

Highly Selective Hydroboration of Terminal Alkenes Catalyzed by a Cobalt Pincer Complex Featuring a Central Reactive N-Heterocyclic Phosphido Fragment.

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ABSTRACT: The application of a cobalt pincer complex, (PP^{Cl}P)CoCl₂, as a precatalyst for the hydroboration of terminal alkenes with pinacolborane (HBPin) is described. The reactions proceed rapidly under mild conditions (room temperature, 30 min) with low catalyst loadings (1 mol %) using KBET₃H (2.1 mol %) as an activator to afford terminal hydroboration products with very high selectivity for the anti-Markovnikov product. The precatalyst is effective towards vinyl arenes and aliphatic alkenes and proceeds to 83-98% conversion with these substrates. However, the functional group tolerance of the catalytic system is somewhat limited, as minimal conversion is observed with internal olefins or when pyridine, ketone, or allyl ether functional groups are present. Deuterium labelling studies and spectroscopic identification of the catalyst deactivation product suggest a (PPP)CoH active species.

INTRODUCTION

Hydrofunctionalization reactions such as hydroboration provide well-established routes to incorporate reactive functional groups into hydrocarbon precursors. Alkene hydroboration is a straightforward method to prepare alkylboronates, which are versatile synthons for the construction of more complex molecules via Suzuki-Miyaura coupling.¹⁻⁴ The most common transition metal catalysts for hydroboration feature precious metals such as Ir and Rh.⁵⁻⁸ However, the environmental and economic concerns associated with the long term use of precious metals has motivated researchers to focus on the development of new catalytic systems based on cheaper and more Earth-abundant first-row transition metals.⁹⁻¹⁵

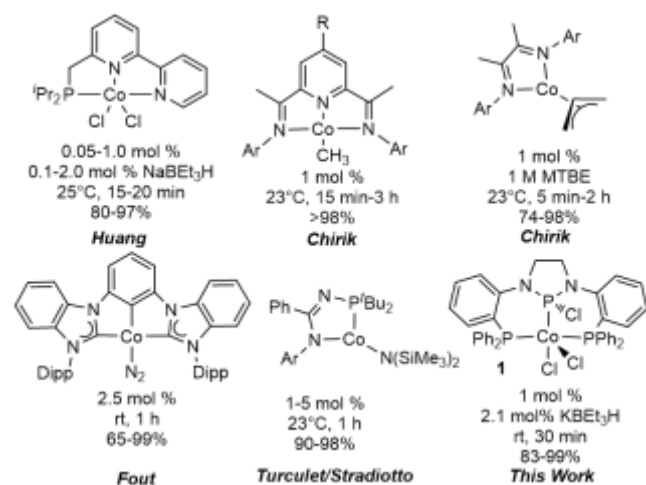


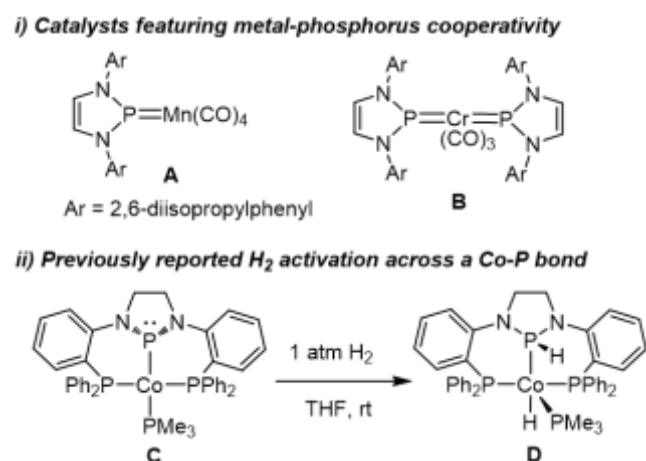
Figure 1. Selected examples of Co catalysts for anti-Markovnikov selective alkene hydroboration.

