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B–H Bond Cleavage via Metal–Ligand Cooperation by Dearomatized Ruthenium Pincer Complexes

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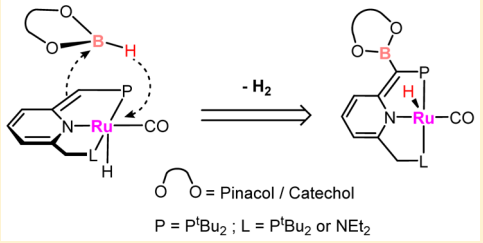
Supporting Information

ABSTRACT: Organic derivatives of boronic acid are widely used reagents useful in various synthetic applications. A fundamental understanding and the exploration of new reaction pathways of boronic reagents with organometallic systems hold promise for useful advancement in chemical catalysis. Herein we present the reactions of simple boranes with dearomatized ruthenium pincer complexes based on PNP (2,6-bis(di-*tert*-butylphosphinomethyl)pyridine) or PNN (2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine) ligands. NMR studies revealed dehydrogenative addition of the borane B–H bond across the metal center and the ligand. Remarkably, new complexes were observed, which contain the boryl moiety at the benzylic carbon of the pincer ligand arm. X-ray crystal structures of new dearomatized boryl pincer complexes were obtained, and DFT calculations revealed mechanistic details of the adduct formation process through a dehydrogenative pathway. In addition, catalytic aryl–boron coupling reactions were explored. The new boryl pincer systems may possibly be useful in future postmodification techniques for ruthenium pincer complexes, as well as in catalytic B–B and B–C coupling reactions.



INTRODUCTION

Organic derivatives of boronic acid have become highly useful reagents in modern synthetic organic chemistry.[1] The unique and sometimes peculiar chemistry of aryl- and alkylborane reagents has been the focus of research for over a century.[2−4] Brown et al. pioneered the field with studies on applicative borane chemistry.[5−7] Ever since, these versatile reagents have found wide use in polymerization reactions,[8−11] medicinal chemistry,[12] organometallic ligand design,[13−16] and various organic synthetic protocols.[17−21] Most outstanding is the use of organo-boronic acids or esters in the catalytic Suzuki–Miyaura carbon–carbon cross-coupling reaction.[22−24] Dehydrogenative borylation of aryls, catalyzed by rhodium(I)[25−30] and iridium-(I)[28−32] complexes, is a recent synthetic method to access these instrumental reagents. To our knowledge, efficient borylation of unactivated arenes using homogeneous ruthenium catalysis has not yet been reported.[30,33,34] Research focus should still be directed toward improved selectivity, substrate scope, and atom efficiency of these reactions. Boron–boron dehydrogenative coupling has also spurred interest as diborons, the products of such coupling reactions, may serve as borylation agents, with the added advantage of being air and moisture stable.[35−38] A fundamental understanding of boron–boron bond formation is in itself of interest.[25,26,39]

The search for key intermediates in catalytic hydroboration reactions has shed light on the nature of borane B–H addition to late-transition-metal complexes and on the dynamics of the metal–boron bond.[40] Presenting a new mode of borane addition to organometallic complexes, Ozerov et al. reported the reversible interaction of boranes and diborons with palladium complexes bearing noninnocent pincer ligands, whereby a boron atom adds to the basic amine group of the ligand and may be detached by hydrolysis.[41] More recently, Leitner et al. disclosed the *Z*-selective hydroboration of terminal alkenes and alkynes using a nonclassical hydride PNP ruthenium pincer complex and were able to isolate a hydrogen-bridged ruthenium–boryl adduct complex.[42] Alkene hydroboration has also been reported using pincer-type iron[43] and cobalt[44] complexes. Chirik et al. demonstrated very recently dehydrogenative B–C_{aryl} coupling by cobalt pincer complexes and isolated a proposed intermediate bearing a σ-boryl ligand attached to the metal center.[45]

Ruthenium PNP (2,6-bis(di-*tert*-butylphosphinomethyl)-pyridine) and PNN (2-(di-*tert*-butylphosphinomethyl)-6-(diethylaminomethyl)pyridine) pincer complexes, previously disclosed by our group,[46−48] are prone to deprotonation at the benzylic position of the ligand, resulting in loss of aromaticity in the ligand backbone (Scheme 1a). The aromatization–dearomatization processes, with no change in the formal oxidation state of the metal, were found to mediate several fundamental catalytic hydrogenation and dehydrogenation reactions.[49−52] It is worth noting that a key intermediate believed to take part in such transformations is a *trans*-dihydride complex, which may also be formed independently by exposure of the dearomatized ruthenium pincer complexes **1**

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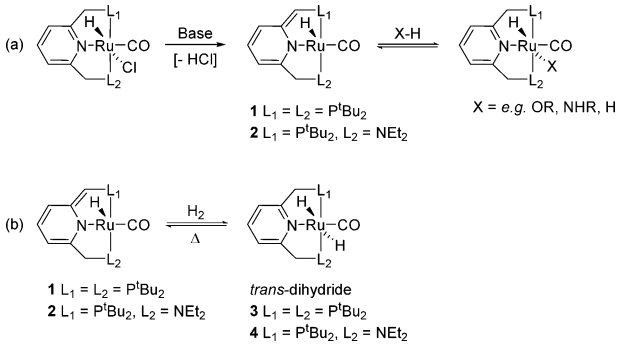
Scheme 1



and **2** to molecular hydrogen (Scheme 1b).[46−48] *trans*-Dihydride complexes **3** and **4** can readily lose H_2 (e.g., by heating) to regenerate the dearomatized starting complexes.

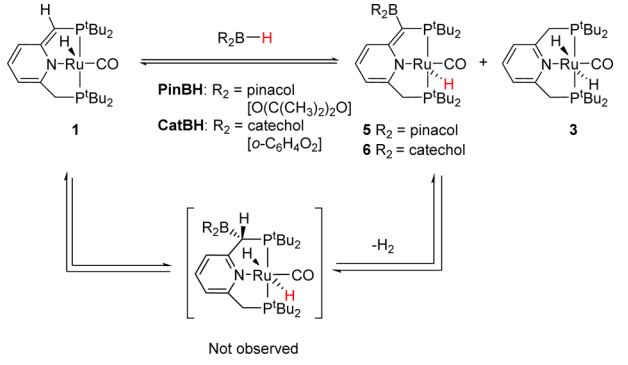
Herein we describe the reactions of 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (pinacol borane, PinBH) and 1,3,2-benzodioxaborole (catechol borane, CatBH) with ruthenium pincer complexes **1** and **2**. Mechanistic details for the reaction of **1** with CatBH are proposed by DFT calculations. Moreover, catalytic B−C_{aryl} coupling reactions are described.

RESULTS AND DISCUSSION

Boronic ester derivatives of the general formula R_2B−H (R_2 = diol) possess duality, since the boron atom is Lewis acidic and hence susceptible to react with the deprotonated ligand of complexes **1** and **2** but is also a strong σ donor, meaning it may tend to directly coordinate to the metal atom.[37,38] We were thus curious to learn which manner would prevail when boranes bearing a B−H bond were added to dearomatized ruthenium pincer complexes.

Reactions of PNP Complex 1. Addition of excess PinBH (3 equiv) to a solution of the dearomatized ruthenium pincer complex **1**, at room temperature, results in a gradual color change from dark green to intense red within 30 min. Analysis of the red product solution by NMR spectroscopy confirmed the formation of two new species: the previously reported *trans*-dihydride PNP complex **3**, known to form upon exposure of complex **1** to hydrogen,[46] and a new species, complex **5** (Scheme 2). Heating the mixture above at 60 °C, preferably in an open system to allow evolution of hydrogen, results in almost full conversion to complex **5**. The $^{31}P\{^1H\}$ NMR spectrum of **5** consists of an AB quartet (84.4, 82.0 ppm), indicative of an asymmetric pincer ligand. In the ^1H NMR spectrum (Figure 1) a high-field hydride signal appears (−24.6 ppm), which is consistent with the expected chemical shift of a hydride in the apical position of a square-pyramidal ruthenium pincer complex.[46,47] Integration of the signal corresponding to the benzylic arm position (2.8 ppm) reveals that only one protonated methylene unit is present in the ligand. Perhaps the most outstanding feature in the ^1H NMR spectrum of **5** is the chemical shift of the pyridine H3 proton, which is significantly shifted downfield to 8.5 ppm.

Scheme 2



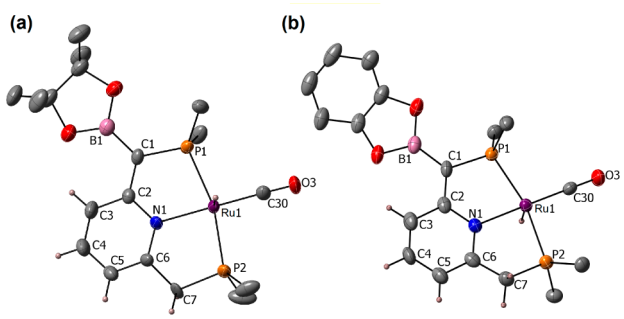


Figure 1. ^1H NMR spectrum (300 MHz, C_6D_6) of complex **5** formed by the reaction of 3 equiv of PinBH with complex **1** at 80 °C for 2 h. Excess PinBH present in the sample is denoted by asterisks. Inset: enlarged aliphatic region.

As shown in Figure 1, complex **5** was identified as a dearomatized complex, formed by borane dehydrogenative addition to the benzylic arm position of the PNP ligand, generating a new boron−carbon bond.

