biased by use of a chiral chelating phospahne on the rhodium center.

RESULTS AND DISCUSSION

Phosphine–Borane and Diboraphosphane Starting Materials. A range of secondary phospahne–boranes with differing electronic and steric properties have been used in this study (1, 2, 3, and 4, Figure 1), which also provide comparison with the previously reported $\text{Ph}_7$ and $\text{Bu}_7$, analogues. The primary phospahne–borane 5 has also been used. Compounds 2 and 3 are known adducts and offer electron-withdrawing and donating aryl groups, respectively. Bis-CF$_3$-substituted 1 is a new complex and offers an alternative to 2. The synthesis of adamantyl-substitutted phospahne, 4, an analogue of 7, has been reported in the patent literature. Compared with the $\text{Bu}_7$ group, adamantyl has a greater steric bulk due to its larger volume and rigid structure. 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 phospahne–boranes, while primary phospahne containing 13 has been synthesized in good isolated yield (85%) by addition of [NBu$_4$][BH$_4$] to the bis-(phospahne)boronium [(CyH$_2$P)$_2$BH$_3$].

Stoichiometric Dehydrocoupling of Secondary Phosphine–Boranes. Addition of 2 equiv of 1 to [Rh(L)(H)$_2$][BArF$_4$] ($L = \text{Ph}_3P(\text{CH}_2)_2P\text{Ph}_3$) in 1,2-$F_2C_6H_4$ solution at 25 °C rapidly (on time of mixing) resulted in the formation of [Rh(L)(H)$_2$][BArF$_4$]·[BArF$_4$], 14 ($R = p-(\text{CF}_3)C_6H_4$, Scheme 3), which was characterized by NMR spectroscopy, ESI-MS (electrospray ionization mass spectrometry), and single crystal X-ray diffraction. Likewise, the use of 2 equiv of phospahne–borane 2 or 3 results in the formation of the analogous complexes 15 ($R = p-(\text{CF}_3)C_6H_4$) and 16 ($R = p-(\text{OMe})C_6H_4$), 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 [Rh(L)(H)$_2$][BArF$_4$]·[BArF$_4$] ($\eta^1$-$\text{H}_2\text{B}·\text{PPbH}_3$), and data for 14 is discussed in detail. The $^{31}$P($^1$H) NMR spectrum of 14 shows four different phosphorys environments. Two of the resonances are broadened significantly compared to the other two, suggesting these phosphorys atoms are bound to a quadrupolar boron center. One of these shows both a large $\text{trans}$-$\text{PP}$ coupling [J($\text{PP}$) 244 Hz] and coupling to $^{103}$Rh [J($\text{RhP}$) 75 Hz], while the other is a broad singlet. The other two signals are sharper and are assigned to the two $^{31}$P environments of the $\text{Ph}_3P(\text{CH}_2)_2P\text{Ph}_3$ ligand. One of these sharper resonances ($\delta$ 29.5, $\text{ddd}$, J($\text{RhP}$) 130, J($\text{PP}$) 35, J($\text{PP}$) 21 Hz) is assigned to the phosphorus atom $\text{trans}$ to the weakly bound $\beta$-B-agostic interaction on the basis of the larger $^{103}$Rh coupling constant, while the other signal ($\delta$ 11.3, $\text{ddd}$, J($\text{RhP}$) 103, J($\text{PP}$) 244, J($\text{PP}$) 35 Hz) is assigned to the phosphorus atom $\text{trans}$ to the coordinated phosphido ligand. In the $^1$H NMR spectrum of 14 one broad, relative integral 3H, signal is observed at $\delta$ −0.78, indicative of a Rh–$\text{H}_2\text{B}·\sigma$ interaction in which the $\text{B}·\text{H}$ bonds are undergoing rapid site exchange on the NMR spectroscopic time scale between terminal and bridging sites. A broad, relative integral 1H, resonance at $\delta$ −6.12 is assigned to a static $\beta$-$\text{B}$-agostic $\text{B}·\text{H}$ 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 $\text{trans}$ disposition to a phospahne. The remaining $\text{BH}_2$($\text{terminal}$) signals are not observed, and it is likely they are coincident with the $\{\text{CH}_2\}$ signals. A sharper signal at $\delta$ −16.21, relative integral 1H, is assigned to a metal–hydride resonance, in which the coupling to both $^{103}$Rh and $^{31}$P