Recent reports from Chirik, Huang, Fout, Lu, and others have demonstrated the use of cobalt^{10,14,16-32} and iron^{20,33-37} complexes as catalysts for the hydroboration of alkenes and some representative examples are shown in Figure 1. Among cobalt examples, Huang and coworkers have reported a highly effective and robust system that incorporates a Co(PNN) precatalyst (PNN = 6-[(dialkylphosphino)methyl]-2,2'-bipyridine) and NaBEt₃H as an activator, which operates at room temperature with ppm catalyst loadings while tolerating a wide variety of functional groups (allyl ethers, tertiary amines, ketones) (Figure 1).²⁹ Fout has similarly developed an effective hydroboration catalyst, (CCC)CoN₂ (CCC = bis(2,6-diisopropylphenylbenzimidazol-2-ylidene)phenyl) that does not require an activator and is functional group tolerant and highly selective for the linear hydroboration product.³⁰ Chirik and coworkers have reported bis(iminopyridine), terpyridine, and α -diimine cobalt(I) alkyl complexes that catalytically hydroborate terminal alkenes with high anti-Markovnikov selectivity without the need for an activator.^{16,17} What sets these complexes apart is their activity towards internal olefins and their ability to perform tandem chain-walking and hydroboration to afford high selectivity terminal hydroboration products. Findlater, Chirik, Zheng, Thomas, and Lu, on the other hand, have reported Co catalysts that are selective for branched/Markovnikov hydroboration products.^{22,26,28,31,32}

Many of the most successful cobalt hydroboration catalysts take advantage of the stability and rigidity imparted by tridentate pincer ligands.^{10,14} We turn our attention herein to a (PPP)⁻ pincer ligand that incorporates an N-heterocyclic phosphido (NHP⁻) moiety in the central donor position flanked by two diarylphosphine sidearms.³⁸ We have previously demonstrated that the tridentate (PPP)⁻ pincer ligand can engage in metal-ligand cooperativity, through either bifunctional substrate activation across the metal-P bond or ligand-assisted redox processes.³⁹⁻⁴⁴

Both stoichiometric and catalytic reactions involving the addition of σ -bonds across metal-ligand bonds have become increasingly prevalent,⁴⁵ with the most extensive studies focusing on metal amide/amine complexes. For example, Hanson and coworkers have shown that catalytic ketone hydrogenation using [(PNHPCy)Co(CH₂SiMe₃)]BAR^F₄ (PNHPCy = bis[(2-dicyclohexylphosphino)ethyl]amine) involves metal-ligand bifunctional catalysis, where the N-H group in the pincer ligand participates in the catalytic cycle.⁴⁶ In contrast, very few examples of metal-phosphorus ligand cooperativity in catalysis have been reported. Gudat and coworkers have shown that a metal phosphonium complex, (*u*NHP^{Dipp})Mn(CO)₄ (**A**), is active for the catalytic dehydrogenation of ammonia borane and (*u*NHP^{Dipp})₂Cr(CO)₃ (**B**) cooperatively activates hydrogen across a Cr-P bond and is active for the photocatalytic hydrogenation of styrene (Scheme 1).^{47,48} Herein, we explore the catalytic activity of (PPP)Co complexes towards alkene hydroboration, hypothesizing that metal-phosphorus cooperativity may be a viable reaction pathway.

Scheme 1. *i)* Examples of catalysts that operative via metal-phosphorus ligand cooperativity.^{47,48} *ii)* Previously reported H₂ activation reaction across the Co-P bond of **C**.⁴¹



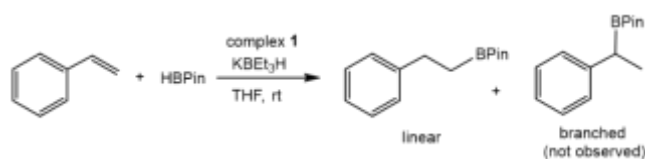
In previous studies in our lab, (PP^{Cl}P)CoCl₂ (**1**) was synthesized and subsequently reduced to the Co^I NHP complex, (PPP)Co(PMe₃) (**C**, Scheme 1). It was found that H₂ and the S-H and O-H bonds of thiophenol and phenol are cleaved across the Co-P bond of **C** to afford new Co^I complexes that contain a functionalized N-heterocyclic phosphine/phosphinito species such as (PP^HP)Co(PMe₃)(H) (**D**) in the case of H₂.^{41,42} Despite its facile reactivity with H₂, **C** was found to be a sluggish alkene hydrogenation catalyst (Table S1), which we attributed to hindrance from the ancillary ligand (PMe₃). In element-hydride bond activation products such as **D**, the hydride ligand was found to be *trans* to the central NHP unit rather than *cis*, with the PMe₃ ligand situated between the NHP-H and Co-H functionalities. We hypothesized that this geometric preference hindered the catalytic viability of metal-ligand cooperative processes in this system, as reductive elimination across the metal-phosphorus bond would require an isomerization step to bring the substituents on the P^{NHP} and Co atoms close enough in proximity to eliminate. Attempts to generate catalytically active reduced species or hydride complexes in the absence of phosphine ligands, however, resulted in dimeric (PPP)Co complexes that were unreactive towards bond activation processes.⁴³ Thus, we turn our attention to the use of **1** as a precatalyst for alkene hydroboration,

