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Conclusive Evidence on the Mechanism of the Rhodium-Mediated Decyanative Borylation

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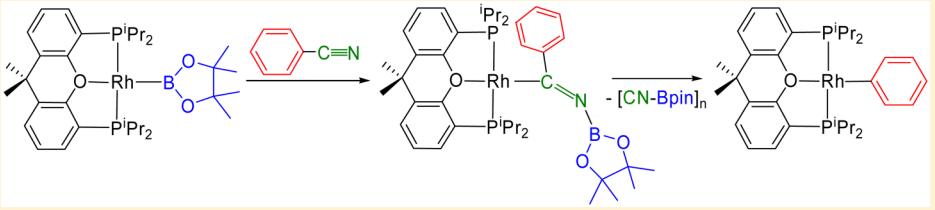
Supporting Information



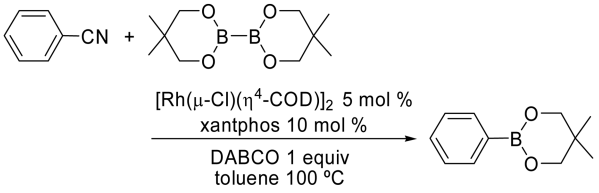
ABSTRACT: The stoichiometric reactions proposed in the mechanism of the rhodium-mediated decyanative borylation have been performed and all relevant intermediates isolated and characterized including their X-ray structures. Complex RhCl{xant(P^{i}Pr$_2$)$_2$} (**1**, xant(P^{i}Pr$_2$)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) reacts with bis(pinacolato)diboron (B$_2$pin$_2$), in benzene, to give the rhodium(III) derivative RhHCl(Bpin){xant(P^{i}Pr$_2$)$_2$} (**4**) and PhBpin. The reaction involves the oxidative addition of B$_2$pin$_2$ to **1** to give RhCl(Bpin)$_2$(xant(P^{i}Pr$_2$)$_2$}, which eliminates ClBpin generating Rh(Bpin){xant(P^{i}Pr$_2$)$_2$} (**2**). The reaction of the latter with the solvent yields PhBpin and the monohydride RhH{xant(P^{i}Pr$_2$)$_2$} (**6**), which adds the eliminated ClBpin. Complex **4** and its catecholboryl counterpart RhHCl(Bcat){xant(P^{i}Pr$_2$)$_2$} (**7**) have also been obtained by oxidative addition of HBR$_2$ to **1**. Complex **2** is the promoter of the decyanative borylation. Thus, benzonitrile and 4-(trifluoromethyl)benzonitrile insert into the Rh−B bond of **2** to form Rh{C(R-C$_6$H$_4$)═NBpin}{xant(P^{i}Pr$_2$)$_2$} (R = H (**8**), *p*-CF$_3$ (**9**)), which evolve into the aryl derivatives RhPh{xant(P^{i}Pr$_2$)$_2$} (**3**) and Rh(*p*-CF$_3$-C$_6$H$_4$){xant(P^{i}Pr$_2$)$_2$} (**10**), as a result of the extrusion of CNBpin. The reactions of **3** and **10** with B$_2$pin$_2$ yield the arylBpin products and regenerate **2**.

INTRODUCTION

Transition metal catalyzed borylation reactions are of great interest because organoboronate esters and boronic acids are useful intermediates in many processes that lead to molecular frameworks with applications ranging from pharmaceutical and agrochemicals to material science.[1] In this context, a powerful tool is the direct borylation of hydrocarbons. These reactions provide products with site-selectivity for C−H bond cleavage that depends upon steric factors.[2]

A major goal of the chemistry of this century is to develop procedures for the selective functionalization of a specific position of a particular organic fragment. A promising alternative to the direct borylation is the use of a directing group suitable to be replaced by a borate ester. The nitrile is a reliable directing group, is common in many organic molecules, and is abundant in nature. On the other hand, the C−CN bond is relatively strong (120−135 kcal mol^{-1}), and its selective rupture remains difficult.[3] As a consequence, the metal-mediated decyanation of nitriles is a challenging target of great importance.[4]

Tobisu, Chatani, and co-workers[5] discovered the decyanative borylation in 2012. They observed that in toluene, at 100 °C, the reaction of a wide range of aryl cyanides with diboranes in the presence of 5 mol % of [Rh(μ-Cl)(η^4-COD)]$_2$ (COD = 1,5-cyclooctadiene), 10 mol % of xantphos (xantphos = 9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene), and 1.0 equiv of 1,4-diazabicyclo[2.2.2]octane (DABCO)[6] leads to arylboronic esters, eq 1.[7] The catalysis is compatible with a variety of



(1)

functional groups. Although this discovery is certainly notable, the nature of the catalyst is not clear, and there is no evidence about the reaction mechanism, mainly because experimental work has not been performed in order to clarify the process.

DFT studies need experimental support to truly contribute to the harmonious development of the field.[8] In spite of this, the groups of Chatani[6] and Yao Fu[9] have only performed calculations, in the effort to gain insight into mechanistic details, assuming the formation of the recently reported complex RhCl(xantphos)[10] as a precatalyst. In both cases, the results suggest a catalytic cycle (Scheme 1) involving four steps: (i) formation of a rhodium(I)-boryl complex resulting from the

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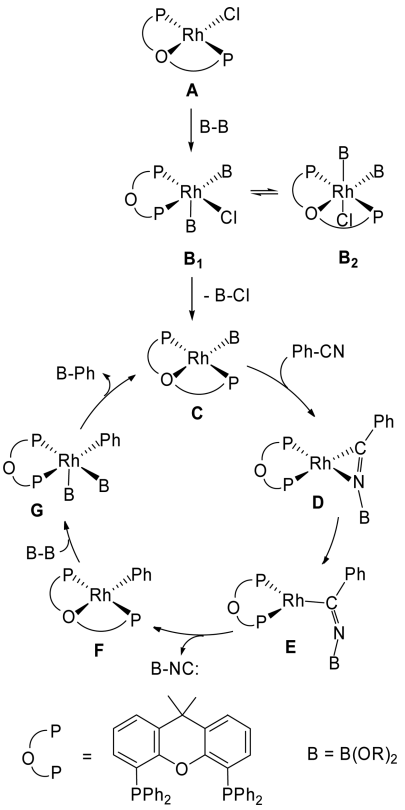
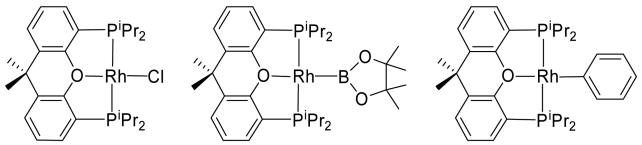
Scheme 1



reaction of RhCl(xantphos) with the diborane (from **A** to **C**), (ii) insertion of the nitrile into the rhodium-boryl bond to form an iminoacyl intermediate (from **C** to **E**), (iii) extrusion of the boryl isocyanide to afford a rhodium(I)-aryl derivative (from **E** to **F**), and (iv) reaction of the latter with the diborane to give the aryl boronic ester and to regenerate the rhodium(I)-boryl especies (from **F** to **C**).

The last step of the proposed cycle has been recently corroborated by us.[11] In addition, we have reported the preparation and X-ray structure of complexes RhCl{xant-(P^iPr_2)$_2$} (**1**), Rh(Bpin){xant(P^iPr_2)$_2$} (**2**), and RhPh{xant-(P^iPr_2)$_2$} (**3**)[11,12] (Chart 1), as a part of a research program on

Chart 1



POP compounds of groups 8 and 9.[13] These 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene (xant(P^iPr_2)$_2$) derivatives are the ^{i}Pr-counterparts of intermediates **A**, **C**, and **F** of the catalytic cycle shown in Scheme 1. In view of this, we decided to investigate the stoichiometric reactions involved in steps i, ii, and iii by using our complexes as models.