![Figure 1. Phosphine–boranes 1–7 and diboraphosphines 8–13.](image-url)
is clearly small and unresolved. The PH group is observed at δ 5.81 that collapses into a singlet in the $^1$H($^3$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–H$_2$B signals, as has been noted previously.$^{31,32}$ Complexes 15 and 16 have similar $^1$H, $^{13}$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-F$_2$C$_6$H$_4$ solution with pentane at −26 °C. The structure of 14 in the solid-state (Figure 2) is fully consistent with the structure 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–P1, 2.778(10) Å] and a β-B-agostic bond [Rh1–B1, 1.913(4) Å]; P4–B2, 1.918(4) Å; Rh1···B1, 2.515(4) Å; Rh1···B2, 2.740(4) Å; Rh1···P1, 7.54(14) Å; Rh1···B4–P4, 121.3(2) Å.

![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, 3.2045(10); P3–B1, 1.913(4); P4–B2, 1.918(4); Rh1···B1, 2.515(4); Rh1···B2, 2.740(4); Rh1···P1, 7.54(14); Rh1···B4–P4, 121.3(2)].

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)(η$^4$-PR$_2$H$_2$)(η$^2$-PR$_2$H$_2$)] [BAR$_4$]$^2$; 17, R = 3,5-(CF$_3$)$_2$C$_6$H$_4$; 18, R = p-(CF$_3$)$_2$C$_6$H$_4$; 19, R = p-(OMe)C$_6$H$_4$ (Scheme 4). This process also results in the liberation of H$_2$ (observed, $^1$H NMR spectroscopy). For 17 and 18 there are additional products formed, assigned as [Rh(L)(η$^4$-PR$_2$H$_2$)][BAR$_4$]$^2$, 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((CF$_3$)$_2$C$_6$H$_4$)$_2$ to [Rh(L)(η$^2$-FC$_6$H$_5$)][BAR$_4$]$^2$.

This mixture of products observed for the electron-withdrawing phosphine substituents (i.e., 1 and 2) contrasts with that found for when R = Ph$_3$, and p-(OMe)C$_6$H$_4$, which yield the dehydrocoupled (e.g., 19 and F, Scheme 2) product in essentially quantitative form (~95% by $^{31}$P($^1$H) NMR spectroscopy). Complex 17 has been synthesized cleanly from direct addition of the preformed dehydrocoupled diboraphosphine product, 10, to [Rh(L)(η$^2$-FC$_6$H$_5$)][BAR$_4$]$^2$, Scheme 5. It was from this reaction that material of 17 suitable for single crystal X-ray diffraction was obtained.

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

![Scheme 4. Dehydrocoupling of Complexes 14–16](image)

$^{[3]}$BAR$_4$$^2$− anions are not shown. Time = 6 h 17/21, 18/22 (25 °C); 8 h 16/19 (35 °C).

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

![Scheme 5. Synthesis of 17 by Direct Addition of the Linear Diboraphosphine 10](image)

$^{[3]}$BAR$_4$$^2$− anions are not shown.

Figure 3 shows the solid-state structure of 17, in which the diboraphosphate acts as a chelate to the Rh(III) center, via a phosphido group and two B-agostic interactions: [Rh(L)(η$^4$-PR$_2$H$_2$)(η$^2$-PR$_2$H$_2$)] [BAR$_4$]$^2$ [R = 3,5-(CF$_3$)$_2$C$_6$H$_4$]. 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$^2$-BH$_2$···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.
also shows unresolved coupling. The $^{11}$B NMR spectrum shows signals (attributed to the chelating phosphine ligand. One of these signals is observed at $\delta = 46.6$ Hz, environments assigned to the BH$_3$ moiety.)