generating a reactive (PPP)Co pincer complex without an ancillary ligand in situ.

RESULTS AND DISCUSSION

Complex **1** was found to be a precatalyst for the hydroboration of terminal alkenes with HBPin in the presence of an activator, KBET₃H. Initial hydroboration experiments were performed using styrene as a model substrate to optimize catalyst loading, reaction time, and concentration (Table 1). In all cases, the linear anti-Markovnikov product was the exclusive product observed at room temperature with no detectable side products from competing reactions such as dehydrogenative borylation. The reaction was found to proceed to 98% yield in 30 min using just 1 mol % catalyst loading of **1** and 2 mol % KBET₃H (Entry 1-3). After just 10 min at room temperature, 80% yield was achieved (Table 1, Entry 5), however, 30 min was required to reach full conversion (Table 1, Entry 3). Varying the concentration of the reaction mixture revealed that more dilute conditions gave a higher yield in the same reaction time (Table 1, Entry 6 and 7). This observation suggests a possible bimolecular catalyst deactivation process. The reaction proceeded to identical conversion in the presence of one drop of Hg, providing one piece of evidence that catalysis is likely homogenous and not attributed to metallic cobalt nanoparticles (Table 1, Entry 4). No hydroboration activity was observed when either the cobalt precatalyst **1** or the KBET₃H activator were omitted from the reaction mixture (Table 1, Entry 8 and 9). Lastly, in a control reaction suggested in a recent paper by Thomas and coworkers,⁴⁹ catalysis proceeded in 96% yield in the presence of TMEDA (Table 1, Entry 10) with no evidence for formation of the TMEDA-BH₃ adduct (by ¹¹B NMR spectroscopy, Figure S34), ruling out decomposition of HBPin to catalytically active boron species. Ultimately, the optimized conditions chosen for the remainder of our studies were 1 mol % **1**, 2.1 mol % KBET₃H, in 3 mL of THF (4-6 mM catalyst concentration) for 30 minutes (Table 1, Entry 3).

Table 1. Optimization of the catalyst loading, time, and concentration for the hydroboration of styrene using **1** as a precatalyst.



Entry	Precatalyst (mol %)	Activator (mol %)	Time (min)	Yield (NMR)
1	1 (10)	KBET ₃ H (20)	60	98
2	1 (5)	KBET ₃ H (10)	60	98
3	1 (1)	KBET ₃ H (2.1)	30	98
4 ^a	1 (1)	KBET ₃ H (2.1)	30	98
5	1 (1)	KBET ₃ H (2.1)	10	80
6 ^b	1 (1)	KBET ₃ H (2.1)	30	98

7 ^c	1 (1)	KBET ₃ H (2.1)	30	88
8	-----	KBET ₃ H (2.1)	30	0
9	1 (1)	-----	30	0
10 ^d	1 (1)	KBET ₃ H (2.1)	30	96

^a One drop of Hg was added. ^b 3 mL of THF, 4 mM catalyst concentration. ^c 1 mL of THF, 12 mM catalyst concentration. ^d 20 mol % TMEDA was added.