Analogous to the formation of complex **5** by reaction of complex **1** with PinBH, the addition of CatBH to complex **1** at room temperature results in the rapid formation of complex **6** (Scheme 2). The pyridine H3 proton of complex **6** is found at 8.5 ppm in the ^1H NMR spectrum, similar to that of complex **5**. This downfield shift of the H3 pyridine proton in complexes **5** and **6** may be explained by through-space electronic deshielding of this proton by the pinacolato or catecholato oxygen atom of the boryl unit, respectively. A similar effect was observed for a CO_2-bearing anionic pincer complex of nickel, previously disclosed by our group.[53] The addition reactions of PinBH and CatBH to complex **1**, and the formation of complexes **5** and **6**, respectively, were performed with an internal standard (1,4-dioxane), confirming quantitative conversion to the latter complexes (see the Supporting Information).

The structure of the new borylated PNP pincer complexes was confirmed by X-ray crystallography of single crystals of complexes **5** and **6** (Figure 2). The square-pyramidal geometry of complexes **5** and **6** resembles that of the parent complex **1**.[46−48] Examination of the bond lengths in the crystal structures of **5** and **6** suggests π delocalization of the C1−C2 formal double bond over the C1−P1 bond (phosphor-ylide resonance donation)[48] and, possibly to some extent, over the C1−B1 bond (alkylidene-borane resonance contribution),[1] with both of these bonds being shorter than the conventional carbon−heteroatom bond lengths.[48,54] Resonance stabilization may account for the ease with which the initial borane adduct loses hydrogen to form the metastable dearomatized product complex. This mode of addition, that is, the boron atom binding to the nucleophilic ligand arm and the borane hydrogen atom residing on the metal, may be expected for the electrophilic boranes.[1,41,53] Our premise is that complexes **5** and **6** are the result of molecular hydrogen loss from aromatic species, bearing a boryl moiety attached to the benzylic arm position of the pincer ligand and two hydrides, trans to each

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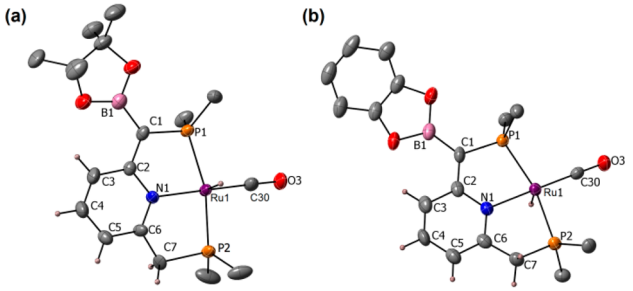
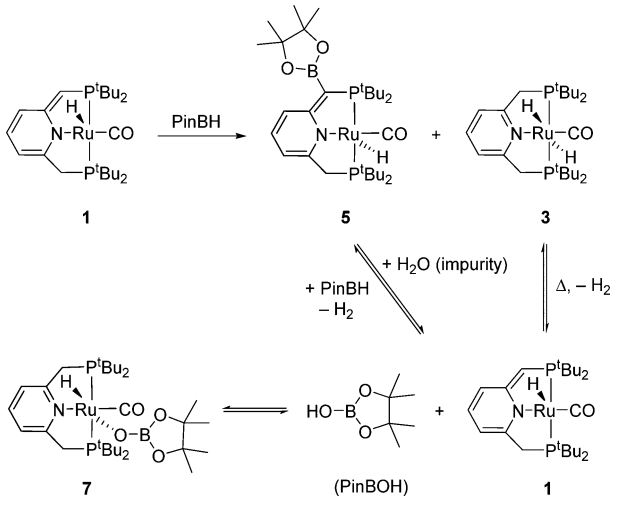


Figure 2. (a) X-ray crystal structure of complex **5** with thermal ellipsoids set at 50% probability. *tert*-Butyl methyl groups and pinacol hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1−C1 1.512(5), C1−C2 1.428(5), P1−C1 1.795(3), P2−C7 1.836(5); C2−C1−B1 121.2(3), B1−C1−P1 124.4(3). (b) X-ray crystal structure of complex **6** with thermal ellipsoids set at 50% probability. *tert*-Butyl methyl groups and catechol hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1−C1 1.503(6), C1−C2 1.422(6), P1−C1 1.803(4), P2−C7 1.833(4); C2−C1−B1 123.1(4), B1−C1−P1 122.4(3).

other, at the metal center (see depiction in Scheme 2). However, no direct evidence has been found for the existence of such saturated intermediates. Nevertheless, coinciding with the formation of the dearomatized adducts, the respective *trans*-dihydride complex **3** (Scheme 2) is consistently observed, indicating the evolution of molecular hydrogen, which is, most probably, trapped by residual starting complex **1** to form complex **3**. Alternatively, one may envision precoordination of the boron atom to the metal center and subsequent transfer of the boryl moiety to the benzylic arm position, in a pseudo boryl migration step.[55] This scenario, however, may be ruled out on the basis of our DFT calculations (vide infra).

It is worth noting that complexes **5** and **6** are highly unstable. Complex **6** undergoes degradation fairly rapidly upon most workup procedures (vide infra). Complex **5** undergoes what seems to be hydrolysis by traces of water in the system.[41] The product of this hydrolysis is the pinacol boronic acid (2-hydroxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, PinBOH), which can then add to the dearomatized complex **1** to form the aromatic boryloxo complex **7** (Scheme 3). PinBOH was independently synthesized and added to complex **1**, forming exclusively complex **7** (see the Supporting Information).

Scheme 3



Having identified a new mode of addition of boranes to complex **1**, we were compelled to deepen our understanding of these reactions. DFT calculations, performed on the reaction of **1** with CatBH, may explain why the boron atom binds preferentially to the arm and not to the metal center and indicate that a *trans*-dihydride species with a boryl ligand bound to the arm is indeed a low-concentration intermediate. The corresponding potential-energy surfaces for two possible reaction pathways are given in Figure 3. Initially, the borane has two options to form an encounter complex with **1**: while coordination of the borane B−H bond to the ruthenium center to generate **A′** is endergonic by 40 kJ mol^{-1}, bond formation of the boron center with the dearomatized ligand arm gives rise to complex **A**, which is located 20 kJ mol^{-1} below the separated starting compounds **1** and CatBH. Note that in **A** the boron center is covalently bound rather than just coordinated to the carbon center, as indicated by the tetrahedral environment (see the Supporting Information), and that the boron-bound hydrogen atom coordinates weakly to the ruthenium center. As a consequence, the B−H bond is elongated by 0.19 Å relative to the free CatBH, while in **A′** the borane B−H bond is only elongated by 0.11 Å. As a result, starting from **A** and **A′**, the barrier for the addition of the B−H bond across the ruthenium center and the ligand arm to give rise to **B** and **B′**, respectively, is 58 kJ mol^{-1} lower for **A** than for **A′**. Thus, under the given experimental conditions, it can be excluded that **B′** is formed from adduct complex **A′**, although **B′** is more stable than **B**. Finally, H_2 elimination from **B** gives rise to the formation of dearomatized **6** via the H_2 intermediate **C** (note that H_2 elimination from **B**, involving the CH_2 arm instead of the boron-containing arm, has a barrier that is higher by 18 kJ mol^{-1} and that the resulting dearomatized complex is 37 kJ mol^{-1} higher in energy; see the Supporting Information). While the barrier **TS B/C** is higher than expected for a process that already occurs at room temperature, the involvement of traces of H_2O might drastically diminish this barrier, as shown previously by our group.[56]

Activation of the borane B−H bond through metal−ligand cooperation distinguishes the ruthenium−carbonyl pincer complexes from the nonclassical hydride ruthenium PNP complex reported by Leitner et al.[42] Whereas for Leitner's complex a hydrogen-bridged boron−ruthenium bond is formed, the square-pyramidal ruthenium−carbonyl pincer complexes **1** and **2** force cleavage of the B−H bond across the metal center and the ligand backbone.

Reactions of PNN Complex 2. The addition pathway in the reactions of PNN pincer complex **2** with PinBH was found to follow the same principles as described above for PNP complex **1**. However, a more dynamic and versatile behavior is observed according to NMR spectroscopy. Upon addition of 3 equiv of PinBH to complex **2** at room temperature, we observed the formation of dearomatized complex **8** (Scheme 4a), analogous to PNP complexes **5** and **6**. Conversion to complex **8** is only partial, with concomitant detection of the *trans*-dihydride complex **4**. The ^{1}H NMR spectrum of complex **8** shows a hydride signal at −26.4 ppm and a downfield-shifted pyridine H3 proton signal at 8.5 ppm. With time and upon heating, several new species appear in solution. Heating is needed to promote conversion of complex **2** and enables hydrogen loss of the *trans*-dihydride complex **4**. After the mixture is heated to 75 °C for 2 h, an additional proton signal at 8.5 ppm is observed in the ^{1}H NMR spectrum, which overlaps with the pyridine H3 proton signal of complex **8**. This