This paper shows the first experimental investigation of the mechanism of the reaction of decyanative borylation, discovered by Tobisu, Chatani, and co-workers in 2012, and describes the formation of the catalytic intermediates, which are isolated and characterized by X-ray diffraction analysis, including *N*-boryl η^1-iminoacyl complexes and the resulting products of their C−C bond cleavage reactions via elimination of boryl isocyanide.

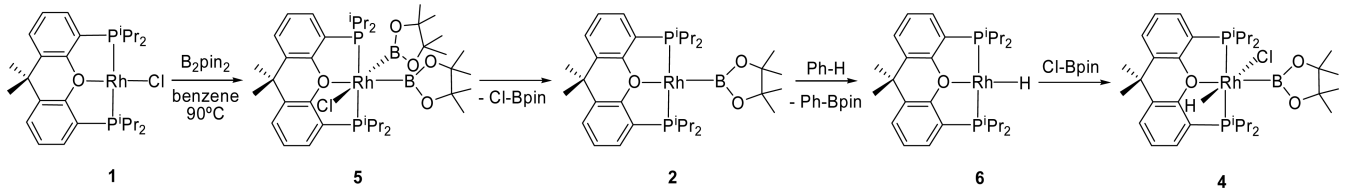
RESULTS AND DISCUSSION

Formation of the Active Species: Rhodium(I)-Boryl versus Hydride-Chloride-Rhodium(III)-Boryl. According to the DFT calculation reported by the Chatani's group,[6] the oxidative addition of diborane to **A** should afford a chloride-rhodium(III)-bis(boryl) derivative (**B** in Scheme 1), which is about 25 kcal mol^{-1} more stable than the reagents. The addition has a small activation barrier of 2.6 kcal mol^{-1}. This rhodium(III) intermediate undergoes reductive elimination of boryl chloride with an activation barrier of about 20 kcal mol^{-1} to give the square-planar rhodium(I)-boryl species **C**, which is believed to be the true catalyst of the reaction. The reductive elimination destabilizes the system by about 17 kcal mol^{-1}.

There are marked differences between the expected one, according to the theoretical calculations, and that experimentally found. In contrast to the DFT results, the treatment of benzene solutions of **1** with 1.0 equiv of bis(pinacolato)diboron (B_2pin_2), at 90 °C, for 20 h leads to the hydride-chloride-rhodium(III)-boryl derivative RhHCl(Bpin){xant(P^iPr_2)$_2$} (**4** in Scheme 2), which was isolated as a white solid in 78% yield, and Ph-Bpin. Complex **4** was characterized by X-ray diffraction analysis. Figure 1 gives a view of its structure. As expected for a pincer coordination of the diphosphine, the Rh(POP) skeleton is T-shaped with the metal center situated in the common vertex and P(1)−Rh−P(2), P(1)−Rh−O(1), and P(2)−Rh−O(1) angles of 157.30(3)°, 81.62(5)°, and 81.98(5)°, respectively. Thus, the coordination geometry around the rhodium atom can be rationalized as a distorted octahedron with the boryl group *trans*-disposed to the oxygen atom of the diphosphine (O(1)−Rh−B(1) = 176.06(12)°) and the hydride *trans*-disposed to the chloride ligand (H(01)−Rh−Cl(1) = 176.5(12)°). The Rh−B bond length of 1.990(4) Å compares well with the Rh(III)−B single bond distances previously reported.[14]

This structure is as that of the related silyl derivatives RhHCl(SiR_3){xant(P^iPr_2)$_2$},[13d] with the Bpin ligand in the position of the silyl group, in agreement with the marked diagonal relationship between boron and silicon, which is also

Scheme 2



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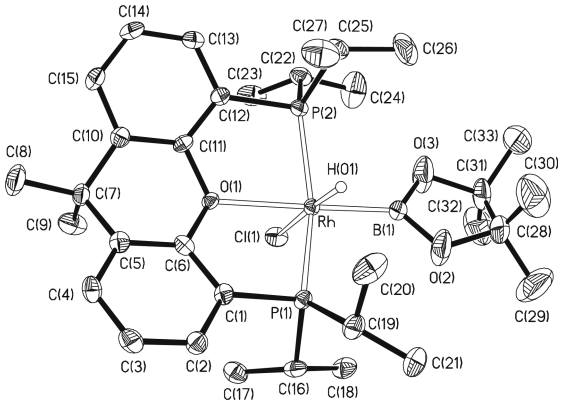

Figure 1. ORTEP diagram of complex **4** (50% probability ellipsoids). Hydrogen atoms (except the hydride) are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−P(1) = 2.2789(8), Rh−P(2) = 2.2893(8), Rh−Cl(1) = 2.4595(8), Rh−O(1) = 2.3019(19), Rh−B(1) = 1.990(4); P(1)−Rh−P(2) = 157.30(3), P(1)−Rh−O(1) = 81.62(5), P(2)−Rh−O(1) = 81.98(5), P(1)−Rh−Cl(1) = 97.57(3), P(2)−Rh−Cl(1) = 96.51(3), P(1)−Rh−B(1) = 97.78(11), P(2)−Rh−B(1) = 97.51(11), O(1)−Rh−Cl(1) = 84.98(5), Cl(1)−Rh−B(1) = 98.97(11), B(1)−Rh−H(01) = 77.7(12), O(1)−Rh−B(1) = 176.06(12), O(1)−Rh−H(01) = 98.3(12), H(01)−Rh−Cl(1) = 176.5(12).

evident in the chemistry of the platinum group metals.[15] The ^{1}H, $^{31}P\{^{1}H\}$, and $^{11}B\{^{1}H\}$ NMR spectra of **4**, in benzene-d_6, at room temperature are consistent with the structure shown in Figure 1. The ^{1}H NMR spectrum shows the hydride resonance at −15.66 ppm as a double triplet with Rh−H and H−P coupling constants of 26.6 and 15.4 Hz, respectively. As expected for equivalent $P^{i}Pr_2$ groups, the $^{31}P\{^{1}H\}$ NMR spectrum contains at 52.8 ppm a doublet with a typical P−Rh(III) coupling constant of 118.4 Hz. In the $^{11}B\{^{1}H\}$ NMR spectrum, the Bpin group displays a broad signal at 36.0 ppm.

Scheme 2 collects the reactions involved in the formation of **4**. In accordance with the theoretical results, complex **1** adds B_2pin_2 to initially afford the bis(boryl)intermediate RhCl(Bpin)$_2$\{xant($P^{i}Pr_2$)$_2$\} (**5**), the $^{i}Pr_2$ counterpart of **B**. This intermediate undergoes reductive elimination of boryl chloride to form the square-planar rhodium(I) boryl complex **2**, which promotes the direct borylation of arenes.[11] In agreement with this, it rapidly reacts with the solvent to give PhBpin (the organic reaction product) and to generate the previously described monohydride RhH\{xant($P^{i}Pr_2$)$_2$\} (**6**),[12,16] which also is an active catalyst for the direct borylation of arenes with both B_2pin_2 and HBpin.[11] The oxidative addition of the previously eliminated boryl chloride to **6** yields **4**. In an effort to confirm this sequence of reactions and to detect some reaction intermediates, we followed the reaction by $^{31}P\{^{1}H\}$ NMR spectroscopy. Figure 2 shows the spectrum after 2.5 h. It contains a resonance at 41.0 ppm, in addition to the characteristic signals of **1** and **4**, which appeared to be due to a rhodium(III) species according to the value of the P−Rh coupling constant, 125.4 Hz. Thinking that this resonance would correspond to the bis(boryl) intermediate **5** (δ_{11B}, 32−42), we added 1.0 equiv of boryl chloride to an NMR tube containing **2** in benzene-d_6. The spectra of the resulting solution confirmed our suspicion and showed the formation of **5**. The presence of four resonances for the methyl groups of the isopropyl substituents of the phosphine, at 1.79, 1.73, 1.01, and 0.90 ppm, and two signals for the methyl substituents of the