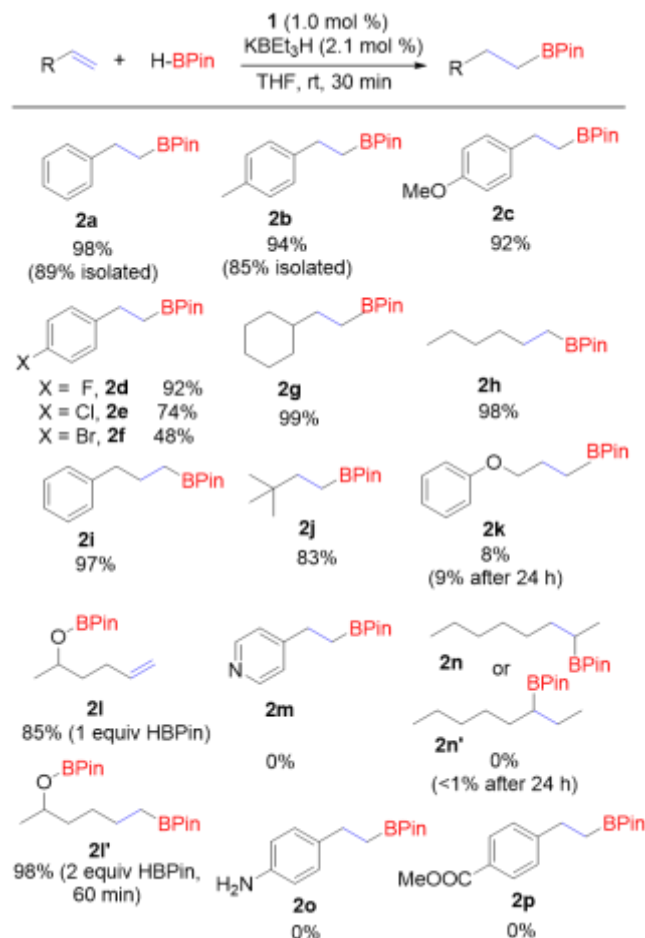
Encouraged by these initial results using styrene, we sought to extend the substrate scope and investigate the limitations of this cobalt-catalyzed reaction by using complex **1** as a precatalyst for the hydroboration of a variety of alkene substrates (Figure 2). The hydroboration of styrene derivatives with both electron-withdrawing and electron-donating substituents in the *para* position proceeded in >90% yields, converting to exclusively the anti-Markovnikov product in all cases (**2a-d**). Although aryl fluorides are well-tolerated (**2d**), the yields obtained for substrates with aryl chloride (**2e**) and aryl bromide (**2f**) functionalities are diminished and decrease in the order F > Cl > Br. The hydroboration of aliphatic terminal alkenes, such as cyclohexylethylene, 1-hexene, and allylbenzene afforded the hydroboration products **2g**, **2h**, and **2i**, respectively, in near-quantitative yield with no evidence for branched products. Hydroboration also proceeded with the more sterically hindered aliphatic substrate *tert*-butylethene, albeit with slightly lower yield of product **2j** (83%). Chain-walking was not observed in any of the aforementioned cases.

The functional group tolerance of the **1**/KBET₃H catalytic system was, however, found to have limitations (Figure 2). The hydroboration of allyl phenyl ether resulted in only 8% yield of **2k** under the optimized reaction conditions, and conversion did not improve with longer reaction time, likely due to deprotection of the allyl ether under the reaction conditions. Catalytic hydroboration of 5-hexen-2-one with one equivalent of HBPIn did not result in hydroboration of the alkene, but instead led to 85% conversion to the ketone hydroboration product **2l** (Figure S29). Under the same conditions but with a 2:1 HBPIn to ketone ratio, hydroboration of both the ketone and alkene functional groups occurs, generating a 7:1 mixture of **2l** to **2l'** after 30 minutes and proceeding to full conversion to **2l'** in 60 min (Figures S30-S31). Hydroboration of 4-vinylpyridine did not proceed to form any detectable **2m**, likely owing to the ability of the pyridine moiety to coordinate to cobalt and deactivate catalysis. Amine and ester functional groups were also shown to interfere with catalysis, as catalytic hydroboration of 4-vinylaniline and 4-acetoxystyrene afforded no conversion to **2o** or **2p**, respectively. Lastly, internal alkenes such as 2-octene were not amenable to the hydroboration protocol and hydroboration products such as **2n** or **2n'** were not formed even with extended reaction times.