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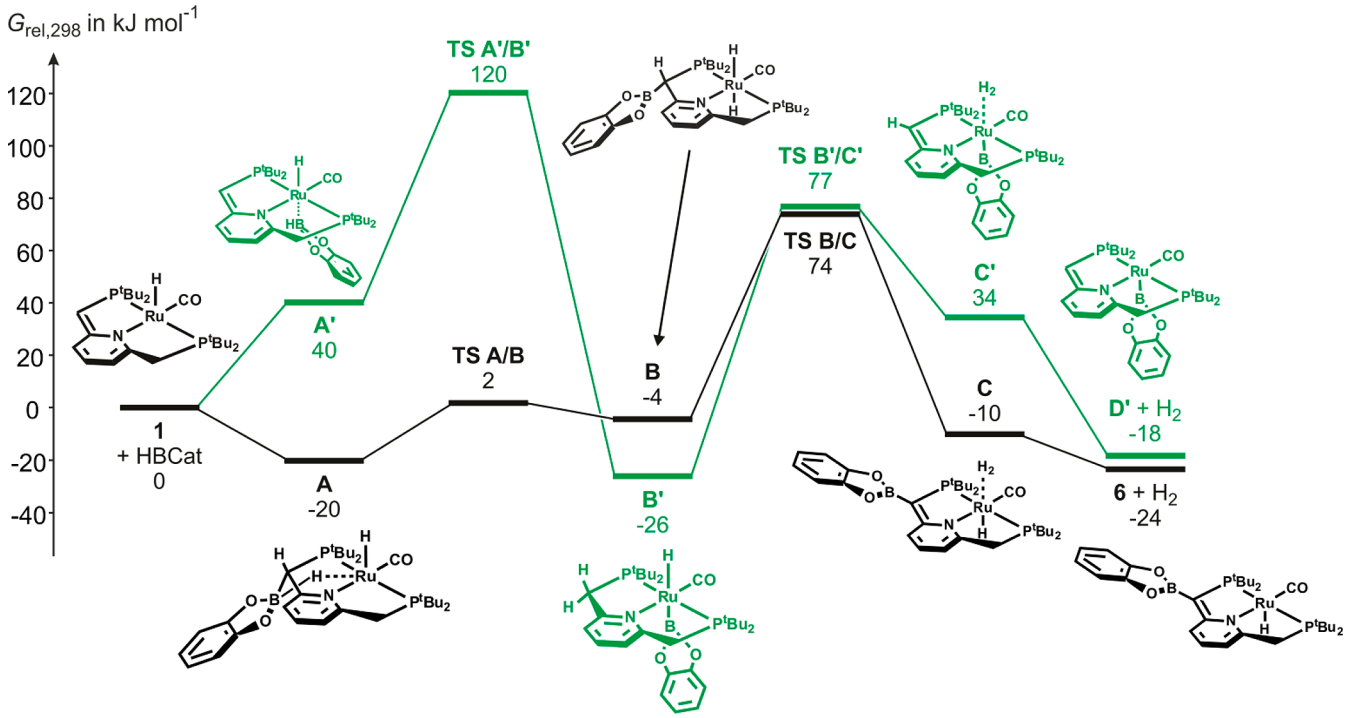
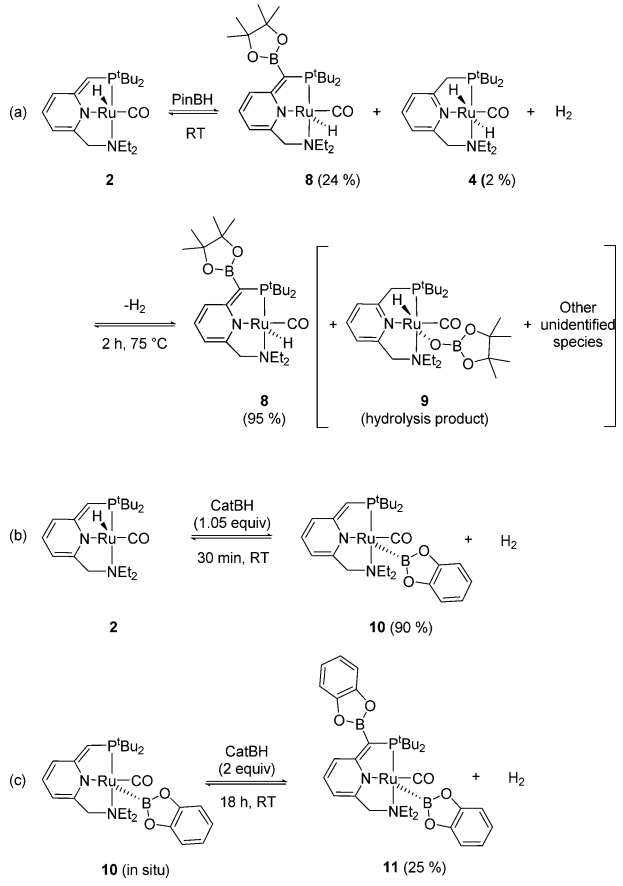


Figure 3. Simplified potential energy surfaces for the reaction of **1** and CatBH. Gibbs free energies (ΔG) are given in kJ mol^{-1} at 298 K. See the Supporting Information for further details.

Scheme 4



additional downfield pyridine H3 proton, with no corresponding hydride signal, may suggest the formation of a doubly borylated species, possessing one boryl unit attached at the ligand benzylic position and a second boryl ligand attached at the metal center. This hypothesis could not be verified explicitly. As is the case with the reaction of PinBH with complex **1**, unwarranted hydrolysis of the PinBH (or the borylated complex **8**) results in the formation of the aromatic boryloxo complex **9** (Scheme 4a), evidenced in the ^{1}H NMR spectrum by a hydride signal at −15.6 ppm and verified by independent synthesis from complex **2** and PinBOH (see the Supporting Information). Unfortunately, high solubility and poor stability prevented the isolation of the minor products in the reaction between **2** and PinBH; hence, their structures could not be unequivocally elucidated. Complex **8** could only be fully characterized by NMR in situ.

The reaction of **2** with the sterically less demanding CatBH proceeds readily at room temperature. The main species identified in solution is complex **10** (Scheme 4b). Several other minor species are observed, which could not be identified. In the ^{1}H NMR spectrum of complex **10**, the methylene porotons of the amine pincer arm appear as a wide AB quartet (4.0, 2.8 ppm), which is indicative of a bulky ligand at the apical position of the complex, inducing disparate chemical environments for each of the geminal methylene protons. The catecholato aromatic protons appear as two multiplets (at 7.0 and 6.7 ppm, two protons each), and a corresponding hydride signal is not observed. A doublet at 3.5 ppm ($^2J_{PH}$ = 3.0 Hz), corresponding to a single proton, implies a double bond at the phosphine pincer arm pointing to a dearomatized species with no borylation at the ligand backbone. The ^{11}B{^{1}H} NMR signal assigned to complex **10** is found at 47.4 ppm, in comparison to 30.7, 33.3, and 30.1 ppm for the benzylic boryl of complexes **5**, **6**, and **8**, respectively, and is well in the range for a metal-bound boryl.[38a] Thus, we conclude that complex **10** is, surprisingly, a dearomatized σ-boryl complex. Such a species, comparable to species **D′** in the DFT study (Figure 3), has not been identified

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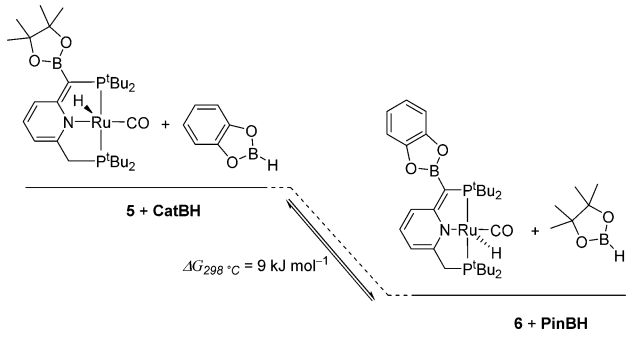
as the major component in any of the aforementioned experiments.

Although the minor species in solution could not be identified in the stoichiometric addition of CatBH to complex **2**, further addition of excess CatBH to complex **10** induces formation of a new double-borylated complex, **11** (Scheme 4c). Complex **11** gives rise to the characteristic pyridine H3 proton ^{1}H NMR signal at 8.5 ppm, and a corresponding hydride signal is not observed. In the aromatic region, four sets of multiplets, pertaining to two catecholato moieties, are observed. Similar to the spectrum of complex **10**, the methylene protons on the amine pincer arm give rise to a wide AB quartet (3.8, 2.9 ppm) in the ^{1}H NMR spectrum, but no signal for a proton on the phosphine ligand arm is observed. Complexes **10** and **11** were characterized by NMR in situ but could not be isolated independently. Several other unidentified complexes and related boron species are formed with time in the reaction of complex **2** with CatBH, as is the case with PinBH. Therefore, the ligand-bound boron atom signal could not be resolved by ^{11}B NMR, restricting the unequivocal spectroscopic assignment of complex **11**.

It is worth noting that the major addition complexes identified after addition of PinBH or CatBH to complex **2** (complexes **8**, **10**, and **11**) appear to be deprotonated at the methylene unit on the phosphine arm of the pincer ligand rather than at the amine arm. Complex **2** was reported to possess a thermodynamic tendency to form addition complexes through the "tautomeric" form of the deprotonated amine pincer arm.[57] In contrast to this, it appears that for the borane addition complexes deprotonation of the phosphine ligand arm is favored, most likely owing to stabilization of the dearomatized form through π delocalization. We cannot, however, preclude the possibility that some of the minor addition complexes formed in solution are, in fact, deprotonated at the amine arm.

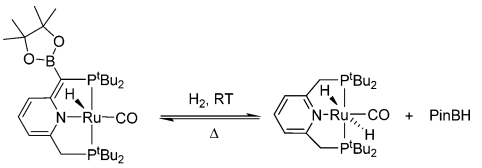
Chemical Exchange Studies. Having established the reactivity pattern of CatBH and PinBH with dearomatized complexes **1** and **2**, we were intrigued to learn more about the mechanism of these reactions. First, the reversibility of the addition was examined. When excess CatBH is added to a solution of pinacol boryl complex **5** in benzene at room temperature, within 2 h quantitative conversion to the corresponding CatBH addition complex **6** becomes evident by NMR. Concomitant formation of free PinBH is also observed (see the Supporting Information). The reverse reaction, that of complex **6** with PinBH to generate **5** and CatBH, was not detected at all, even upon heating. According to DFT calculations, the reaction of complex **5** with free CatBH to yield complex **6** and free PinBH is exergonic by 9 kJ mol^{-1} (Scheme 5). Assuming that **5** + CatBH and **6** + PinBH are in rapid equilibrium (without further calculations of possible intermediates and barriers), the relative ratio of **5** + CatBH to **6** + PinBH corresponds to ca. 1:38. According to this value, complex **5** may be expected to be undetectable by NMR spectroscopy, all the more in the presence of excess CatBH in solution. As is shown in Figure 2, the boron−carbon bond in catechol boryl complex **6** is slightly shorter than that of pinacol boryl complex **5**. Although the difference is negligible, it may stand testament to the formation of a stronger B−C bond in the case of complex **6**, making it less prone to substitution with PinBH. Moreover, the outcome of the exchange experiments is in line with the fact that CatBH is slightly more Lewis acidic[1] and less sterically hindered than PinBH.