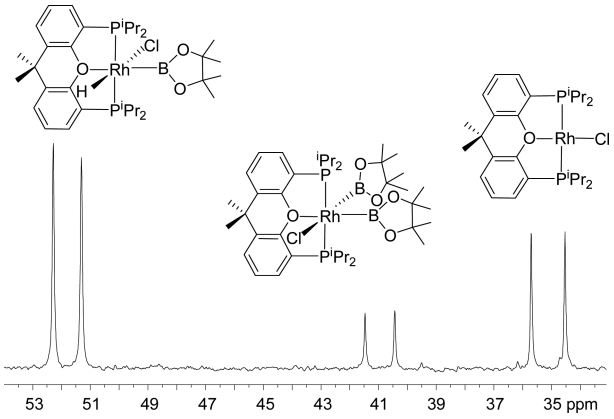

Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction of RhCl\{xant($P^{i}Pr_2$)$_2$\} (**1**) with B_2pin_2, at 90 °C in benzene, after 2.5 h, showing the formation of RhHCl(Bpin)\{xant($P^{i}Pr_2$)$_2$\} (**4**) via the bis(boryl) intermediate RhCl(Bpin)$_2$\{xant($P^{i}Pr_2$)$_2$\} (**5**).

central heterocycle, at 1.16 and 1.06 ppm, in the ^{1}H NMR spectrum, strongly support the mutually *cis* disposition of the boryl ligands. In the presence of 1 equiv of DABCO complex **4** is also formed. However, instead of **5**, the square-planar rhodium(I)-boryl derivative **2** is detected as an intermediate (Figure 3). In order to corroborate the participation of the

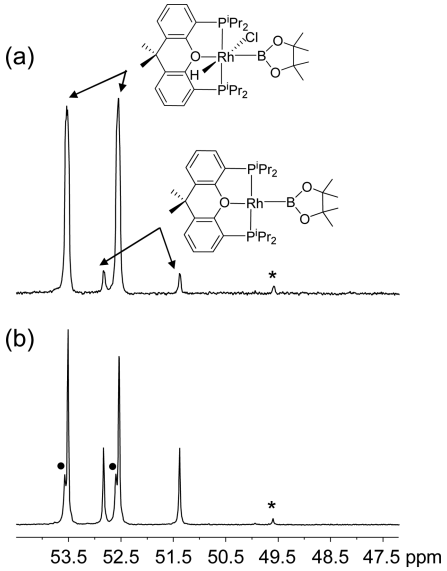

Figure 3. $^{31}P\{^{1}H\}$ NMR spectra of the reaction of RhCl\{xant($P^{i}Pr_2$)$_2$\} (**1**) with B_2pin_2 in the presence of 1 equiv of DABCO after 5.5 h at 90 °C in benzene (a), and in benzene-d_6 (b) showing the formation of RhHCl(Bpin)\{xant($P^{i}Pr_2$)$_2$\} (**4**), via Rh(Bpin)\{xant($P^{i}Pr_2$)$_2$\} (**2**). (●) Isotopomer RhDCl(Bpin)\{xant($P^{i}Pr_2$)$_2$\}. * indicates diphosphine oxide.

monohydride **6**, we also added boryl chloride to a NMR tube containing a benzene-d_6 solution of **6**, and as expected, complex **4** was instantaneously formed. The participation of **6** in the formation of **4** is also supported by the presence of about 0.5 deuterium atoms in the hydride position of the resulting product from the addition of B_2pin_2 to **1** in benzene-d_6. The remaining 0.5 hydrogen atoms result from a D/H exchange process between the intermediate RhD\{xant($P^{i}Pr_2$)$_2$\} (**6**-d_1) and the methyl groups of the isopropyl substituents of the phosphine.

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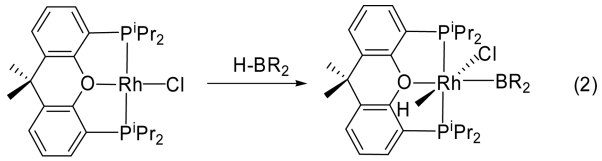
These results demonstrate that, in fact, the addition of $B_2(OR)_4$ to **A** affords **C** via rhodium(III) intermediates $RhCl\{B(OR)_2\}_2(POP)$ (**B**) although, in the absence of nitrile, rhodium(III) compounds $RhHCl\{B(OR)_2\}(POP)$ are formed as a result of a side reaction of **C** with the solvent and subsequent addition of $Cl-B(OR)_2$ to the resulting square-planar rhodium(I)-monohydride complexes. In order to demonstrate that species **C** is certainly the catalyst of the decyanative borylation we have performed the catalysis under the same conditions as those employed by Tobisu, Chatani, and co-workers using complex **2**, 4-(trifluoromethyl)-benzonitrile, and B_2pin_2. After 15 h, the decyanative borylation product 4-(trifluoromethyl)phenyl boronic acid pinacol ester was formed in quantitative yield.

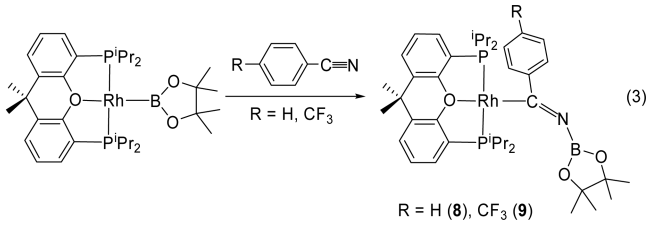
Complex **4** was also prepared in an isolated yield of 80% by means of the HBpin oxidative addition to **1**. Similarly, the addition of 4.0 equiv of catecholborane (HBcat) to the latter leads to the catecholboryl counterpart $RhHCl(Bcat)\{xant(P^iPr_2)_2\}$ (**7**), which was isolated as a white solid in 78% yield, eq 2. In agreement with **4**, the ^1H NMR spectrum of **7**, in



benzene-d_6, at room temperature shows the hydride resonance at −14.96 ppm as a double triplet with H−Rh and H−P coupling constants of 26.5 and 14.4 Hz, respectively. In the $^{31}P\{^1H\}$ NMR spectrum, the equivalent P^iPr_2 groups display a doublet (J_{P-Rh} = 109.9 Hz) at 57.7 Hz, whereas the $^{11}B\{^1H\}$ NMR spectrum contains a broad signal at 40.9 ppm. The high stability of these rhodium(III) species toward the reduction of their metal center must be pointed out. In contrast to **4** and **7**, the dihydride counterparts $RhH_2(BR_2)\{xant(P^iPr_2)_2\}$ (BR_2 = Bpin, Bcat) eliminate molecular hydrogen to yield the corresponding rhodium(I) boryl derivatives.[11] This difference in behavior is a new fact indicating that d_6-$Rh\{xant(P^iPr_2)_2\}$ species containing the π donor chloride ligand are more reluctant to undergo reductive elimination than those without any π donor ligand.[12,13d]

Insertion of the Nitrile: Nature of the Iminoacyl Intermediate. In their original paper,[5a] Tobisu, Chatani, and co-workers proposed that once the rhodium(I)-boryl species **C** is formed, the insertion of the C−N triple bond of the substrate into the Rh−B bond should lead to an "iminylrhodium" species as a result of the migration of the boryl group to the electrophilic carbon atom of the nitrile, in contrast with the typical regiochemistry of the borylation of polar unsaturated multiple bonds,[17] and assuming a nucleophilic boron.[18] Later, on the basis of DFT calculations, the formation of a square-planar η^2-iminoacyl intermediate **D**, which evolved to the T-shaped η^1-iminoacyl species **E**, was proposed.[6,9]

We were interested in knowing if N-boryl substituted η^1-iminoacyl intermediates could be really formed and their nature. A few N-boryl substituted η^2-iminoacyl transition metal complexes had been previously isolated,[19] and it has been proven that N-silyl substituted η^2-iminoacyl intermediates played a main role in the C−C bond activation of alkyl and aryl nitriles.[20] Thus, we studied the insertion reaction starting from **2**, which was prepared by reaction of **6** with HBpin according to the previously described method.[11] At room temperature, the treatment of toluene solutions of this square-planar rhodium(I) boryl complex with 1.0 equiv of benzonitrile and 4-(trifluoromethyl)benzonitrile gave rise to the instantaneous formation of the unprecedented square-planar derivatives $Rh\{C(R\text{-}C_6H_4)=NBpin\}\{xant(P^iPr_2)_2\}$ (R = H (**8**), *p*-CF_3 (**9**)), which were isolated as orange solids in 91% (**8**) and 74% (**9**) yield, eq 3.