NMR spectrum shows three different environments. One of these signals ($\delta = 12.8$ Hz) also shows large $^{31}$P-$^{31}$P coupling ($J(PP) = 260$ Hz) suggesting a trans position relative to the phosphido center. The other two environments are broad, typical of those assigned to the chelating phosphine ligand. One of these signals ($\delta = 12.8$) also shows large $^{31}$P-$^{31}$P coupling ($J(PP) = 260$ Hz) suggesting a trans position relative to the phosphido center.

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 ($R = Ph$). The $^{31}$P($^1$H) NMR spectrum shows four different phosphorus environments. Two of these signals are well-resolved and show coupling to $^{103}$Rh, $\delta = 46.6$ Hz and $\delta = 12.8$ Hz, and are attributed to the chelating phosphine ligand. One of these signals ($\delta = 12.8$) also shows large $^{31}$P-$^{31}$P coupling ($J(PP) = 260$ Hz) suggesting a trans position relative to the phosphido center.

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Prior to the formation of the parallel product 21 ($R = 3.5\text{-}CF_3\text{C}_6\text{H}_3$) an intermediate is observed that has been characterized by $^1$H and $^{31}$P($^1$H) NMR spectroscopy as $[\text{Rh}(\text{L})\text{H}(\text{CH}_{2}\text{PR}_2\text{H})][\text{BH}_3]$ 20, i.e., a complex that sits directly between 14 and 21 by loss of one $\text{BH}_3$ fragment (Scheme 6). Complex 20 results from P–B bond cleavage, formally of the $\sigma$-H$_3$B–Pr$_2$H ligand, to afford a complex with a $\beta$-agostic interaction from a phosphido borane ligand (as for 14) and a simple Pr$_2$H 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 $^{31}$P NMR spectroscopy), allowing for its identification and assignment of its spectroscopic parameters.

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, 2.2260(12); Rh1–P3, 2.3925(10); Rh1…B2, 2.280(5); Rh1–P3–B1, 110.88(15); B1–P4–B2, 107.5(2).
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 $f(PP)$ coupling with another phosphine environment. In the high-field region of the $^1$H NMR spectrum a broad doublet is observed at $\delta$ –7.06 [$f(HP)$ = 76 Hz] which is assigned to the $\beta$-B-agostic interaction, while there is a relatively sharper one at $\delta$ –9.61 [$f(HP)$ = 165 Hz] assigned to Rh–H, and again $^{103}$Rh coupling is not resolved. These assignments were confirmed by $^1$H/$^{11}$B, $^1$H/$^{31}$P and $^1$H/$^{31}$P correlation experiments.

Addition of 2 equiv of the bulky and electron rich phosphine–borane H$_3$B·P(adamantyl)$_2$H, 4, to [Rh(L)($\eta^6$-FC$_6$H$_5$)][BArF$_4$] in 1,2-F$_2$C$_6$H$_4$ solution at 25 °C rapidly results in a color change from orange to purple and the formation of the new $\sigma$ bound Rh(I) phosphine–borane complex [Rh(L)($\eta^6$-H$_2$B·P(adamantyl))][BArF$_4$], 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 [Rh(L)($\eta^6$-FC$_6$H$_5$)][BArF$_4$].

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

\[ \text{Ad} = \text{adamantyl} \]

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 H$_3$B·PPh$_2$H (6). Interestingly we have recently reported that for H$_3$B·PPh$_2$H P–B bond cleavage is also observed during dehydrocoupling catalysis being accomplished by a further dehydrocoupling step, through which bis(phosphine)boronium salts are ultimately formed. Similar complexes can be prepared on rhodium using H$_2$B·PPh$_2$H and PPh$_3$ under stoichiometric conditions. 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 dianinoboranes from amine–boranes and amines catalyzed by alkaline earth catalysts. 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, it was of interest to explore whether the proposed dehydrocoupling mechanism for secondary phosphine–boranes using [Rh(L)($\eta^6$-FC$_6$H$_5$)$_2$][BArF$_4$] 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.