Scheme 5



Probing for the reversibility of the boron−carbon bond formation, spin-saturation transfer (SST) ^{1}H NMR experiments were conducted for complex **5** in the presence of excess PinBH (see the Supporting Information). Despite our expectations, no chemical exchange signal was observed between bound and free pinacol borane even at elevated temperatures (up to 70 °C). Further, we investigated the reaction of boryl complexes **5** and **6** with hydrogen. Thus, applying 1.5 bar of H_2 pressure (corresponds to ca. 2 equiv) to an NMR tube containing a benzene solution of complex **5** results in gradual formation of the corresponding *trans*-dihydride complex **3** and formation of free PinBH (Scheme 6 and the Supporting Information). In

Scheme 6



contrast, the PNP catechol-boryl complex **6** is reluctant to undergo hydrogenation. The reaction of **6** with hydrogen results in only partial conversion to complex **3**, accompanied by rapid formation of an unidentified precipitate. Generally, the catechol boryl complexes **6**, **10**, and **11** seem to be unstable in solution and tend to gradually undergo degradation. We speculate that the catechol boryl complexes form ionic borate complexes through disproportionation of catechol borane or the corresponding boronic acid.[58] The product of this presumable process gives rise to very broad signals in the NMR spectra (see Supporting Information) and is insoluble in nonpolar solvents. Elucidation of this observed degradation process and its products are beyond the scope of this article.[59]

The dynamic behavior observed in the reactions of complex **2** with PinBH and CatBH and the possibility of boron to coordinate directly to the ruthenium atom suggest complex **2** as a potential catalyst for dehydrogenative coupling reactions of boranes (vide infra).

The observed trends and differences in complex formation when switching from PinBH to CatBH and between pincer complexes **1** and **2** suggest a largely steric control over the outcome of these reactions between the bifunctional pincer complexes and the dual-natured boranes. It is also quite likely that steric hindrance prevents the formation of a ruthenium−boron bond in the case of borane addition to the bulky PNP complex **1**. Clearly, when steric bulk is not detrimental, a σ-

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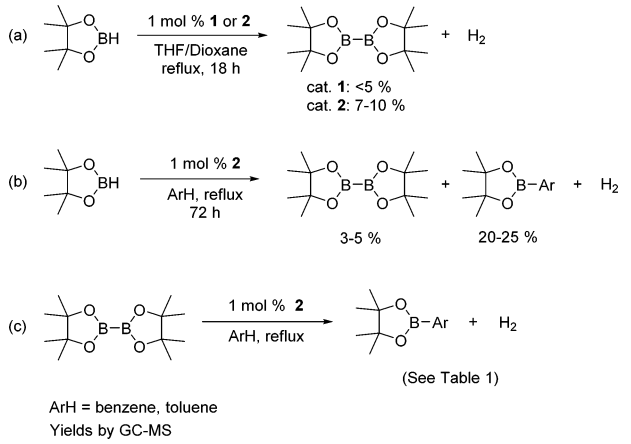
boryl complex is the kinetic product, as seen in the case of CatBH addition to complex **2**. σ-Boryl ligands are known to exert a strong *trans* influence, which is on the order of that of a hydride ligand.[26,38a,60] The formation of **10** is most likely the result of the strong *trans* influence of the catechol boryl ligand, promoting loss of the *trans* hydride ligand in cooperation with the benzylic arm proton, as molecular hydrogen. Thus, while hydrogen loss to yield dearomatized complexes **5**, **6**, and **8** may be thermodynamically favored by the possible π delocalization around the boron−carbon bond on the ligand, complex **10** may be thermodynamically favored in the dearomatized form due to the strong *trans* influence of the ruthenium-bound boryl ligand.

Catalytic Cross-Coupling Reactions. The facile activation of boranes by ruthenium pincer complexes, its observed fluctuation, and the ease with which dehydrogenation seems to occur led us to probe catalytic dehydrogenative coupling reactions.[25−36,46,47,61] Initially, 0.5 M PinBH was refluxed in THF for 18 h with 1 mol % of complex **1** or **2** (Scheme 7a).

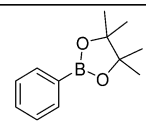
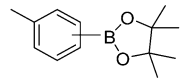
Scheme 7



Complex **2** showed some reactivity, albeit very poor: less than 10% conversion (by GC-MS) to the corresponding diboron species bis(pinacolato)diboron (PinBBPin) was observed under these conditions. Complex **1** was even less active under the same conditions. Unexpectedly, when the same reaction was conducted in benzene, after 18 h two products were observed by GC-MS (Scheme 7b): the diboron species PinBBPin and the B−C_{aryl} cross-coupling product with the solvent phenyl-(pinacol)borane (PhBPin). Although B−C coupling products are expected to be thermodynamically favored over B−B coupling products,[26,30,61a] C−H activation by this type of ruthenium pincer complex has not yet been observed. Reports of B−C_{aryl} cross coupling of nonactivated arenes catalyzed by homogeneous ruthenium catalysts are also scarce.[33,34] Conducting the reactions in higher-boiling solvents (1,4-dioxane, toluene) or for longer times (up to 72 h) only marginally improved the yields. Nevertheless, since PinBBPin was observed to be formed in situ in reactions leading to aryl borylation and since this reagent is relatively air and moisture stable,[35−38] we attempted B−C_{aryl} cross coupling catalysis with PinBBPin as the borylation agent (Scheme 7c).

Table 1 summarizes the reactions of complex **2** with PinBBPin in benzene (entry 1) and toluene (entry 2). The use of PinBBPin results in the same cross-coupling products as expected for PinBH but with superior yields. Poor thermal stability as well as evaporation of PinBH in the open reaction

Table 1. Cross-Coupling Reactions of PinBBPin Catalyzed by Complex 2[a]

Entry	Arene	Time	Product	Yield[b]
1	Benzene	72 h		37 %
2	Toluene	72 h	 meta/para (2:1)	56 %

[a]Conditions: 0.5 M PinBBPin (2 equiv) in respective arene solution, 1 mol % catalyst loading, reactions under reflux conditions (oil bath temperature 90 °C for benzene, 120 °C for toluene), under an argon atmosphere. [b]Isolated yields, obtained by elution of the evaporated mixture through SiO_2 with pentane. The purity was determined to be >95% by ^{1}H NMR.

system may contribute to this difference in reactivity.[36] Higher yields were obtained for toluene, rather than benzene, as a substrate for aryl borylation. This is most probably due to the higher boiling point (and thus reaction temperature) of toluene. The products of toluene borylation, catalyzed by 1 mol % of **2**, were isolated in 56% yield and found to consist of the meta- and para-borylated isomers in a statistical 2:1 ratio, respectively. Negligible amounts of the ortho- and benzyl-borylated isomers could also be detected by GC-MS. Catalytic borylations of other arenes with PinBBPin were attempted as well, albeit with poor isolated yields (see the Supporting Information). Nevertheless, in all cases a statistical isomeric outcome was obtained, befitting steric control in aryl borylation. Similar steric selection was reported with the more efficient iridium and rhodium borylation catalysts,[25,27,29,30−32] as well as with cobalt pincer complexes.[45]

In order to assess whether borylation by PinBBPin is analogous in mechanism to PinBH, we examined the adduct formation of PinBBPin with the pincer complexes **1** and **2**. Although heating is needed to promote reactivity, B−B bond activation seems to follow the same pathways as observed for B−H activation of the substrate PinBH. Thus, the predominant products of heating complex **1** with PinBBPin are complex **5** and PinBH (Scheme 8a). The *trans*-dihydride complex **3** and hydrogen are also formed (see the Supporting Information), indicating an indirect pathway from the starting mixture to the product complexes. Heating complex **2** with excess PinBBPin results in only partial conversion to form a mixture of composition similar to that observed for stoichiometric reactions with PinBH (Scheme 8b). Prolonged heating of complex **2** with PinBBPin (18 h at 80 °C) does not result in substantial conversion to new boryl complexes, yet ^{1}H NMR and GC-MS monitoring of the mixture heated in C_6D_6 reveals the formation of the B−C cross-coupling product: phenyl-(pinacol)borane-d_5 (see the Supporting Information). Thus, we reason that reactions of the diboron species PinBBPin and borane species PinBH follow a similar mechanism. The reaction of the diboron serves as an efficient stepping stone toward B−C coupling reactions, while the borane PinBH is prone to hydrolysis or oxidation and is a less viable precursor for open system reactions.