Both compounds were characterized by X-ray diffraction analysis. The structures prove their formation and reveal marked differences with the optimized structures resulting from the DFT calculations. The structure of **8** has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 4 shows a drawing of one of them.

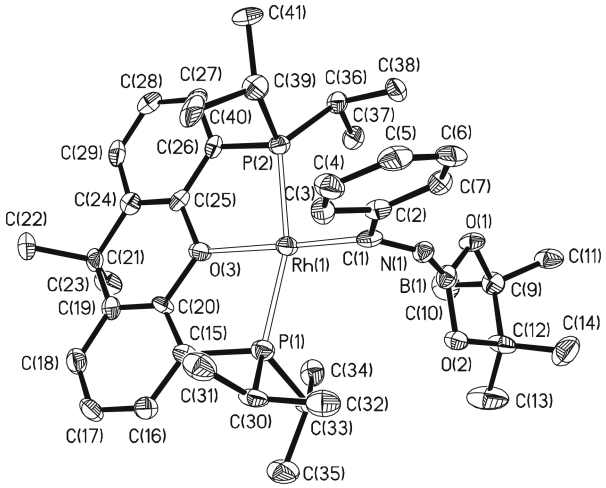


Figure 4. ORTEP diagram of complex **8** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−P(1) = 2.2693(17), 2.2489(18); Rh(1)−P(2) = 2.2460(17), 2.2583(18); Rh(1)−C(1) = 1.943(6), 1.955(6); Rh(1)−O(3) = 2.249(4), 2.287(4); C(1)−N(1) = 1.298(7), 1.279(7); N(1)−B(1) = 1.388(8), 1.377(8); P(1)−Rh(1)−P(2) = 162.42(6), 162.34(6); P(1)−Rh(1)−O(3) = 81.84(11), 80.74(11); P(2)−Rh(1)−O(3) = 81.49(11), 81.61(11); P(1)−Rh(1)−C(1) = 100.97(18), 99.99(18); P(2)−Rh(1)−C(1) = 96.01(18), 97.52(18); O(3)−Rh(1)−C(1) = 175.6(2), 174.8(2); Rh(1)−C(1)−N(1) = 124.1(5), 125.2(5); C(1)−N(1)−B(1) = 143.3(6), 142.7(6); Rh(1)−C(1)−C(2) = 121.8(4), 119.9(4); C(2)−C(1)−N(1) = 114.1(5), 114.9(5).

In contrast to the optimized structures of **D** and **E**, the diphosphine acts as tridentate with P(1)−Rh(1)−P(2), P(1)−Rh(1)−O(3), and P(2)−Rh(1)−O(3) angles of 162.42(6)° and 162.34(6)°, 81.84(11) and 80.74(11)°, and 81.49(11)° and 81.61(11)°, respectively. Thus, the geometry around the rhodium atom is almost square-planar with the η^1-C donor ligand *trans* disposed to the oxygen atom (C(1)−Rh(1)−O(3)

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= 175.6(2)° and 174.8(2)°). The greatest deviation from the best plane through Rh(1), C(1), P(1), O(3), and P(2) atoms is 0.0868(16) Å in one molecule and −0.0488(18) Å in the other one, involved with P(2) and Rh(1), respectively. The Rh(1)−C(1) bond lengths of 1.943(6) and 1.955(6) Å and the C(1)−N(1) distances of 1.298(7) and 1.279(7) Å are consistent with single and double bonds between the respective atoms, whereas the angles around C(1), between 125° and 114°, are in accordance with a sp^2-hybridization at C(1). The N(1)−B(1) bond lengths of 1.388(8) and 1.377(8) Å, along with the C(1)−N(1)−B(1) angles of 143.3(6)° and 142.7(6)°, suggest a notable double bond character for the N(1)−B(1) bond and, therefore, a significant allenic nature of the η^1-C donor ligand. This is a consequence of the empty p orbital at the boron, which allows additional nitrogen to boron π donation.

The structure of **9** (Figure 5) resembles that of **8** with P(1)−Rh−P(2), P(1)−Rh−O(1), P(2)−Rh−O(1), and C(1)−Rh−

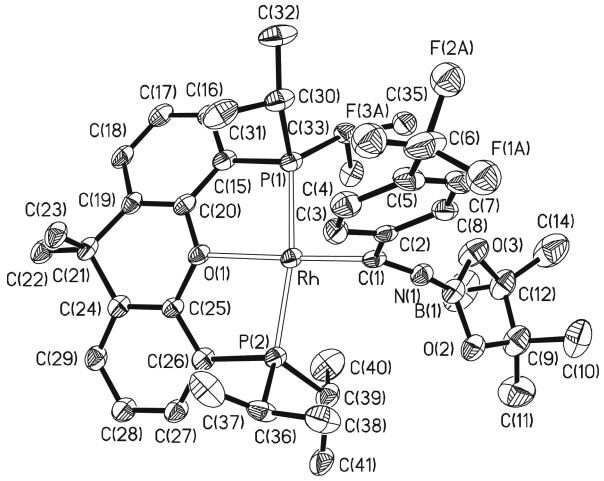
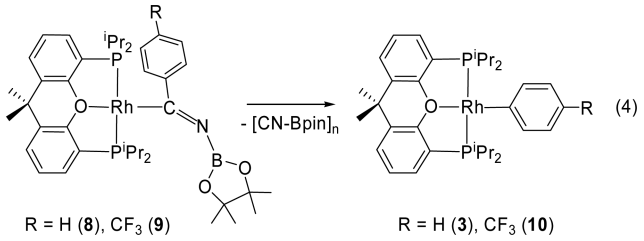


Figure 5. ORTEP diagram of complex **9** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−P(1) = 2.2606(18), Rh−P(2) = 2.2450(18), Rh−C(1) = 1.946(6), Rh−O(1) = 2.246(4), C(1)−N(1) = 1.274(8), N(1)−B(1) = 1.399(9); P(1)−Rh−P(2) = 160.30(6), P(1)−Rh−O(1) = 82.44(12), P(2)−Rh−O(1) = 82.72(11), P(1)−Rh−C(1) = 96.39(18), P(2)−Rh−C(1) = 98.65(18), O(1)−Rh−C(1) = 178.5(2), Rh−C(1)−N(1) = 129.2(5), Rh−C(1)−C(2) = 116.1(5), C(1)−N(1)−B(1) = 155.5(6), C(2)−C(1)−N(1) = 114.6(6).

O(1) angles of 160.30(6)°, 82.44(12)°, 82.72(11)°, and 178.5(2)°, respectively. The Rh−C(1), C(1)−N(1), and N(1)−B(1) distances of 1.946(6), 1.274(8), and 1.399(9) Å are statistically identical to the respective bond lengths of **8**. The C(1)−N(1)−B(1) angle of 155.5(6)° also supports some allenic nature for the C(*p*-CF_3-Ph)═NBpin ligand, and its comparison with that of **8** reveals a marked influence of the substituent at C(1) on the N−B bond.

The $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **8** and **9**, in benzene-d_6, at room temperature are consistent with the structures shown in Figures 4 and 5. In the $^{13}C\{^1H\}$ NMR spectra the resonance due to the metalated carbon atom C(1) appears at about 209 ppm as a double triplet with C−Rh and C−P coupling constants of about 43 and 10 Hz, respectively. The Bpin group displays a broad resonance at about 27 ppm in the $^{11}B\{^1H\}$ NMR spectra, whereas the equivalent $^iPr_2P$ groups give rise to a doublet ($J_{P-Rh} \approx 187-191$ Hz) at about 37 ppm in the $^{31}P\{^1H\}$ NMR spectra.