**In situ** investigations using stoichiometric quantities of primary phosphine–boranes H$_3$B·PPh$_2$H resulted in immediate reaction when combined with [Rh(L)($\eta^6$-FC$_6$H$_5$)][BArF$_4$], 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 H$_3$B·PPh$_2$H where single products...
are formed analogous to 14−16.31 However, reaction of \([\text{Rh}(L)(\eta^8-\text{FC}_{6}\text{H}_{5})][\text{BARF}_{4}]\) with a slight excess of \(\text{H}_{2}\text{B}(\text{PCy})_{2}\) 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, \([\text{Rh}(L)(\sigma_{\text{PCy}}\text{H}-\text{BH})\eta^1-\text{H}(\text{B}-\text{PCy})\text{H}][\text{BARF}_{4}]\), as a proposed diastereomeric pair (Scheme 8). This stereoisomerism comes from \(\text{P}−\text{H}\) 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 \(^{31}\text{P}\{\text{H}\}\) 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 \(^{31}\text{P}\) environments in each diastereomer, and show characteristic \(J(\text{RhP})\) coupling constants consistent with a \(\text{Rh}(III)\) center. Complex overlapping multiplets at \(\delta=11.8\) [2 × ddd] represent the resonances for both diastereomers of the second chelated phosphorus center, which is \(\text{trans}\) to the phosphide position, displaying a large \(\text{trans}\) \(PP\) coupling constant \([J(\text{PP})\sim200\text{ Hz}]\) in addition to coupling to \(^{103}\text{Rh}\) and \(\text{cis}^{31}\text{P}\). The remaining 4 signals are broad indicating the phosphorus centers are bound to a quadrupolar \(^{11}\text{B}\) nucleus. Of these, peaks at \(\delta=1110.0\) and 32.1 are assigned to the phosphine centers of each diastereomer \(\text{trans}\) to the chelating phosphine \([J(\text{PP})\sim200\text{ Hz}]\), and resonances at \(\delta=39.8\) and 44.2 as assigned to phosphorus centers in the \(\sigma\)-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 phosphide group is part of a chelate ring. The \(^{1}H\) 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 \(\text{H}, \text{BH}_{2}\)), \(\delta=7.9\) (1 \(\text{H}, \text{Rh}−\text{H}−\text{B}\)), \(\delta=17.5\) (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 \([\text{Rh}(L)(\text{PH}_2\text{Cy})_2]^{\text{−}}\), analogous to 21/22, was also observed. NMR spectroscopic and ESI-MS analysis suggests that the dehydrocrouiling products formed are direct analogues of 17. This mixture of diastereomers can also be synthesized cleanly by direct reaction of \([\text{Rh}(L)(\eta^8-\text{PC}_{6}\text{H}_{4})][\text{BARF}_{4}]\) with the preformed diaboraphosphine \(\text{H}_{2}\text{B}(\text{PCy})\text{H}_{2}-\text{PCyH}_{2}\) (13) in 1,2-\(\text{F}_{2}\text{C}_{6}\text{H}_{4}\) solution at 25 °C (Figure 5 for the solid-state structure). Immediate measurement of the \(^{31}\text{P}\{\text{H}\}\) 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 \(^{31}\text{P}\{\text{H}\}\) 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 \(\text{trans}\) to the \(\text{B}\)-agostic site, while the signals for the phosphorus \(\text{trans}\) to the phosphido group overlap at \(\delta=10.7\), and display characteristic \(J(\text{PP})\) coupling \([255\text{ Hz}]\). The broad resonances of the diboraphosphine 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 \(^{1}H\) NMR spectrum of 26a/26b shows a slight downfield shift of the \(\text{Rh}−\text{H}\) hydride resonance to \(\delta=16.1\), when compared to 25a/25b, while the \(\eta^1-\text{BH}_2\)-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 \(^{31}\text{P}\{\text{H}\}\) 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 \([\delta=34.5, 16.2, 10.7, \text{and }−14.9]\) 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 \(\text{P}−\text{B}\) bond forming process. Leaving this solution for one week resulted in no significant change to this ratio, suggesting equilibrium had been reached. We suggest the mechanism for equilibration involves reductive elimination of the phosphido and hydride ligands to form a \(\text{Rh}(I)\) \(\sigma\)-phosphine−borane complex, similar to E in Scheme 2, which then undergoes rapid oxidative addition of the other \(\text{P}−\text{H}\) 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