In comparing the catalytic activity of the **1**/KBET₃H system to known cobalt hydroboration catalysts, we find that both the activity and selectivity of the present system are excellent, but the system is limited compared to other reported catalysts in the context of functional group tolerance. Comparing the system with (dppCCC)CoN₂, it becomes clear that **1**/KBET₃H is more active towards sterically hindered substrates, but (dppCCC)CoN₂ is superior in functional group tolerance as it tolerates ketone and allyl ether functionalities.³⁰

Although **1** operates under similarly mild conditions and with similar reaction times to (PNN)CoCl₂, the latter catalyst is functional at much lower catalyst loading (0.05 mol %) and is more functional group tolerant.²⁹ The activity of precatalyst **1** is comparable to Chirik's Co(I) alkyl catalysts, but a notable difference is the inactivity of **1**/KBET₃H towards internal olefins.^{16,17}

Figure 2. Substrate scope for the catalytic hydroboration of alkenes using **1** as a precatalyst.

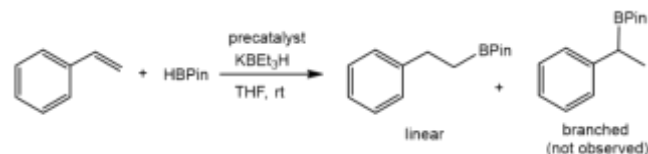


^a The long induction period required for this reaction suggests that the active species may not be a homogeneous (PPP)Rh catalyst.

To assess whether the catalytic hydroboration activity was specific to mononuclear (PPP)Co complexes, several additional complexes were screened as precatalysts for the hydroboration of styrene (Table 2). The symmetric Co^I dimer (PPP)₂Co₂ was found to be inactive as a catalyst/precatalyst for alkene hydroboration (Table 2, Entry 1-2).⁴³ The Co^{II} hydride dimer [(PPP)CoH]₂ was found to be inactive as a catalyst for the hydroboration of styrene even when KBET₃H was added (Table 2, Entry 3-4). On the other hand, the chloride-bound Co^{II} dimer [(PPP)CoCl]₂ does display moderate catalytic activity when KBET₃H is added and produces the linear hydroboration product in 61% yield (Table 2, Entry 6), implying that some quantity of catalytically active species can be generated from this complex under the reaction conditions. Nonetheless, the diminished catalytic activity of the dimeric complexes strongly suggests that the active species is a monometallic complex. To assess the importance of cobalt and its role in the catalytic cycle, we also screened the catalytic activity of nickel and rhodium

complexes previously reported by our group. (PPP)NiCl⁵⁰ was found to be catalytically inactive for the hydroboration of styrene under the optimized reaction conditions, even with a much higher catalyst loading and longer reaction times (Table 2, Entry 7). Catalytic styrene hydroboration using the rhodium complex (PP^{Cl}P)RhCl⁴⁴ in the presence of KBET₃H, on the other hand, did afford a yield of anti-Markovnikov hydroboration product similar to that of **1** (Table 2, Entry 8). However, the reaction using the Rh precatalyst was not homogeneous and a long induction period was observed, leading to some ambiguity whether the active species is truly a (PPP)Rh complex.

Table 2. Screening of the catalytic activity of additional metal complexes as catalysts/precatalysts for alkene hydroboration, demonstrating that catalytic activity is specific to **1**.



Entry	Precatalyst (mol %)	Activator (mol %)	Time (min)	Yield (NMR)
1	(PPP) ₂ Co ₂ (2)	-----	30	< 1%
2	(PPP) ₂ Co ₂ (2)	KBET ₃ H (4)	30	< 1%
3	[(PPP)CoH] ₂ (2)	-----	30	< 1%
4	[(PPP)CoH] ₂ (2)	KBET ₃ H (4)	30	< 1%
5	[(PPP)CoCl] ₂ (2)	-----	30	< 1%
6	[(PPP)CoCl] ₂ (1)	KBET ₃ H (2)	30	61 %
7	(PPP)NiCl (10) ⁵⁰	KBET ₃ H (20)	2 - 48 h	< 1%
8 ^a	(PP ^{Cl} P)RhCl (1) ⁴⁴	KBET ₃ H (2)	30	93 %

To gain further mechanistic insights into the catalytic hydroboration reaction using **1**, a deuterium labeling experiment was performed with deuterated pinacolborane (DBPin). Upon performing a catalytic styrene hydroboration reaction with DBPin under optimized reaction conditions, deuterium was incorporated into the desired linear alkylboronate ester product with a roughly 0.85 to 1 distribution of deuterium at the terminal and benzylic positions (Figures 3 and S31). These observations are consistent with the presence of a borane-derived cobalt hydride/deuteride intermediate over the course of catalysis and suggest that the alkene insertion step is reversible and occurs without selectivity but that reductive elimination can only occur from a linear alkyl intermediate. The detection of a significant amount of deuterium incorporation into the terminal position of the hydroboration product suggests that the rate of reversible alkene insertion/ β -hydride elimination is competitive with the rate of C-B reductive elimination.