Phenyl Migration. In spite of that DFT results indicate that the formation of **F** from **D** and **E** is an endoergic process by 21.0 and 14.0 kcal mol^{-1},[6] respectively; the heating of toluene solutions of **8** and **9**, at 50 °C, for 72 h leads to the aryl derivatives **3** and Rh(*p*-CF_3-C_6H_4){xant(P^iPr_2)$_2$} (**10**). Their formation results from the extrusion of boryl isocyanide, which polymerizes to afford an air-sensitive, insoluble, yellow solid containing an IR band at 2116 cm^{-1}, eq 4. In agreement with



(4)

the participation of these aryl derivatives in the catalysis, the reactions of both **3** and **10** with B_2pin_2 yield the corresponding aryl-Bpin and regenerate the rhodium(I)-boryl compound **2**.

Complex **10** was isolated as a red solid in 72% yield and characterized by X-ray diffraction analysis. The structure (Figure 6) proves its formation. As expected, the coordination

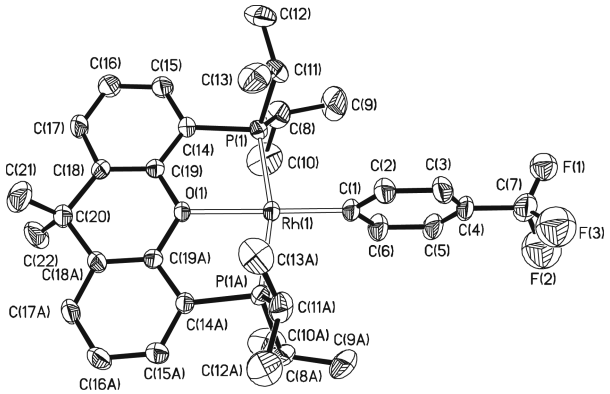


Figure 6. ORTEP diagram of complex **10** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−P(1) = 2.2434(10), Rh−C(1) = 1.983(6), Rh(1)−O(1) = 2.221(4); P(1)−Rh(1)−P(1A) = 164.09(5), P(1)−Rh(1)−O(1) = 82.24(2), P(1)−Rh(1)−C(1) = 97.71(2), O(1)−Rh−C(1) = 178.6(2).

geometry around the rhodium atom is almost square-planar with the diphosphine coordinated in a *mer*-fashion (P(1)−Rh−P(1A) = 164.09(5)° and P(1)−Rh−O(1) = 82.24(2)°) and the aryl group *trans* disposed to the oxygen atom (C(1)−Rh−O(1) = 178.6(2)°). The greatest deviation from the best plane through Rh, C(1), O(1), P(1), and P(1A) atoms is 0.0174(24) Å and involves Rh. The metalated aromatic ring lies perpendicular to the coordination plane with a dihedral angle of 90°. The Rh−C(1) distance of 1.983(6) Å compares well with those found in the reported square-planar rhodium(I)-aryl complexes (1.84−2.10 Å).[11,21] In the $^{13}C\{^1H\}$ NMR spectrum in benzene-d_6, at room temperature the most noticeable resonance is that corresponding to C(1), which appears at 173.8 ppm as a double triplet with C−Rh and C−P coupling constants of 40.9 and 11.8 Hz, respectively. In agreement with equivalent $^iPr_2P$ groups, the $^{31}P\{^1H\}$ NMR spectrum contains at 37.5 ppm a doublet with a typical P−Rh(I) coupling constant of 173.5 Hz.

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CONCLUDING REMARKS

This study shows the stoichiometric reactions forming the catalytic cycle of the rhodium-mediated decyanative borylation of nitriles and the X-ray structures of the main intermediates of the catalysis.

The true catalyst of the process is certainly a square-planar Rh{B(OR)$_2$}(POP) derivative which is formed, via a rhodium(III)-bis(boryl) intermediate, through the oxidative addition of B$_2$(OR)$_4$ to the catalytic precursor RhCl(POP) and subsequent reductive elimination of boryl chloride. In the absence of substrate the catalyst evolves into a rhodium(III) derivative RhHCl{B(OR)$_2$}(POP), as a consequence of the borylation of the solvent (toluene) and the oxidative addition of the eliminated boryl chloride to the resulting monohydride.

Once the catalyst is generated, the insertion of the C−N triple bond of the substrates RCN into the Rh−B bond affords square-planar Rh[C(R)═N{B(OR)$_2$}](POP) species, with the diphosphine acting as *mer*-tridentated and the formed η^1-C-donor ligand showing a significant allenic nature. No evidence of the participation of square-planar η^2-iminoacyl and T-shaped η^1-iminoacyl intermediates has been found. Complexes Rh[C(R)═N{B(OR)$_2$}](POP) evolve into rhodium(I)-aryl derivatives as a result of the extrusion of boryl isocyanide, which polymerizes in the reaction medium. The reactions of the rhodium(I)-aryl compounds with B$_2$(OR)$_4$ yield the products of the catalysis, closing the cycle.

Too many catalytic cycles of relevant organic reactions are reported on the basis of simple speculations, even some of them without taking into account basic concepts of organometallics. Other times, DFT calculations replace experimental evidence, which can be easily obtained. In contrast to these uses, here, we report the mechanism of a novel reaction recently discovered on the basis of the experimental study of each elemental stage of the process, the isolation of all relevant intermediates, and their spectroscopic and structural characterization, including the X-ray structures.

EXPERIMENTAL SECTION

General Information. All reactions were carried out with rigorous exclusion of air using Schlenk-tube techniques or in a drybox. Pentane was obtained oxygen- and water-free from an MBraun solvent purification apparatus and was stored over P_2O_5 in the drybox, while toluene, benzene, and benzonitrile were dried, distilled, and stored under argon. Pinacolborane, B$_2$pin$_2$, and 4-(trifluoromethyl)-benzonitrile were purchased from commercial sources and used without further purification. Catecholborane was purchased from commercial sources and distilled in a Kugelrohr distillation oven. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}, ^{11}B{^{1}H}, and ^{19}F NMR spectra were recorded on Bruker 300 ARX, Bruker Avance 300 MHz, Bruker Avance 400 MHz, or Bruker Avance 500 MHz instruments. Chemical shifts (expressed in parts per million) are referenced to residual solvent peaks (^{1}H, ^{13}C{^{1}H}), external 85% H_3PO_4 (^{31}P{^{1}H}), BF_3·OEt$_2$ (^{11}B{^{1}H}), or $CFCl_3$ (^{19}F). Coupling constants J and N are given in hertz. Attenuated total reflection infrared spectra (ATR-IR) of solid samples were run on a PerkinElmer Spectrum 100 FT-IR spectrometer. C, H, and N analyses were carried out in a PerkinElmer 2400 CHNS/O analyzer. High-resolution electrospray mass spectra were acquired using a MicroTOF-Q hybrid quadrupole time-of-flight spectrometer (Bruker Daltonics, Bremen, Germany). RhCl{xant(P^{i}Pr$_2$)$_2$} (**1**),[13d] Rh(Bpin){xant(P^{i}Pr$_2$)$_2$} (**2**),[11] and ClBpin[22] were prepared by published methods.