![Diagram](image)

**[BarF]** anions are not shown.

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 \([\text{Rh(BDPP)}(\text{dppe})]^+\) and free 13 (by \(^{31}\text{P}\) and \(^{11}\text{B}\) NMR spectroscopy). We have not explored whether there is enantiocontrol at the central \(\text{PCyH} unit\) arising from this PB coupling event on release from the metal.

For these experiments with \(\text{H}_2\text{B-PCyH}_2\) 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 \(\text{H}_2\text{B-PPH}_2\) and \(\text{H}_2\text{B-PPH}_2\cdot\text{BH}_2\cdot\text{PPH}_2\cdot\text{H}_2\), which on addition to \([\text{Rh}(L)(\eta^6\text{-FC}_6\text{H}_5)]\)[BarF] gave the corresponding Rh(I) \(\sigma\)-phosphine–borane complexes with no P–H activation.\(^{33}\) Such selectivity for primary over secondary phosphines in P–H activation at a metal center has been described previously for both phosphine\(^{30}\) and phosphine–borane ligands.\(^{27}\) In particular it has been shown that addition of \(\text{H}_2\text{B-PPH}_2\) to \(\text{Pt}(\text{PEt}_3)_2\text{H}(\text{PPH}_2\cdot\text{BH}_2)\) results in exchange of the metal bound phosphido 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 \((90 \, ^\circ\text{C}, 5 \, \text{mol \%}, [\text{Cat.}] = [\text{Rh}(L)(\eta^6\text{-FC}_6\text{H}_5)]\)[BarF] 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 \(4 \, \text{h}\) (Table 1). The reaction at this temperature is not selective, and although the main product is the linear diboraphosphine, there are products that we tentatively identify as the cyclic oligomers \((\text{BH}_2\text{P})_n\) \((n = 3, 4)\).\(^{20,55}\) Our results are broadly in line with the previously reported catalyzed dehydrocoupling of 2 using \([\text{Rh}(\text{COD})\text{Cl}]_2\), which, at a slightly lower temperature \((60\, ^\circ\text{C}, 16\, \text{h}, \text{melt})\), affords the linear diboraphosphine product in 69% isolated yield, while at 100 \(^\circ\text{C}\) only the cyclic oligomers are isolated. The mechanism of formation of the higher cyclic oligomers, \((\text{BH}_2\text{P})_n\), remains to be resolved.\(^{20}\) For electron-donating \(3\) the reaction is slower using the \([\text{Rh}(L)(\eta^6\text{-FC}_6\text{H}_5)]\)[BarF]...
catalyst (8 h) but overall is more selective. For R = Ph we have previously shown that [Rh(L)(η^6-FC_6H_5)][BH_3] catalyzes dehydrocoupling to give the corresponding linear diboraphosphine in greater than 95% conversion after 4 h. For secondary phosphine–boranes, H_3B-PPh_2H 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 (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 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 H_3B-PPh_2 that being under melt conditions (90 °C) would promote such a substitution.