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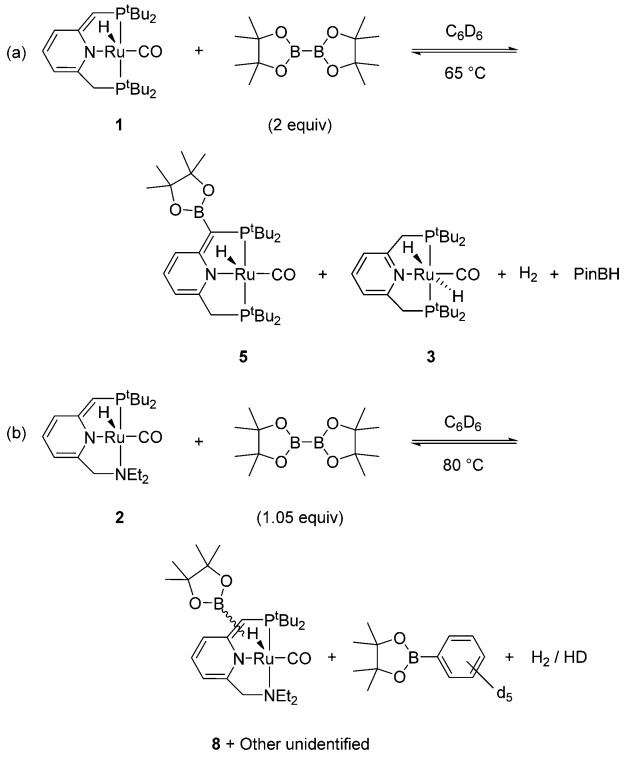
Scheme 8



SUMMARY AND CONCLUSIONS

Facile addition of boranes to ruthenium−carbonyl pincer complexes bearing dearomatized PNP or PNN ligands was shown to involve metal−ligand cooperation. The Lewis acidic boron atom is inclined to reside on the benzylic arm position of the ligand, whereas the hydride adds to the metal center. Notwithstanding, complexes bearing a boryl ligand attached to the ruthenium atom were also identified. Both benzyl-boryl and σ-boryl complexes readily lose dihydrogen to form new dearomatized pincer complexes. In addition to these new dearomatized pincer complexes, several other boryl complexes were observed in solution. These minor, dynamic species may be the catalytically active species for the boron−boron as well as aryl−boron dehydrogenative coupling reactions observed. Further catalysis experimentation is currently being pursued in our group, both with ruthenium and with other late-transition-metal pincer complexes.

EXPERIMENTAL SECTION

General Considerations. Dearomatized ruthenium complexes **1** and **2** and the *trans*-dihydride complex **3** were synthesized according to previously reported methods.[46,47] Pinacol borane (PinBH), catechol borane (CatBH), and bis(pinacolato)diboron (PinBBPin) were purchased from commercial sources and used without further purification. Pinacol boronic acid (PinBOH) was synthesized by hydrolysis of PinBH on the basis of a previously reported method.[62] All solvents used were dried and distilled according to known procedures to ensure their purity and the absence of water. All reactions were carried out inside a nitrogen atmosphere glovebox or using Schlenk techniques to ensure oxygen- and water-free environments. Catalytic cross-coupling reactions were carried out under an argon atmosphere. Gas chromatography was carried out on an HP 5973 (MS detector) instrument equipped with a 30 m column (Restek 5 MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas. ^{1}H, ^{13}C, ^{11}B, and ^{31}P NMR spectra were recorded using Bruker AMX-300, AMX-400, or AMX-500 NMR spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra are reported in ppm downfield from tetramethylsilane and referenced to residual protonated solvent shifts.[63] ^{31}P NMR chemical shifts are referenced to an external 85% solution of phosphoric acid in D_2O. ^{11}B NMR chemical shifts are referenced to an external 15% solution of BF_3−diethyl etherate (ca. 50% in ether) in $CDCl_3$. Abbreviations used in the NMR spectral assignments: br, broad; s, singlet; d, doublet; dd, doublet of doublets; t, triplet; q, quartet; m, multiplet; v, virtual.

Computational Methods. All calculations were performed using Gaussian 09 (Revision C.01).[64] The Perdew−Burke−Ernzerhof (PBE) generalized-gradient approximation (GGA) functional was used for geometry optimizations,[65,66] and the PBE0 hybride version of Adamo and Barone was used for energy calculations.[65−67] For geometry optimizations and frequency calculations, the split-valence basis set Def2-SVP of Ahlrichs and co-workers was used for all atoms,[68] and for ruthenium the corresponding ECP was added.[69] In the energy calculations, the Dunning cc-pVTZ basis set was used for H, B, C, N, and O,[70] Wilson's cc-pV(D+d)Z was used for P,[71] and Peterson's cc-pVTZ-PP basis set−RECP combination was used for Ru.[72] When the PBE functional was used, density fitting basis sets, specifically the fitting sets generated using the automatic generation algorithm implemented in Gaussian 09, were employed in order to speed up the calculations.[73,74] The accuracy of the DFT method was improved by adding the empirical dispersion correction as recommended by Grimme.[75,76] The older version (DFTD2) is available in Gaussian 09 (with analytical gradients and Hessians) and was used during geometry optimizations and frequency calculations;[75] our version of Gaussian 09 was locally modified to allow its use for any DFT functional rather than just for the limited set of functionals as included in the commercially available version. The newer and more accurate DFTD3 version was used as an a posteriori correction to the PBE0 energies obtained from Gaussian 09;[76] a locally modified version of the stand-alone program written by Grimme was used.[77] Only the singlet states of the various ruthenium-containing species were considered in the calculations.

Detailed Characterization of Borylated Pincer Complexes. *[Ru(PNP^{tBu}*-BPin)](H)(CO)] (**5**).* To a vigorously stirred solution of PinBH (9.0 mg, 0.07 mmol) in benzene or THF (0.3 mL) in a dry nitrogen glovebox was added slowly a solution of complex **1** (12.3 mg, 0.023 mmol) in the same solvent (0.3 mL). The dark red solution was left to stir vigorously in an open vial at room temperature for 30 min. NMR spectroscopy showed formation of complex **5** alongside the *trans*-dihydride complex **3** in a 10:1 ratio. Alternatively, PinBH (9.0 mg, 0.07 mmol) was added to a solution of complex **1** (12.3 mg, 0.23 mmol) in C_6D_6 in a J. Young NMR tube equipped with a condenser. The system was connected to a Schlenk line, and the mixture was heated to 80 °C for 2 h under an argon atmosphere. Attempts to obtain complex **5** in higher purity resulted in formation of complex **7** (see below). Single crystals suitable for X-ray diffraction were obtained from a concentrated pentane solution of the obtained mixture stored at −20 °C under a dry nitrogen atmosphere. Spectroscopic data: ^{1}H NMR (300 MHz, C_6D_6, δ) 8.54 (d, $^{3}J_{HH}$ = 9.1 Hz, 1H, Py-H3), 6.85−6.77 (m, 1H, Py-H4), 5.86 (d, $^{3}J_{HH}$ = 6.5 Hz, 1H, Py-H5), 2.86 (d, $^{2}J_{PH}$ = 8.0 Hz, 2H, Py-CH_2P), 1.71 (d, $^{3}J_{PH}$ = 13.0 Hz, 9H, PC(CH_3)$_3$), 1.30 (d, $^{3}J_{PH}$ = 11.6 Hz, 9H, PC(CH_3)$_3$), 1.20 (s, 6H, BPin-(CH_3)$_2$), 1.19 (s, 6H, BPin-(CH_3)$_2$), 1.06 (d, $^{3}J_{PH}$ = 12.0 Hz, 9H, PC(CH_3)$_3$), 1.00 (d, $^{3}J_{PH}$ = 11.6 Hz, 9H, PC(CH_3)$_3$), −24.61 (dd, $^{2}J_{PH}$ = 16.5, 14.7 Hz, 1H, Ru-*H*) ppm; ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, δ) 84.4, 82.0 (ABq, $^{2}J_{PP}$ = 211.4 Hz) ppm; ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, δ) 210.32 (d, $^{2}J_{PC}$ = 10.3 Hz, Ru-CO), 180.52 (dd, $^{2}J_{PC}$ = 15.3, $^{3}J_{PC}$ = 5.4 Hz, PyC2), 159.94 (dd, $^{2}J_{PC}$ = 7.5, $^{3}J_{PC}$ = 5.0 Hz, PyC6), 132.97 (PyC4), 119.12 (dd, $^{3}J_{PC}$ = 16.70, $^{4}J_{PC}$ = 1.3 Hz, PyC3), 104.28 (d, $^{3}J_{PC}$ = 10.67 Hz, PyC5), 81.08 (BPin(*C*(CH$_3$)$_2$) 63 (br, m, Py=*C*(BPin)), 44.77 (d, $^{1}J_{PC}$ = 19.11, P-C(CH$_3$)$_3$), 37.19 (d, $^{1}J_{PC}$ = 14.0 Hz, Py-CH$_2$-P), 35.52 (dd, $^{1}J_{PC}$ = 20.9, $^{3}J_{PC}$ = 2.9 Hz, P-C(CH$_3$)$_3$), 35.28 (dd, $^{1}J_{PC}$ = 12.4, $^{3}J_{PC}$ = 2.9 Hz, P-C(CH$_3$)$_3$), 34.18 (dd, $^{1}J_{PC}$ = 15.6, $^{3}J_{PC}$ = 2.7 Hz, P-C(CH$_3$)$_3$), 31.97 (dd, $^{2}J_{PC}$ = 6.0, $^{4}J_{PC}$ = 1.2 Hz, PC(CH$_3$)$_3$), 29.50 (dd, $^{2}J_{PC}$ = 5.2, $^{4}J_{PC}$ = 1.1 Hz, PC(CH$_3$)$_3$), 29.17 (dd, $^{2}J_{PC}$= 4.5, $^{4}J_{PC}$ = 0.8 Hz, PC(CH$_3$)$_3$), 25.10 (d, $^{2}J_{PC}$ = 5.4 Hz PC(CH$_3$)$_3$), 24.64 (BPin(CH$_3$)$_4$) ppm; ^{11}B{^{1}H} NMR (128 MHz,

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C_6D_6, δ) 30.7 (br) ppm. Crystal data: $C_{30}H_{54}BNO_3P_2Ru$, brown, 0.12 × 0.10 × 0.02 mm^3, monoclinic, $P2_1/n$ (No. 14), a = 7.6760(15) Å, b = 30.854(6) Å, c = 13.989(3) Å, β = 98.87(3)° from 20 degrees of data, T = 120(2) K, V = 3273.5(11) Å^3, Z = 4, formula weight 650.56, D_c = 1.320 Mg m^{-3}, μ = 0.606 mm^{-1}. Data collection and processing: Nonius KappaCCD diffractometer, Mo Kα (λ = 0.71073 Å), graphite monochromator, 26518 reflections collected, $-9 \le h \le 9$, $-39 \le k \le 39$, $-17 \le l \le 17$, frame scan width 0.5°, scan speed 1.0° per 120 s, typical peak mosaicity 0.97°, 7191 independent reflections (R_{int} = 0.0610). The data were processed with Denzo-Scalepack. Solution and refinement: structure solved by direct methods with SHELXS-97, full-matrix least-squares refinement based on F^2 with SHELXL-97, 373 parameters with 0 restraints, final R1 = 0.0499 (based on F^2) for data with $I > 2\sigma(I)$ and R1 = 0.0649 on 7191 reflections, goodness of fit on F^2 = 1.064, largest electron density peak 1.327 e Å^{-3}, deepest hole −0.802 e Å^{-3}.