Reaction of RhCl{xant(P^{i}Pr$_2$)$_2$} (1) with Bis(pinacolato)-diboron: Preparation of RhHCl(Bpin){xant(P^{i}Pr$_2$)$_2$} (4). A solution of **1** (230.1 mg, 0.40 mmol) in toluene was treated with the stoichiometric amount of B$_2$pin$_2$ (100.7 mg, 0.40 mmol), and the resulting solution was heated in an oil bath at 90 °C for 20 h. After this time, it was concentrated to dryness to afford a pale brownish residue. Addition of pentane (4 mL) afforded a white solid that was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 219.0 mg (78%). Anal. Calcd for $C_{33}H_{53}BClO_3P_2Rh$: C, 55.91; H, 7.54. Found: C, 56.32; H, 7.25. HRMS (electrospray, m/z) calcd for $C_{33}H_{53}BO_3P_2Rh$ [M − Cl]$^+$: 673.2618; found: 673.2647. IR (cm^{-1}): ν(Rh−H) 2094 (w), ν(C−O−C) 1109 (m). ^{1}H NMR (400.16 MHz, C_6D_6, 298 K): δ 7.22 (m, 2H, CH-arom POP), 7.10 (dd, J_{H-H} = 7.7, J_{H-H} = 1.3, 2H, CH-arom POP), 6.92 (dd, 2H, J_{H-H} = 7.6, J_{H-H} = 7.6, CH-arom POP), 2.85 (m, 2H, PCH(CH$_3$)$_2$), 2.38 (m, 2H, PCH(CH$_3$)$_2$), 1.79 (dvt, J_{H-H} = 7.3, N = 16.2, 6H, PCH(CH_3)$_2$), 1.63 (dvt, J_{H-H} = 7.3, N = 15.1, 6H, PCH(CH_3)$_2$), 1.40 (dvt, J_{H-H} = 7.2, N = 15.8, 6H, PCH(CH_3)$_2$), 1.35 (s, 3H, CH$_3$), 1.26 (s, 12H, Bpin), 1.16 (s, 3H, CH$_3$), 0.95 (dvt, J_{H-H} = 7.1, N = 14.9, 6H, PCH(CH_3)$_2$), −15.66 (dt, J_{H-Rh} = 26.6, J_{H-P} = 15.4, 1H, Rh−H). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 154.8 (vt, N = 12.3, C-arom POP), 132.2 (vt, N = 5.0, C-arom POP), 130.8 (s, CH-arom POP), 127.4 (s, CH-arom POP), 126.1 (vt, N = 24.1, C-arom POP), 124.3 (vt, N = 4.8, CH-arom POP), 82.0 (s, C Bpin), 34.9 (s, C(CH$_3$)$_2$), 34.4 (s, C(CH$_3$)$_2$), 29.4 (vt, N = 21.6, PCH(CH$_3$)$_2$), 28.2 (dvt, J_{Rh-C} = 3.0, N = 30.0, PCH(CH$_3$)$_2$), 27.5 (s, C(CH$_3$)$_2$), 25.7 (s, CH$_3$ Bpin), 21.5 (s, PCH(CH$_3$)$_2$), 20.3 (vt, N = 5.6, PCH(CH$_3$)$_2$), 20.0 (s, PCH(CH$_3$)$_2$), 19.8 (vt, N = 5.6, PCH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, C_6D_6, 298 K): δ 52.8 (d, J_{P-Rh} = 118.4). ^{11}B{^{1}H} NMR (128.38 MHz, C_6D_6, 298 K): δ 36.0 (br).

Reaction of RhCl{xant(P^{i}Pr$_2$)$_2$} (1) with Bis(pinacolato)-diboron in an NMR Tube: Detection of RhCl(Bpin)$_2${xant-(P^{i}Pr$_2$)$_2$} (5). In an NMR tube a solution of **1** (40 mg, 0.069 mmol) in benzene (0.5 mL) was treated with the stoichiometric amount of B$_2$pin$_2$ (17.6 mg, 0.069 mmol), and the resulting solution was heated at 90 °C in an oil bath. The reaction was periodically checked by ^{31}P{^{1}H} and ^{11}B{^{1}H} NMR spectroscopy. After 2.5 h the ^{31}P{^{1}H} NMR spectrum shows signals corresponding to RhHCl(Bpin){xant-(P^{i}Pr$_2$)$_2$} (**4**), RhCl(Bpin)$_2${xant(P^{i}Pr$_2$)$_2$} (**5**), and RhCl{xant(P^{i}Pr$_2$)$_2$} (**1**) in a ratio 53:15:32. The ^{11}B{^{1}H} NMR spectrum show peaks assigned to PhBpin (br, δ 30.9) and ClBpin (br, δ 27.5), in addition to those assigned to **4** and **5**. After 20 h the ^{31}P{^{1}H} NMR spectrum shows the quantitative conversion to RhHCl(Bpin){xant(P^{i}Pr$_2$)$_2$} (**4**).

Reaction of Rh(Bpin){xant(P^{i}Pr$_2$)$_2$} (2) with ClBpin. Spectroscopic Detection of RhCl(Bpin)$_2${xant(P^{i}Pr$_2$)$_2$} (5). In an NMR tube a solution of **2** (20 mg, 0.030 mmol) in benzene-d_6 was treated with ClBpin (4.8 μL, 0.030 mmol). The immediate and quantitative conversion to **5** was observed by ^{1}H, ^{31}P{^{1}H}, and ^{11}B{^{1}H} NMR spectroscopies. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 7.20 (m, 2H, CH-arom POP), 7.12 (d, J_{H-H} = 7.5, 2H, CH-arom POP), 6.96 (t, 2H, J_{H-H} = 7.5, CH-arom POP), 3.09 (m, 2H, PCH(CH$_3$)$_2$), 2.92 (m, 2H, PCH(CH$_3$)$_2$), 1.79 (dvt, J_{H-H} = 6.8, N = 14.9, 6H, PCH(CH_3)$_2$), 1.73 (dvt, J_{H-H} = 7.5, N = 16.0, 6H, PCH(CH_3)$_2$), 1.37 (s, 12H, Bpin), 1.16 (s, 3H, CH$_3$), 1.11 (s, 12H, Bpin), 1.06 (s, 3H, CH$_3$), 1.01 (dvt, J_{H-H} = 8.1, N = 14.0, 6H, PCH(CH_3)$_2$), 0.90 (dvt, J_{H-H} = 7.0, N = 13.4, 6H, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 41.0 (d, J_{P-Rh} = 125.4). ^{11}B{^{1}H} NMR (96.29 MHz, C_6D_6, 298 K): δ 32−42 (very br).

Reaction of RhCl{xant(P^{i}Pr$_2$)$_2$} (1) with Bis(pinacolato)-diboron in the Presence of DABCO. Two NMR tubes were charged with **1** (40 mg, 0.047 mmol), B$_2$pin$_2$ (11.3 mg, 0.047 mmol), and DABCO (5.0 mg, 0.069 mmol). To the first NMR tube was added 0.5 mL of benzene, and to the second was added 0.5 mL of benzene-d_6. After that, both tubes were introduced in an oil bath at 90 °C, and the tubes were periodically checked by ^{31}P{^{1}H} NMR spectroscopy. After 5.5 h the ^{31}P{^{1}H} NMR spectra of both tubes show the formation of RhHCl(Bpin){xant(P^{i}Pr$_2$)$_2$} (**4**) and Rh(Bpin){xant-(P^{i}Pr$_2$)$_2$} (**2**). Additionally, the ^{31}P{^{1}H} NMR spectrum of the reaction performed in benzene-d_6 showed the presence of the isotopomer of **4** RhDCl(Bpin){xant(P^{i}Pr$_2$)$_2$}. Ratio **4**:**2** in benzene is 94:6. Ratio **4** (plus its isotopomer):**2** in benzene-d_6 is 77:23.

Reaction of RhH{xant(P^{i}Pr$_2$)$_2$} (6) with ClBpin. A solution of **6** (37.0 mg, 0.067 mmol) in benzene-d_6 (0.5 mL) in an NMR tube was treated with ClBpin (70 μL, 0.070 mmol). The immediate and

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quantitative conversion to RhHCl(Bpin){xant(P^iPr_2)$_2$} (**4**) was observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies.