**Catalytic Dehydrocoupling of Primary Phosphine–Boranes.** [Rh(L)(η^6-FC_6H_5)][BH_3] also acts as a catalyst for the dehydrocoupling of primary phosphine–boranes. Under melt conditions (90 °C, 5 mol %, 4 h) H_3B-PPh_2 is dehydrocoupled to give a major product which is identified by 31P NMR spectroscopy as being polymeric (BH_3PPhH)_n by comparison with previously reported data for purified material coming from the [Rh(COD)_2][OTf] catalyzed process ([δ ~49.3, δ(1H) ~350 Hz, 1,2-F_2C_6H_4] lit.: δ ~48.9, δ(1H) 360 Hz, CDCl_3]. There were also other species observed ~5 ~55, which could be reduced in relative concentration (to ~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 conditions (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 dehydropolymerization. Positive mode ESI-MS (electrospray mass spectrometry) of the melt reaction product demonstrated polymerization, showing repeat units of [H-(PPhHBH_2PPh_2)] up to n = 10 (Supporting Information). Similar analyses have been reported for amine–borane dehydropolymerization.12,14,58 That these polymers are terminated by {PPh_2} groups rather than {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 H_3B-PCy_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 [Rh(PPh_2PCH_2CH_2CH_2PPh_2)] fragment have been determined. This demonstrates that the complex that precedes dehydrocoupling to form a linear diboraphosphine has a σ bond 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 steric plays a role in this process.

A significant observation is that, for primary phosphine–boranes, which are precursors to polyphosphinoboranes, use of the [Rh(PPh_2PCH_2CH_2CH_2PPh_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 flame-dried 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. Under non-melt conditions (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 dehydropolymerization. Positive mode ESI-MS (electrospray mass

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Scheme 11. Competition Experiments between Linear Diboraphosphines**

![Scheme 11](image-url)
(adamantyl)HP-BH$_3$ (4), and Cy$_2$P-BH$_3$ (5) were prepared by the same method as Me$_2$P-BH$_3$, but with the phosphine changed. (4-Trifluoromethylphenyl)PH-BH$_3$ (2) and (3,5-bis(trifluoromethyl)-phenyl)PCl were prepared according to literature procedures reported by Clark et al. NMR spectra were recorded on a Bruker AVD 500 MHz spectrometer at room temperature unless otherwise stated. In 1,2-C$_6$H$_4$F$_2$, 1H NMR spectra were referenced to the center of the downfield solvent multiplet (6.70 ppm) and 13C and 31P NMR spectra were referenced against 85% H$_3$PO$_4$ (external) and BF$_3$·Et$_2$O (external), respectively. The spectrometer was precooled and preshimmed using a CD$_2$C (0.1 mL) and 1,2-C$_6$H$_4$F$_2$ (0.3 mL) sample. Chemical shifts are quoted in ppm and coupling constants in Hz. ESI-MS were recorded on a Bruker microOTOF instrument. All in 1H NMR 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 H$_2$B(PR$_2$H) [R = 3,5-Bis(trifluoromethyl)phenyl] (1). A solution of 3,5-bis(trifluoromethyl)phenyl)PCl (1.48 g, 3.0 mol) in diethyl ether (5 mL) was added dropwise to a diethyl ether (20 mL) suspension of LiBH$_4$ (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, CDCl$_3$): δ 8.18 (br s, 1 H, p-Ar-H), 8.09 (br s, 2 H, o-Ar-H), 6.58 (dm, δ$_{JHH}$ = 388 Hz, 1 H, PH), 0.3–2.0 (br m, 3 H, BH). 31P-{1H} NMR (121 MHz, CDCl$_3$): δ 4.7 (br s, PH). 11B (160 MHz, CDCl$_3$): δ −41.7 (br s, BH). 13C F NMR (282 MHz, CDCl$_3$): δ −62.9 (s, CF). EI-MS (70 eV) m/z (%) = 458 (62) [M−BH$_3$]$.\textsuperscript{+}$. Anal. Found: C 40.71%, H 2.02%. Calcd for C$_9$H$_7$BP$_2$: C 40.69%, H 2.14%.

**Synthesis of (Adamantyl)PH-BH$_3$ (4).** (Adamantyl)PH-BH$_3$ was prepared under the same conditions as Me$_2$P-BH$_3$, but with (adamantyl)PH instead of PMe$_2$.