[Ru(PNP^{tBu}-BCat)(H)(CO)]* (**6**). In a dry nitrogen glovebox, to a vigorously stirred solution of CatBH (2.7 mg, 0.023 mmol) in benzene or THF (0.3 mL) was added slowly a solution of complex **1** (11.7 mg, 0.022 mmol) in the same solvent (0.3 mL). The bright red solution was stirred vigorously in an open vial at room temperature for 30 min. NMR spectroscopy showed formation of complex **6** in ca. 95% yield alongside the *trans*-dihydride complex **3**. Further attempts at purification resulted in the formation of bis(catecholato)borate ionic species.[59] Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a benzene/pentane solution of the obtained mixture at room temperature under a dry nitrogen atmosphere. Spectroscopic data: ^{1}H NMR (300 MHz, C_6D_6, δ) 8.46 (d, $^3J_{HH}$ = 9.0 Hz, 1H, Py-H$_3$), 7.12 (dd, $^3J_{HH}$ = 5.6, $^4J_{HH}$ = 3.4 Hz, 2H, BCat-H$_{3,6}$), 6.89 (overlaps catechol signals, m, 1H, Py-H$_4$), 6.84 (dd, $^3J_{HH}$ = 5.7, $^4J_{HH}$ = 3.3 Hz, 2H, BCat-H$_{4,5}$), 5.94 (d, $^3J_{HH}$ = 6.7 Hz, 1H, Py-H$_5$), 2.86 (d, $^2J_{PH}$ = 6.8 Hz, 2H, Py-CH_2-P), 1.71 (dd, $^3J_{PH}$ = 11.0, $^5J_{PH}$ = 3.2 Hz, 9H, PC(CH_3)$_3$), 1.25 (dd, $^3J_{PH}$ = 10.2, $^5J_{PH}$ = 2.5 Hz, 9H, PC(CH_3)$_3$), 1.03 (dd, $^3J_{PH}$ = 10.6, $^5J_{PH}$ = 2.7 Hz, 9H, PC(CH_3)$_3$), 0.97 (dd, $^3J_{PH}$ = 9.9, $^5J_{PH}$ = 3.0 Hz, 9H, PC(CH_3)$_3$), −24.71 (t, $^2J_{PH}$ = 15.7 Hz, 1H, Ru-*H*) ppm; ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, δ) 83.8, 82.6 (ABq, $^2J_{PP}$ = 214.5 Hz) ppm; ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, δ) 209.94 (d, $^2J_{PC}$ = 8.9 Hz, 5Ru-CO), 180.02 (dd, $^2J_{PC}$ = 14.0, $^3J_{PC}$ = 6.4 Hz, PyC2), 160.36 (dd, $^2J_{PC}$ = 6.7, $^3J_{PC}$ = 5.5 Hz, PyC6), 149.49 (BCatC1,6), 134.06 (PyC4), 123.23 (BCatC2,5), 118.64 (dd, $^3J_{PC}$ = 14.4, $^4J_{PC}$ = 1.3 Hz, PyC3), 112.94 (BCatC3,4), 105.99 (d, $^3J_{PC}$ = 9.7 Hz, PyC5), 65.87−64.70 (br, m, Py=*C*(BCat)-P), 44.34 (dd, $^1J_{PC}$ = 17.2, $^3J_{PC}$ = 2.2 Hz, P-*C*(CH$_3$)$_3$), 37.16 (d, $^1J_{PC}$ = 13.1 Hz, Py-CH$_2$-P), 35.45 (dd, $^1J_{PC}$ = 18.83, $^3J_{PC}$ = 4.5 Hz, P-*C*(CH$_3$)$_3$), 35.38 (dd, $^1J_{PC}$ = 11.2, $^3J_{PC}$ = 3.4 Hz, P-*C*(CH$_3$)$_3$), 34.14 (dd, $^1J_{PC}$ = 14.9, $^3J_{PC}$ = 3.7 Hz, P-*C*(CH$_3$)$_3$), 31.78 (d, $^2J_{PC}$ = 4.5 Hz, PC(*C*H$_3$)$_3$), 29.53 (d, $^2J_{PC}$ = 4.3 Hz, PC(*C*H$_3$)$_3$), 29.41 (d, $^2J_{PC}$ = 3.5 Hz, PC(*C*H$_3$)$_3$), 29.13 (d, $^2J_{PC}$ = 3.5 Hz, PC(*C*H$_3$)$_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, THF, δ) 33.3 (br) ppm. Crystal data: $C_{30}H_{46}BNO_3P_2Ru$, red plate, 0.28 × 0.20 × 0.05 mm^3, monoclinic, $P2_1/c$, a = 8.2384(2) Å, b = 17.5293(3) Å, c = 21.3522(4) Å, β = 92.9126(9)° from 7032 reflections, T = 120(2) K, V = 3079.56(11) Å^3, Z = 4, formula weight 642.50, D_c = 1.386 Mg m^{-3}, μ = 0.644 mm^{-1}. Data collection and processing: Nonius KappaCCD diffractometer, Mo Kα (λ = 0.71073 Å), MiraCol optics, graphite monochromator, $0 \le h \le 10$, $0 \le k \le 21$, $-26 \le l \le 26$, $2\theta_{max}$ = 54.42°, frame scan width 1.0°, scan speed 1.0° per 120 s, typical peak mosaicity 1.178, 43396 reflections collected, 7270 independent reflections (R_{int} = 0.054). The data were processed with HKL-scalepack. Solution and refinement: structure solved with Shelxs-97, full-matrix least-squares refinement based on F^2 with SHELXL-97, 359 parameters with 0 restraints, final R1 = 0.0469 (based on F^2) for data with $I > 2\sigma(I)$, R1 = 0.0548 on 5825 reflections, goodness of fit on F^2 1.244, largest electron density peak 0.601 e Å^{-3}, largest hole −0.735 e Å^{-3}.

[Ru(PNP^{tBu})(H)(OBPin)(CO)] (**7**). In a dry nitrogen glovebox, a solution of complex **1** (10.5 mg, 0.020 mmol) and PinBOH (2.9 mg, 0.020 mmol) in 0.6 mL of C_6D_6 was mixed in an NMR tube for 20 h. NMR spectroscopy of the yellow solution showed full conversion to complex **7**. Spectroscopic data: ^{1}H NMR (400 MHz, C_6D_6, δ) 6.87 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Py-H3), 6.66 (d, $^3J_{HH}$ = 7.7 Hz, 2H, Py-H2,4), 3.73, 3.02 (ABq of vt, $^2J_{HH}$ = 15.9 Hz, J_{PH} = 3.2 Hz, 4H, Py-(CH_2-P)$_2$), 1.49 (vt, J_{PH} = 6.5 Hz, 18H, P-C(CH_3)$_3$), 1.26 (s, 12H, Ru−BPin-(CH_3)$_4$), 1.14 (vt, J_{PH} = 6.14 Hz, 18H, P-C(CH_3)$_3$), −16.11 (t, $^2J_{PH}$ = 19.9 Hz, 1H, Ru-*H*) ppm; ^{31}P{^{1}H} NMR (160 MHz, C_6D_6, δ) 91.56 (s) ppm; ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ) 209.81 (t, $^2J_{PC}$ = 11.8 Hz, Ru-*C*O), 163.58 (vt, J_{PC} = 4.7 Hz, PyC2,6), 136.49 (PyC4), 119.58 (vt, J_{PC} = 4.5 Hz, PyC3,5), 78.14 (Ru-O−B(OC(CH$_3$)$_2$)$_2$), 37.31 (vt, J_{PC}= 5.8 Hz, Py-(CH$_2$-P)$_2$), 36.96 (vt, J_{PC} = 5.3 Hz, P-C(CH$_3$)$_3$), 35.05 (vt, J_{PC} = 9.9 Hz, P-*C*(CH$_3$)$_3$), 30.47 (vt, J_{PC} = 3.0 Hz, P-C(CH$_3$)$_3$), 29.81 (vt, J_{PC} = 3.0 Hz, P-C(*C*H$_3$)$_3$), 26.00 (Ru-O-B(OC(*C*H$_3$)$_2$)$_2$) ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, δ) 23 (br, overlaps that of PinBOH) ppm.