Decyanative Borylation of 4-(Trifluoromethyl)benzonitrile with Bis(pinacolato)diboron Catalyzed by Rh(Bpin){xant-(P^iPr_2)$_2$} (2). In an argon filled glovebox an Ace pressure tube was charged with 4-trifluoromethylbenzonitrile (85.6 mg, 0.5 mmol), B_2pin_2 (254 mg, 1.0 mmol), **2** (67.2 mg, 0.1 mmol), DABCO (56.1 mg, 0.5 mmol), and toluene (0.5 mL). The resulting mixture was stirred at 100 °C for 15 h. After this time the pressure tube was cooled to room temperature, and the suspension was filtered. After the volatiles were evaporated under reduced pressure, ^{1}H, ^{11}B{^{1}H}, ^{19}F, and ^{13}C{1H} NMR spectra showed the quantitative decyanative borylation of 4-(trifluoromethyl)benzonitrile to give 4-(trifluoromethyl)phenylboronic acid pinacol ester. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.90 (d, J_{H-H} = 7.7, 2H, CH), 7.58 (d, J_{H-H} = 7.7, 2H, CH), 1.33 (s, 12H, CH_3). ^{13}C{^{1}H} NMR (100.5 MHz, $CDCl_3$, 298 K): δ 134.9 (s, CH), 132.5 (q, J_{C-F} = 32.1, *C*-CF_3), 125.3 (q, J_{C-F} = 271.2, CF_3), 124.0 (q, J_{C-F} = 3.8, CH), 84.1 (s, C), 24.8 (s, CH_3). ^{11}B{^{1}H} NMR (128.30 MHz, $CDCl_3$, 298 K): δ 30.7 (s). ^{19}F NMR (376.49 MHz, $CDCl_3$, 298 K): δ −63.5. These data agree with previously reported data.[23]

Reaction of RhCl{xant(P^iPr_2)$_2$} (1) with Pinacolborane: Preparation of RhHCl(Bpin){xant(P^iPr_2)$_2$} (4). Pinacolborane (47 μL, 0.31 mmol) was added to a solution of **1** (121.4 mg, 0.21 mmol) in toluene (0.5 mL). After the resulting solution was stirred for 10 min, it was concentrated to dryness to afford a white residue. Addition of pentane afforded a white solid that was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 116 mg (78%). ^{1}H, ^{31}P{^{1}H}, and ^{11}B{^{1}H} NMR spectra are identical to those obtained for this compound starting from RhCl{xant(P^iPr_2)$_2$} and B_2pin_2.

Reaction of RhCl{xant(P^iPr_2)$_2$} (1) with Catecholborane: Preparation of RhHCl(Bcat){xant(P^iPr_2)$_2$} (7). Catecholborane (109.4 μL, 1.02 mmol) was added to a solution of **1** (146.0 mg, 0.25 mmol) in toluene (0.5 mL). After the resulting solution was stirred for 10 min, the solvent was removed in vacuo to afford a white residue, which was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 150 mg (78%). Anal. Calcd for $C_{33}H_{45}BClRhO_3P_2$: C, 56.56; H, 6.47. Found: C, 56.80; H, 6.52. HRMS (electrospray, *m*/*z*): calcd for $C_{33}H_{45}BO_3P_2Rh$ [M − Cl]$^+$: 665.1992; found: 665.2122. IR (cm^{-1}): ν(Rh−H) 2108 (w); ν(C−O−C) 1092 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.23 (m, 2H, Bcat), 7.10 (dd, J_{H-H} = 7.5, J_{H-H} = 1.4, 2H, CH-arom POP), 6.91 (dd, J_{H-H} = 7.5, J_{H-H} = 7.5, 2H, CH-arom POP), 6.89 (m, 2H, Bcat), 6.74 (m, 2H, CH-arom POP), 2.72 (m, 2H, PC*H*(CH_3)$_2$), 2.18 (m, 2H, PC*H*(CH_3)$_2$), 1.61 (dvt, J_{H-H} = 7.4, *N* = 15.9, 6H, PCH(CH_3)$_2$), 1.47 (dvt, J_{H-H} = 7.4, *N* = 16.4, 6H, PCH(CH_3)$_2$), 1.34 (s, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.14 (dvt, J_{H-H} = 7.3, *N* = 16.1, 6H, PCH(CH_3)$_2$), 0.93 (dvt, J_{H-H} = 7.1, *N* = 15.5, 6H, PCH(CH_3)$_2$), −14.96 (dt, J_{H-Rh} = 26.5, J_{H-P} = 14.4, 1H, Rh−H). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 154.5 (vt, *N* = 12.7, Carom POP), 150.5 (s, C−O Bcat), 132.2 (vt, *N* = 5.4, Carom POP), 130.9 (s, CH-arom POP), 128.1 (s, CH-arom POP), 125.0 (vt, *N* = 25.8, Carom POP), 124.6 (vt, *N* = 5.3, CH-arom POP), 121.4 (s, CH Bcat), 111.3 (s, CH Bcat), 34.8 (s, *C*(CH_3)$_2$), 34.4 (s, C(CH_3)$_2$), 22.8 (vt, *N* = 23.7, PCH(CH_3)$_2$), 28.1 (s, C(CH_3)$_2$), 27.9 (dvt, J_{C-Rh} = 2.3, *N* = 28.5, PCH(CH_3)$_2$), 21.7 (s, PCH(CH_3)$_2$), 19.8 (vt, *N* = 5.2, PCH(CH_3)$_2$), 19.6 (s, PCH(CH_3)$_2$), 19.1 (vt, *N* = 6.7, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 57.7 (d, J_{P-Rh} = 109.9). ^{11}B{^{1}H} NMR (96.29 MHz, C_6D_6, 298 K): δ 40.9 (br).

Reaction of Rh(Bpin){xant(P^iPr_2)$_2$} (2) with Benzonitrile: Preparation of Rh{C(Ph)═NBpin}{xant(P^iPr_2)$_2$} (8). Benzonitrile (46 μL, 0.45 mmol) was added to a solution of **2** (300 mg, 0.45 mmol) in toluene (2 mL). The resulting mixture was stirred for 5 min at room temperature. After this time, it was concentrated to dryness to afford an orange residue. Addition of pentane (1 mL) afforded an orange solid that was washed with pentane (1 × 0.5 mL) and dried in vacuo. Yield: 315 mg (91%). Anal. Calcd for $C_{40}H_{57}BNO_3P_2Rh$: C, 61.95; H, 7.41; N, 1.81. Found: C, 61.63; H, 7.73; N, 1.98. HRMS (electrospray, *m*/*z*): calcd for $C_{34}H_{45}NOP_2Rh$ [M − Bpin]$^+$: 648.2026. Found: 648.1990. IR (cm^{-1}): ν(C═N) 1649 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.90 (d, J_{H-H} = 7.8, 2H, CH Ph), 7.31 (t, J_{H-H} = 7.8, 2H, CH Ph), 7.23−7.14 (m, 3H, 1H Ph + 2 CH-arom POP), 7.06 (d, J_{H-H} = 7.7, 2H, CH-arom POP), 6.86 (t, J_{H-H} = 7.7, 2H, CH-arom POP), 2.56 (m, 4H, PC*H*(CH_3)$_2$), 1.37 (s, 12H, CH_3 Bpin), 1.30−1.22 (m, 18H, PCH(CH_3)$_2$ + C(CH_3)$_2$), 1.16 (dvt, J_{H-H} = 6.9, *N* = 14.0, 12H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.78 MHz, C_6D_6, 298 K): δ 209.7 (dt, J_{C-Rh} = 42.3, J_{C-P} = 9.6, Rh−C), 155.2 (vt, *N* = 15.0, Carom POP), 148.7 (dt, J_{C-Rh} = 3.2, J_{C-P} = 3.2, C_{ipso} Ph), 131.2 (s, CH Ph), 131.0 (s, CH-arom POP), 130.8 (vt, *N* = 4.9, Carom POP), 127.9, 127.6 (both s, CH Ph), 126.9 (s, CH-arom POP), 125.3 (vt, *N* = 16.0, Carom POP), 123.9 (s, CH-arom POP), 80.8 (s, C Bpin), 34.2 (s, *C*(CH_3)$_2$), 32.8 (s, C(CH_3)$_2$), 25.6 (s, CH_3 Bpin), 25.2 (dvt, J_{C-Rh} = 2.9, *N* = 17.8, PCH(CH_3)$_2$), 19.6 (br, PCH(CH_3)$_2$), 18.1 (s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 36.5 (d, J_{P-Rh} = 190.8). ^{11}B NMR (92.29 MHz, C_6D_6, 298 K): δ 26.7 (br).