2H NMR (300 MHz, CDCl$_3$): δ 3.61 (dm, 1 H, δ$_{JHP}$ = 379 Hz, PH), 2.11 to 1.83 (30 H, adamantyl-CH), 0.41 to −0.15 (br m, 3 H, BH). 31P-{1H} NMR (121 MHz, CDCl$_3$): δ 40.1 (br m, PH). 11B (160 MHz, CDCl$_3$): δ −44.8 (br d, BH). Anal. Found: C 75.78%, H 10.71%. Calcd for C$_{20}$H$_{24}$BP: C 75.89%, H 10.84%.

**Synthesis of H$_2$B(PR$_2$H)$_2$-PR$_2$H (R = 3,5-Bis(trifluoromethyl)phenyl) (10); 4-Trifluoromethylphenyl (11); 4-Methoxyphenyl (12).** A Youngs flask charged with 0.25 mmol of R$_2$PH-BH$_3$ (118 mg of 1, 84 mg of 2, 65 mg of 3) and 5 mol% of [Rh(dppp)(C$_6$H$_4$F$_2$)]$^+$ (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, CDCl$_3$): δ 8.09 to 7.89 (12 H, Ar–H), 7.32 (dm, δ$_{JHP}$ = 412 Hz, 1 H, PH), 2.45 (br m, 2 H, BH$_3$), 1.11 (br m, 3 H, BH). 31P-{1H} NMR (121 MHz, CDCl$_3$): δ −1.7 (br s, PRH). 11B (160 MHz, CDCl$_3$): δ −33.2 (br s, BH$_3$). Anal. Found: C 40.90%, H 1.83%. Calcd for C$_{20}$H$_{25}$B$_2$P$_2$: C 40.76%, H 1.93%.

Details follow for 11. 1H NMR (500 MHz, CDCl$_3$): δ 7.77 to 7.52 (16 H, Ar–H), 7.04 (dt, δ$_{JHP}$ = 426 Hz, δ$_{JHH}$ = 7.8 Hz, 1 H, PH), 2.37 (br m, 2 H, BH$_3$), 1.02 (br m, 3 H, BH). 31P-{1H} NMR (202 MHz, CDCl$_3$): δ −3.5 (br s, PRH). 11B (160 MHz, CDCl$_3$): δ −33.7 (br s, BH$_3$).
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)–(C6H,F)][BARf4] (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, BARf4), 7.69 (s, 4H, BARf4), 4.40 (vbr, 1H, BH), 3.10–2.12 (8H, 3CH3 dpp3 + BH3), −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, JRh,P = 111°, JH,P = 36°, 36H, P(3CH3)PPh3), 29.5 (m, JRh,P(trans) = 260°, Rh-PR3BH3), JRh,P(phen) = 1.20 (br, 1H, B–H), −6.2 (s, BARf4), −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%.