[Ru(PNN-BPin)(H)(CO)]* (**8**). In a dry nitrogen glovebox, PinBH (10.2 mg, 0.08 mmol) was added to a solution of **2** (18 mg, 0.04 mmol) in 0.5 mL of C_6D_6 in an NMR tube. The mixture was mechanically shaken for 30 min, after which ^{1}H and ^{31}P NMR spectra were recorded, showing a mixture comprising ca. 24% complex **8**, alongside the *trans*-dihydride complex **4** (2%) and the starting complex **2** (74%). The solution was heated and intermittently shaken for 2 h at 75 °C, upon which the solution turned dark red. NMR spectroscopy showed formation of complex **8** in ca. 95% yield (1% starting complex **2** and the rest unidentified complexes). Traces of molecular hydrogen were also observed in solution (4.46 ppm, s). Spectroscopic data: ^{1}H NMR (300 MHz, C_6D_6, δ) 8.51 (d, $^3J_{HH}$ = 9.2 Hz, 1H, Py-H$_3$), 6.83 (m, 1H, Py-H$_4$), 5.63 (d, $^3J_{HH}$ = 6.5 Hz, 1H, Py-H$_5$), 3.3, 2.9 (ABq, $^2J_{HH}$ = 13.9 Hz, 2H, Py-CH_2-N), 2.89−2.58 (m, 1H, N-CH*H*-CH$_3$), 2.60−2.46 (1H, m, N-C*H*H-CH$_3$), 2.22−2.09 (m, 1H, N-C*H*H-CH$_3$), 1.95 (m, 1H, N-CH*H*-CH$_3$), 1.68 (d, $^3J_{PH}$ = 14.2 Hz, 9H, PC(CH_3)$_3$), 1.44 (d, $^3J_{PH}$ = 12.7 Hz, 9H, PC(CH_3)$_3$), 1.19 (br, 12H, Py=C-BPin-(CH_3)$_4$), 0.86−0.76 (t, $^3J_{HH}$ = 7.1 Hz, 3H, N-CH$_2$CH_3), 0.70 (t, $^3J_{HH}$ = 7.4 Hz, 3H, N-CH$_2$CH_3), −26.39 (d, $^2J_{PH}$ = 24.5 Hz, 1H, Ru-H) ppm; ^{31}P{^{1}H} NMR (121 MHz, C_6D_6, δ) 105.42 (s) ppm; ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, δ) 208.13 (d, $^2J_{PC}$ = 10.0 Hz, Ru-CO), 176.98 (PyC2, d, $^2J_{PC}$ = 12.0 Hz), 155.61 (PyC6), 132.81 (PyC$_4$), 119.24 (d, $^3J_{PC}$ = 12.08 Hz, PyC$_3$), 102.74 (br, PyC$_5$), 81.05 (BPin(*C*(CH$_3$)$_2$)), 68.07 (br, Py=C−BPin), 64.64 (Py-CH$_2$-N), 54.53 (N-CH$_2$CH$_3$), 50.04 (N-CH$_2$CH$_3$), 41.69 (d, $^1J_{PC}$ = 24.6 Hz, P-*C*(CH$_3$)$_3$), 35.72 (d, $^1J_{PC}$ = 24.2 Hz, P-*C*(CH$_3$)$_3$), 31.54 (d, $^2J_{PC}$ = 5.2 Hz, PC(*C*H$_3$)$_3$), 29.85 (d, $^2J_{PC}$ = 3.6 Hz, P-C(*C*H$_3$)$_3$), 25.06 (BPin-(*C*H$_3$)$_2$), 25.11 (BPin-(*C*H$_3$)$_2$), 10.73 (NCH$_2$*C*H$_3$), 10.72 (NCH$_2$*C*H$_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, δ) 31.0 (br) ppm.

[Ru(PNN)(H)(OBPin)(CO)] (**9**). In a dry nitrogen glovebox, a solution of complex **2** (10.4 mg, 0.023 mmol) and PinBOH (3.3 mg, 0.023 mmol) in 0.6 mL of C_6D_6 was mixed in an NMR tube for 30 min. NMR spectroscopy of the yellow solution showed full conversion to complex **9**. Spectroscopic data: ^{1}H NMR (400 MHz, C_6D_6, δ) 6.90 (t, $^3J_{HH}$ = 7.7 Hz, 1H, Py-H4), 6.56 (d, $^3J_{HH}$ = 7.8 Hz, 1H, Py-H5), 6.47 (d, $^3J_{HH}$ = 7.7 Hz, 1H, Py-H3), 5.1, 3.1 (ABq, $^2J_{HH}$ = 15.9 Hz, 2H, Py-CH_2-N), 3.55 (m, 1H, N-C*H*HCH$_3$), 3.44 (td, $^2J_{HH}$ = 13.6, $^3J_{HH}$ = 6.7 Hz, 1H, N-C*H*HCH$_3$), 3.04, 2.80 (ABq, $^2J_{HH}$ = 16.71 Hz, 2H, Py-CH_2-P), 2.60 (dq, $^2J_{HH}$ = 14.2, $^3J_{HH}$ = 7.2 Hz, 1H, N-C*H*HCH$_3$), 2.42 (ddd, $^2J_{HH}$ = 12.8, $^3J_{HH}$ = 6.9, $^4J_{PH}$ = 2.5 Hz, 1H, N-C*H*HCH$_3$), 1.38 (overlap) (d, $^3J_{PH}$ = 13.0 Hz, 9H, PC(CH_3)$_3$), 1.36 (overlap) (s, 12H, O-BOPin(CH_3)$_4$), 1.23 (d, $^3J_{PH}$ = 12.9 Hz, 9H, P-C(CH_3)$_3$), 1.05−1.00 (m (overlapping with excess PinBOH methyls, 6H, N-(CH$_2$CH_3)$_2$), −15.72 (d, $^2J_{PH}$ = 27.6 Hz, 1H, Ru-*H*); ^{31}P{^{1}H} NMR (160 MHz, C_6D_6, δ) 112.02 (s) ppm; ^{13}C{^{1}H} NMR (100 MHz, C_6D_6, δ) 208.82 (dd, $^2J_{PC}$ = 16.5 Hz, Ru-CO), 161.34 (d, $^2J_{PC}$ = 4.2 Hz, PyC2), 161.27 (d, $^3J_{PC}$ = 2.1 Hz, PyC6), 136.01 (PyC4), 119.38 (d, $^3J_{PC}$ = 9.2 Hz), 119.01 (PyC5), 78.46 (Ru-O-B(OC(CH$_3$)$_2$)$_2$), 64.04 (Py-CH$_2$-N), 53.73 (N-CH$_2$CH$_3$), 49.46 (N-CH$_2$CH$_3$), 37.53 (d, $^1J_{PC}$ = 11.7 Hz, P-*C*(CH$_3$)$_3$), 37.43 (d, $^1J_{PC}$ = 19.3 Hz, Py-CH$_2$-P), 34.86 (d, $^1J_{PC}$ = 23.9 Hz, P-*C*(CH$_3$)$_3$), 30.37 (d, $^2J_{PC}$ = 2.7 Hz, P-C(CH$_3$)$_3$), 29.77 (d, $^2J_{PC}$ = 4.7 Hz, P-C(CH$_3$)$_3$), 25.72 (N-CH$_2$CH$_3$), 25.53 (Ru-O-B(OC(CH$_3$)$_2$)$_2$), 24.64 (N-CH$_2$CH$_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, δ) 23 (br, overlaps that of PinBOH) ppm.

[Ru(PNN)(BCat)(CO)]* (**10**). In a dry nitrogen glovebox, a C_6D_6 solution (0.3 mL) of complex **2** (15.0 mg, 0.033 mmol) was added slowly to a vigorously stirred solution of CatBH (4.5 mg, 0.037 mmol)

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in C_6D_6 (0.3 mL). The bright red solution was stirred vigorously in an open vial at room temperature for 30 min. NMR spectroscopy showed formation of complex **10** in ca. 90% conversion, with other unidentified complexes and unreacted excess CatBH. When the addition was performed in a closed NMR tube that was vigorously shaken, molecular hydrogen was also observed in solution (4.47 ppm, s, 1:3 to complex **10**; see the Supporting Information). Spectroscopic data: ^{1}H NMR (500 MHz, C_6D_6, δ) 7.04 (dd, $^3J_{HH}$ = 5.9, $^4J_{HH}$ =3.5 Hz, 2H, BCat-H4,5), 6.71 (dd, $^3J_{HH}$ = 5.7, $^4J_{HH}$ = 3.3 Hz, 2H, BCat-H2,5), 6.52 (ddd, $^3J_{HH}$ = 8.6, 6.4, $^5J_{HH}$ = 1.9 Hz, 1H, Py-H4), 6.40 (d, $^3J_{HH}$ = 9.0 Hz, 1H, Py-H3), 5.40 (d, $^3J_{HH}$ = 6.4 Hz, 1H, Py-H5), 4.05 (d, $^2J_{HH}$ = 13.7 Hz, 1H, Py-C*H*HN), 3.45 (d, $^2J_{PH}$ = 3.0 Hz, 1H, Py=C*H*-P), 2.82 (dd, $^2J_{HH}$ = 13.8, $^5J_{HH}$ = 1.8 Hz, 1H, Py-CH*H*–N), 2.67–2.58 (m, 1H, N-C*H*HCH$_3$), 2.43 (dq, $^2J_{HH}$ = 13.8, $^3J_{HH}$ = 7.0 Hz, 1H, N-CH*H*CH$_3$), 2.27 (dq, $^2J_{HH}$ = 14.4, $^3J_{HH}$ = 7.2 Hz, 1H, N-C*H*HCH$_3$), 1.97 (ddq, $^2J_{HH}$ = 14.4, $^3J_{HH}$ = 7.2, $^4J_{PH}$ 2.7 Hz, 1H, N-CH*H*CH$_3$), 1.33 (d, $^3J_{PH}$ = 12.5 Hz, 9H, P-C(C*H*$_3$)$_3$), 1.15 (d, $^3J_{PH}$ = 14.1 Hz, 9H, P-C(C*H*$_3$)$_3$), 0.68 (t, $^3J_{HH}$ = 7.2 Hz, 3H, N-CH$_2$C*H*$_3$), 0.50 (t, $^3J_{HH}$ = 7.2 Hz, 3H, N-CH$_2$C*H*$_3$) ppm; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ) 84.88 (s) ppm; ^{13}C{^{1}H} NMR (125 MHz, C_6D_6, δ) 206.40 (d, $^2J_{PC}$ = 9.4 Hz, Ru-CO), 169.05 (d, $^2J_{PC}$ = 15.5 Hz, PyC2), 156.18 (PyC6), 150.75 (BCat-C1,6), 132.34 (PyC4), 121.25 (BCat-C2,5), 115.04 (d, $^3J_{PC}$ = 17.5 Hz, PyC3), 111.23 (BCat-C3,4), 97.30 (PyC5), 64.80 (Py-CH$_2$-N), 64.16 (d, $^1J_{PC}$ = 56.0 Hz, Py=CH-P), 54.49 (N-CH$_2$CH$_3$), 47.58 (N-CH$_2$CH$_3$), 40.85 (d, $^1J_{PC}$ = 25.3 Hz, P-C(CH$_3$)$_3$), 35.07 (d, $^1J_{PC}$ = 28.2 Hz, P-C(CH$_3$)$_3$), 29.21 (PC(CH$_3$)$_3$), 28.85 (N-CH$_2$CH$_3$), 9.94 (PC(CH$_3$)$_3$), 9.57 (N-CH$_2$CH$_3$) ppm; ^{11}B{^{1}H} NMR (128 MHz, C_6D_6, δ) 47.4 (br) ppm.