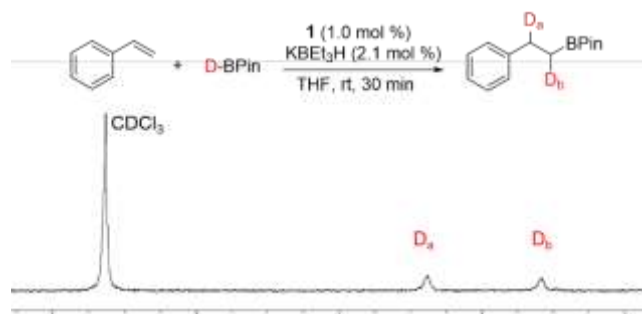


Figure 3. ²H NMR spectrum of the product obtained upon styrene hydroboration with DBPin catalyzed by **1** in the presence of KBET₃H.

To probe the identity of the active metal catalyst, trapping experiments were performed with trimethylphosphine (PMe₃). When PMe₃ is added at the outset of the catalytic reaction, there is no detectable conversion to the desired alkylboronate ester product. Likewise, when PMe₃ is added while the reaction is in progress, the reaction is halted. In both cases, the final metal-containing species was spectroscopically identified as (PP^HP)Co(PMe₃)(H) (**B**).⁴¹

Under standard catalytic conditions without the addition of PMe₃, spectroscopic analysis of the metal-containing species at the end of the reaction revealed a single compound identified as the catalytically inactive Co^{II} dimer [(PPP)CoH]₂ (Figure S32).⁴³ The identification of this dimeric species upon reaction completion allows several key mechanistic conclusions to be drawn: (1) Catalyst deactivation occurs via dimerization once the alkene and HBPIn substrates have been consumed. (2) The chloride substituent on phosphorus has been removed from **1** upon catalyst activation with KBET₃H. Indeed, we previously reported that treatment of **1** with 3.2 equiv KBET₃H generates [(PPP)CoH]₂, which can be isolated in 90% yield.⁴³ (3) Prior to dimerization at the completion of the catalytic reaction, the NHP⁻ phosphorus center is available to participate in the catalytic cycle. (4) The active species likely remains in the Co^{II} state throughout the catalytic cycle and a Co^{I/III} cycle is not operative. Although we cannot conclusively draw a mechanism for the catalytic alkene hydroboration reaction, these conclusions strongly suggest that the active species is a Co^{II} hydride monomer (PPP)CoH (**I**). Square planar Co(II) hydride species have been previously proposed as catalytically active species in related studies, but have proven to be reactive to isolate.^{51,52} Further studies will be required to determine whether metal-ligand cooperativity is operative or whether catalysis proceeds from **I** via an entirely metal-based olefin insertion / σ -bond metathesis pathway.

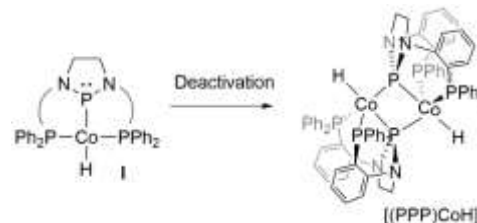


Figure 4. Proposed catalytically active species and known deactivation product.

CONCLUSION

In conclusion, a catalytic system for the hydroboration of alkenes has been developed using a cobalt complex bearing a tridentate (PPP) ligand featuring a central N-heterocyclic phosphido donor as a precatalyst. When (PP^{Cl}P)CoCl₂ is activated in situ using KBet₃H, hydroboration of terminal alkenes with HBPIn proceeds in high anti-Markovnikov selectivity at room temperature in 30 minutes. A deuterium labeling experiment confirmed the intermediacy of a cobalt hydride, likely (PPP)CoH, and generation of a primary alkyl intermediate during the catalytic cycle. Upon completion of the catalytic reaction, the catalytically inactive dimer species [(PPP)CoH]₂ is observed spectroscopically as the sole metal-containing species, providing further evidence for the intermediacy of (PPP)CoH. Future studies will focus on exploring the mechanism of this catalytic reaction in more detail, expanding upon the catalytic applications of the (PPP)Co system, and optimizing the catalyst design.