Method A follows. To a Youngs flask charged with [Rh(dpp3)(C6H5F)][BARf4] (11 mg, 0.034 mmol) and 1 equiv of PHR5 (10 mg, 0.034 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)(C6H,F)][BARf4] (50 mg, 0.034 mmol) and 2 equiv of H2BPR-H (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 (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, 8H, BARf4), 7.69 (s, 4H, BARf4), 3.30 (d, JPR = 362 Hz, 1H, BH), 2.87 (d, JPR = 412 Hz, 1H, PH), 2.45–1.56 (66H, dpp3 CH3 and adamantyl-H), −0.24 (br, 3H, BH). 31P{1H} NMR (202 MHz, 1,2-F2C6H4) δ 60.4 (dd, JPR,P(trans) = 266 Hz, JPR,P(phen) = 142 Hz, 30H, P(3CH3)PPh3), 30.5 (s, P(3CH3)PPh3), 22.8 (s, JPR,P(trans) = 163 Hz, JPR,P(phen) = 30 Hz, PPh3(C3H3)), 6.6 (dd, JPR,P(trans) = 270 Hz, JPR,P(phen) = 114 Hz, JPR,P(trans) = 30 Hz, PPh3(C3H3)). 11B{1H} NMR (160 MHz, 1,2-F2C6H4): δ −6.0 (s, BARf4), −42.2 (br, BH). 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)(PHR5)][BARf4] [R = 3,5-Bis-(trifluoromethyl)phenyl] (21). Method A follows. To a Youngs flask charged with [Rh(dpp3)(C6H,F)][BARf4] (50 mg, 0.034 mmol) and 2 equiv of H2BPR-H (32 mg of 1) was added 1,2-F2C6H4 (5 mL). The solution was stirred at room temperature for 24 h. The formation of (gaseous) H2 gas was 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)–(C6H,F)][BARf4] (20 mg, 0.034 mmol) and 2 equiv of PHR5 (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, 8H, BARf4), 7.69 (s, 4H, BARf4), 6.41 (dm, JPR = 375 Hz, 2H, PH), 2.62 (br, 4H, 2 CH2 dpp3), 2.17 (m, 2H 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%.
BH$_2$, CyH), and showed that the complexes rapidly decomposed when exposed to 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, C$_6$H$_5$F: δ 8.32 (s, 8 H, $\text{BH}_2^+$), 7.61 (s, 4 H, $\text{BH}_2^+$), 5.63 (m, 2 H, Ar–H), 5.43 (m, 2 H, Ar–H), 5.10 (m, 1 H, Ar–H), 4.38 (m, 2 H, Ph–CH$_2$), 1.40 (m, 2 H, CH$_2$), 0.78 (m, 6 H, CH$_3$), 0.72 (m, 4 H, $\text{BH}_2^+$) and 0.77 (m, 6 H, $\text{BH}_2^+$) were observed as signals of isomers and were characterized 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 13C NMR spectra of 27a and 27b which, along with the presence of $\text{H}_2$, show that the complexes rapidly undergo dehydrocoupling to form complexes of 28. The 13C 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 26a and 26b, based on coupling constants and approximate integrations) and tentatively assigned the individual diastereomers (Scheme 5S, Supporting Information) by inspection of a model.

Method B follows. To a Youngs flask charged with [Rh(dppp)(CH$_2$F)]$^+$(50 mg, 0.034 mmol) and 1 equiv of CyH$_2$P(BH$_2$)Cy (0.56 mmol) in a solution in $\text{C}_6\text{H}_5\text{F}$ (4 mL). Complexes 26a and 26b were characterized as a mixture in solution by NMR spectroscopy and ESI-MS. The 13C 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 5S, Supporting Information) by inspection of a model.

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(CH₃)₃P²¹⁵P₃H₂·BH₃, 3.6 (br d, in ν(trans) = approximately 208 Hz, Rh-Pᴴ3Cpy-C, −12.1 (br s, in ν(trans) = approximately 208 Hz, Rh-Pᴴ3Cpy-C, −42.1 (br s, Rh−H), 13.5 (br s, R−H, NH) ppm. See Supporting Information for further details.

**Synthesis of [Rh(BDPP)(PCy₂H₂PCH₂H₂P)][BArF₄]** [28a, 28b, 28c] and [28d]. Method A follows. [Rh(BDPP)(C₆H₅F)][BH₄] was prepared on an NMR scale from [Rh(BDPP)(nbd)][BF₄] (0.020 g, 0.0133 mmol) as above. This solution was transferred to a NMR tube containing CyH₂P.trans·BH₃. The solution was heated to 90 °C for 18 h. The resulting solid was dissolved in 1,2-C₆H₄F₂ (0.248 g, 2.0 mmol) was dissolved in toluene (10 mL) either in the presence of no catalyst or with 1,2-C₆H₄F₂ (0.027 mmol) and the solution was heated to re-precipitate. The solvent was decanted and the solid washed with hexane (25 mL) to yield a pale yellow precipitate. The author information section of the manuscript is as follows:

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**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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(56) In principle there should be four diastereoisomers for 25 as both P-centers are stereogenic. However, we assume that the second center (which is next to the BH3) is far enough removed from the metal center so as not to influence the 31P or 1H chemical shifts significantly.

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