[Ru(PNN-BCat)(BCat)(CO) (**11**).* In a dry nitrogen glovebox, to a solution of complex **10** (90%, prepared in situ, see above) in 0.6 mL of C_6D_6 was added 1.8 equiv of CatBH (7.0 mg, 0.058 mmol), and the solution was stirred under nitrogen overnight. NMR spectroscopy showed 25% conversion to complex **11**. Further attempts to purify complex **11** out of the mixture failed. Characterization was possible in situ, with the aid of 2D NMR techniques. Spectroscopic data: ^{1}H NMR (500 MHz, C_6D_6, δ) 8.50 (d, $^3J_{HH}$ = 9.1 Hz, 1H, Py-H3), 7.16–7.13 (m, 2H, Ru-BCat-H3,6), 7.08 (dd, $^3J_{HH}$ = 5.6, $^4J_{HH}$ = 3.5 Hz, 2H, Py=C-BCat-H3,6), 6.95–6.91 (m, 2H, Py-H4), 6.82 (dd, $^3J_{HH}$ = 5.8, $^4J_{HH}$ = 3.2 Hz, 2H, Ru-BCat-H4,5), 6.78 (dd, $^3J_{HH}$ = 5.8, $^4J_{HH}$ = 3.2 Hz, 2H, Py=C-BCat-H3,6), 5.84 (d, $^3J_{HH}$ = 6.8 Hz, 1H, Py-H5), 3.84 (d, $^2J_{HH}$ = 14.0 Hz, 1H, Py-C*H*H-N), 2.92 (m, 1H, N-C*H*HCH$_3$), 2.91 (m, 1H, Py-CH*H*-N), 2.62 (m, 1H, N-C*H*HCH$_3$), 2.14 (m, 1H, N-CH*H*CH$_3$), 1.82 (m, 1H, N-CH*H*CH$_3$), 1.56 (d, $^3J_{PH}$ = 14.9 Hz, 9H, P-C(C*H*$_3$)$_3$), 1.36 (d, $^3J_{PH}$ = 11.4 Hz, 9H, P-C(C*H*$_3$)$_3$), 0.70 (t, $^3J_{HH}$ = 6.9 Hz, 3H, N-CH$_2$C*H*$_3$), 0.44 (t, $^3J_{HH}$ = 7.1 Hz, 3H, N-CH$_2$C*H*$_3$) ppm; ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, δ) 97.53 (s) ppm; ^{13}C{^{1}H} NMR (126 MHz, C_6D_6, δ) 207.10 (d, $^2J_{PC}$ = 10.0 Hz, Ru-CO), 176.05 (PyC2), 155.16 (PyC6), 150.63 (Ru-BCatC1,6), 149.31 (Py=C-BCatC1,6), 134.12 (PyC4), 121.73 (Ru-BCatC2,5), 121.33 (Py=C-BCatC2,5), 119.51 (d, $^3J_{PC}$ = 14.23 Hz, PyC3), 111.43 (Py=C-BCatC3,4), 111.10 (Ru-BCatC3,4), 105.06 (PyC5), 65.86 (Py-CH$_2$-N), 55.38 (N-CH$_2$CH$_3$), 48.18 (N-CH$_2$CH$_3$), 43.3 (br, Py=C-BCat), 42.57 (d, $^1J_{PC}$ = 23.4 Hz, P-C(CH$_3$)$_3$), 36.33 (d, $^1J_{PC}$ = 24.8 Hz, P-C(CH$_3$)$_3$), 30.91 (PC(CH$_3$)$_3$), 29.97 (PC(CH$_3$)$_3$), 10.53 (N-CH$_2$CH$_3$), 8.64 (N-CH$_2$CH$_3$) ppm; ^{11}B NMR could not be resolved in the mixture.

General Procedure for Catalytic Boron–Boron Coupling Reactions, Demonstrated for 1 with PinBH in THF. In a dry nitrogen glovebox, complex **1** (6.0 mg, 0.011 mmol), cyclooctane (internal standard, 0.1 mmol), and PinBH (145.0 mg, 1.13 mmol) were dissolved in THF (2.5 mL) in a Schlenk flask equipped with a condenser. The red solution was refluxed under an argon atmosphere (oil bath temperature 75 °C). The reaction was monitored by GC-MS analysis until no increase in conversion was observed. The product was not isolated due to low yields.

General Procedure for Catalytic Aryl Borylation Reactions, Demonstrated for 2 with PinBBPin in Benzene. In a dry nitrogen glovebox, complex **2** (14.3 mg, 0.031 mmol), cyclooctane (internal standard, 0.1 mmol), and PinBBPin (380 mg, 1.6 mmol) were dissolved in benzene (3 mL) in a Schlenk flask equipped with a condenser. The red solution was refluxed under an argon atmosphere. The conversion was monitored by GC-MS analysis. The solution after the reaction was fully evaporated under high vacuum, removing solvent and cyclooctane (and unreacted borane). The residue after evaporation was weighed, and 0.1 mmol of 1,4-dioxane was added as an internal standard. $CDCl_3$ (0.5 mL) was added, and the yield was calculated from the appropriate signals in the ^{1}H NMR spectra. For isolation, the residue after evaporation was eluted through a silica column with *n*-pentane or 1/9 ethyl acetate/*n*-pentane.

Reaction of 5 with CatBH. In a dry nitrogen glovebox, CatBH (3.2 mg, 0.027 mmol) was added to a solution of complex **5** (9.7 mg, 0.015 mmol, containing 20% complex **7**) in C_6D_6 (0.6 mL) in an NMR tube. The ^{1}H NMR spectrum taken immediately after mixing showed complete disappearance of residual complex **7**. Further shaking of the sample at room temperature resulted in quantitative conversion to catechol boryl complex **6** within 2 h (see the Supporting Information).

Reaction of 5 with H_2. *Warning!* H_2 is an explosive gas, and proper measures should be taken for its safe handling. In a dry nitrogen glovebox, a solution of complex **5** containing 20% complex **7** (21 mg, ca. 0.032 mmol) in C_6D_6 (0.6 mL) in a J. Young NMR tube was pressurized three times to 1.5 bar of H_2 (ca. 2 equiv in the gas phase) and then shaken overnight at room temperature. Changes were monitored by NMR. Within minutes, the *trans*-dihydride complex **3** appeared, with disappearance of complex **7** and subsequently disappearance of complex **5**. Free PinBH could also be observed (see the Supporting Information).

Substoichiometric Reactions of 1 with PinBBPin. In a dry nitrogen glovebox, PinBBPin (8.6 mg, 0.036 mmol, 2.1 mol equiv) was added to a solution of **1** (17.7 mg, 0.033 mmol) in C_6D_6 (0.6 mL) in an NMR tube. ^{1}H and ^{31}P NMR spectra were recorded at room temperature and during heating. Complexes **5** and the *trans*-dihydride **3** formed in a ca. 1:1 ratio at room temperature; however, with heating, all species converted to complex **5**. Free hydrogen as well as free PinBH (detected by ^{11}B NMR) could also be detected by ^{1}H NMR (see the Supporting Information).

Substoichiometric Reactions of 2 with PinBBPin. In a dry nitrogen glovebox PinBBPin (4.7 mg, 0.02 mmol, 2 mol equiv) was added to a solution **2** of (8.0 mg, 0.018 mmol) in C_6D_6 (0.5 mL) in an NMR tube. The mixture showed no reaction at room temperature by ^{1}H NMR. After the solution was heated to 80 °C for 18 h, a ^{1}H NMR spectrum showed that only a small fraction of the starting complex **2** had reacted. The product complexes were not identified, except for 1.5% of complex **8** that was clearly formed. A signal at 1.10 ppm indicated the formation of deuterated phenyl(pinacol)borane (PhBPin-d_5) in 37% conversion relative to PinBBPin (see the Supporting Information). GC-MS confirmed the formation of the deuterated PhBPin.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, tables, figures, and CIF files giving crystallographic data for **5** and **6**, NMR spectra of boryl addition complexes, detailed exchange experiments, catalytic borylation of substituted arenes, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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