EXPERIMENTAL SECTION

General Considerations. Unless otherwise noted, all manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. Glassware was oven-dried before use. Tetrahydrofuran and hexanes were degassed by sparging with ultra-high purity argon and dried via passage through columns of drying agents using a Seca solvent purification system from Pure Process Technologies. CDCl₃ was purchased from Cambridge Isotopes Laboratories and used without further purification. (PP^{Cl}P)CoCl₂ (**1**) was synthesized according to literature procedures.⁴¹ CoCl₂ was purchased from Strem Chemicals, Inc. (anhydrous, 99+%) and further dried under vacuum at 130 °C overnight prior to use. Hexamethylbenzene was purified by sublimation. Allyl phenyl ether was purified by drying over CaH₂ overnight, followed by vacuum distillation and degassing via repeated freeze pump-thaw cycles. Dry allyl phenyl ether was stored over 4 Å molecular sieves before use. Styrene derivatives were filtered over basic alumina to dry and remove stabilizers and stored in the glovebox at -35 °C. All alkenes were stored over 4 Å molecular sieves before use. HBPIn was purchased from Acros Organics and KBet₃H was purchased from Sigma Aldrich as a 1 M solution in THF, and both were used without further purification. All other reagents and solvents were obtained from commercial sources and used without further purification. NMR spectra were recorded at ambient temperature unless otherwise stated on a Bruker DPX 400 MHz or Bruker 600 MHz Avance III HD instrument. ¹H and ¹³C NMR chemical shifts were referenced using residual solvent resonances and are reported in ppm. ¹⁹F NMR chemical shifts are referenced using an external standard (1% trifluoroacetic acid, -76.5 ppm). ¹¹B NMR chemical shifts are referenced using an external standard (BF₃•Et₂O, 0 ppm).

General Catalytic Alkene Hydroboration

Procedure. To a 20 mL vial equipped with a stir bar, **1** (1.0 mol %), THF (3 mL), HBPIn (1.0 equiv), and the alkene substrate (1.0 equiv) were added and stirred for 1 min. KBet₃H (2.1 mol %, 1.0 M solution in THF) was added to the stirring solution via a glass syringe and the reaction was stirred at room temperature for 30 min. *To determine NMR yields:* Upon completion, the solvent was removed in vacuo. Hexamethylbenzene (0.10 equiv, 1.0 M in CDCl₃) was added to the remaining oily residue via a glass syringe, and the resulting solution was diluted further with CDCl₃. ¹H NMR spectroscopy was used to determine the yield by integration of the methyl BPin resonance (1.22-1.25

ppm) relative to the resonance of the internal standard (hexamethylbenzene, 2.23 ppm). *To determine isolated yields:* The reaction was removed from the glovebox, concentrated under reduced pressure, and purified by flash chromatography with 20:1 hexanes/ethyl acetate to afford the desired alkylboronate ester. Complete experimental procedures and characterization data for **2a-2j** are provided on pages S3-S7 of the Supporting Information file.

Deuterium Labelling Experiment with DBPin.

DBPin was synthesized using a modified literature procedure.⁵³ To a stirring solution of BD₃-THF (1.0 mL, 1.0 mmol) under argon at 0 °C was added pinacol (118 mg, 1.00 mmol). The reaction was allowed to warm to room temperature and was stirred for 2 h. The solution of DBPin was used without further purification.

To a 20 mL vial equipped with a stir bar, **1** (0.012 g, 0.015 mmol), THF (3 mL), DBPin (312.3 µL, 0.312 mmol), and styrene (35.9 µL, 0.312 mmol) were added and stirred for 1 min. KBet₃H (32.7 µL, 1.0 M solution in THF, 0.032 mmol) was added to the stirring solution via a glass syringe and the reaction was stirred at room temperature for 30 min. Upon completion, an aliquot of the reaction was removed for analysis by ²H NMR spectroscopy.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/

characterization data for hydroboration products, NMR spectra for hydroboration products, ³¹P NMR spectra of metal-containing species observed upon catalyst deactivation.

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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 interests.

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TOC Graphic