Reaction of Rh(Bpin){xant(P^iPr_2)$_2$} (2) with 4-(Trifluoromethyl)benzonitrile: Preparation of Rh{C(*p*-CF_3−C_6H_4)═NBpin}{xant(P^iPr_2)$_2$} (9). 4-(Trifluoromethyl)benzonitrile (63.6 mg, 0.37 mmol) was added to a solution of **2** (250 mg, 0.37 mmol) in toluene (2 mL). The resulting mixture was stirred for 5 min at room temperature. After this time, it was concentrated to dryness to afford an orange residue. Addition of pentane (1 mL) afforded an orange solid that was washed with pentane (1 × 0.5 mL) and dried in vacuo. Yield: 231 mg (74%). Anal. Calcd for $C_{41}H_{56}BF_3NO_3P_2Rh$: C, 58.38; H, 6.69. Found: C, 58.64; H, 6.31. HRMS (electrospray, *m*/*z*): calcd for $C_{35}H_{44}ONF_3P_2Rh$ [M − Bpin]$^+$: 716.1900. Found: 716.1897. IR (cm^{-1}): ν(C═N) 1606 (w), ν(C−O−C) 1061 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.86 (d, J_{H-H} = 7.9, 2H, CH, *p*-CF_3-C_6H_4), 7.59 (d, J_{H-H} = 7.9, 2H, *p*-CF_3-C_6H_4), 7.23 (m, 2H, CH-arom POP), 7.04 (d, J_{H-H} = 7.7, 2H, CH-arom POP), 6.84 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 2.50 (m, 4H, PC*H*(CH_3)$_2$), 1.36 (s, 12H, CH_3), 1.23 (m, 18H, PCH(CH_3)$_2$ + C(CH_3)$_2$), 1.11 (dvt, J_{H-H} = 6.8, *N* = 14.7, 12H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (125.78 MHz, C_6D_6, 298 K): δ 209.3 (dt, J_{C-Rh} = 43.6, J_{C-P} = 9.9, Rh−C), 155.2 (vt, *N* = 16.0, Carom POP), 151.1 (m, C_{ipso} Ph), 139.7 (t, J_{C-F} = 2.5, CH, Ph), 131.2 (s, CH-arom POP), 130.9 (s, CH-arom POP), 130.7 (s, Carom POP), 129.9 (q, J_{C-F} = 31.4, *C*-CF_3), 127.9 (q, J_{C-F} = 271.9, −CF_3), 124.8 (vt, *N* = 16.8, Carom POP), 124.1 (s, CH-arom POP), 123.8 (q, J_{C-F} = 3.7, CH, Ph), 81.1 (s, C Bpin), 34.2 (s, *C*(CH_3)$_2$), 32.8 (s, C(CH_3)$_2$), 25.6 (s, CH_3 Bpin), 25.2 (vt, *N* = 18.4, PCH(CH_3)$_2$), 19.3 (vt, *N* = 8.2, PCH(CH_3)$_2$), 18.6 (s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 37.0 (d, J_{P-Rh} = 187.6). ^{19}F{^{1}H} NMR (282.33 MHz, C_6D_6, 298 K): δ −61.4 (s). ^{11}B NMR (92.29 MHz, C_6D_6, 298 K): δ 26.5 (br).

Preparation of RhPh{xant(P^iPr_2)$_2$} (3). Rh{C(Ph)═NBpin}-{xant(P^iPr_2)$_2$} (**8**) (200 mg, 0.26 mmol) was dissolved in toluene (3 mL), and the resulting solution was heated at 50 °C for 72 h (the progress of the reaction was periodically checked by ^{31}P{^{1}H} NMR spectroscopy). During this time a yellow solid precipitated from the red solution. The mixture was cooled to room temperature, and it was filtered, obtaining a red solution that was evaporated to dryness. Addition of pentane (5 mL) afforded a red solid, which was further washed with pentane (6 × 1 mL) and was dried in vacuo. Yield: 53.0 mg (33%). ^{31}P{^{1}H} NMR spectroscopy shows that the reaction is quantitative, but the isolated yield is low due to the high solubility of the complex in pentane. ^{1}H and ^{31}P{^{1}H} NMR spectra agree well with those previously reported for this compound.[11]

Preparation of Rh(*p*-CF_3-C_6H_4){xant(P^iPr_2)$_2$} (10). Rh{C(*p*-CF_3−C_6H_4)═NBpin}{xant(P^iPr_2)$_2$} (**9**) (200 mg, 0.24 mmol) was dissolved in toluene (3 mL), and the resulting solution was heated at 50 °C for 72 h (the progress of the reaction was periodically checked by ^{31}P{^{1}H} NMR spectroscopy). During this time a yellow solid precipitated from the red solution. The mixture was cooled to room temperature, and it was filtered, obtaining a red solution that was evaporated to dryness. Addition of pentane (2 mL) afforded a red solid that was washed with pentane (2 × 1 mL) and dried in vacuo. Yield: 68 mg (72%). Anal. Calcd for $C_{34}H_{44}F_3OP_2Rh$: C, 59.14; H, 6.42. Found: C, 59.43; H, 6.18. HRMS (electrospray, *m*/*z*): calcd for $C_{34}H_{44}F_3OP_2Rh$ [M + H]$^+$ 691.1962; found 691.1947. IR (cm^{-1}): ν(C−O−C) 1093 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.07 (d, J_{H-H} = 8.0, 2H, *p*-CF_3-Ph), 7.39 (d, J_{H-H} = 8.0, 2H, *p*-CF_3-Ph),

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7.22 (m, 2H, CH-arom POP), 7.03 (dd, J_{H-H} = 7.6, J_{H-H} = 1.6, 2H, CH-arom POP), 6.84 (t, J_{H-H} = 7.6, 2H, CH-arom POP), 2.28 (m, 4H, PC*H*$(CH_3)_2$), 1.21 (s, 6H, CH_3), 1.11 (m, 24H, PCH$(CH_3)_2$). $^{13}C\{^1H\}$ NMR (75.47 MHz, C_6D_6, 298 K): δ 173.8 (dt, J_{C-Rh} = 40.9, J_{C-P} = 11.8, Rh−C), 155.7 (vt, *N* = 16.0, C-arom POP), 139.4 (t, J_{C-P} = 2.8, *o*-C*H* *p*-CF_3-Ph), 131.0 (s, C-arom POP), 127.7 (s, CH-arom POP), 127.5 (q, J_{C-F} = 270.0, CF_3), 124.9 (vt, *N* = 15.5, Carom), 123.9 (vt, *N* = 3.7, CH-arom POP), 120.6 (m, *m*-CH, *p*-CF_3−Ph), 119.9 (q, J_{C-F} = 31.1, *C*-CF_3), 33.7 (s, *C*$(CH_3)_2$), 32.7 (s, C$(CH_3)_2$), 25.0 (dvt, J_{C-Rh} = 2.9, *N* = 18.2, P*C*H$(CH_3)_2$), 19.0 (vt, *N* = 8.3, PCH$(CH_3)_2$), 18.2 (s, PCH$(CH_3)_2$). $^{31}P\{^1H\}$ NMR (121.49 MHz, C_6D_6, 298 K): δ 37.5 (d, J_{P-Rh} = 173.5). ^{19}F NMR (282.33 MHz, C_6D_6, 298 K): δ −60.2 (t, J_{F-H} = 2.0).

Structural Analysis of Complexes 4, 8, 9, and 10. Crystals suitable for the X-ray diffraction were obtained by slow evaporation of pentane (**8**, **9**, **10**) or by diffusion of pentane into solutions of **4** in toluene. X-ray data were collected on a Bruker Smart APEX or APEX DUO difractometers equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.710 73 Å) operating at 50 kV and 40 mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (**8**, **10**), 20 s (**4**), 30 s (**9**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[24] The structures were solved by the Patterson (Rh atoms) or direct methods and conventional Fourier techniques and refined by full-matrix least-squares on F^2 with SHELXL97.[25] Anisotropic parameters were used in the last cycles of refinement for all non-hydrogen atoms. The hydrogen atoms were observed or calculated and refined freely or using a restricted riding model. The hydride ligand of complex **4** was observed in the difference Fourier maps but refined too close to the metal, so a restrained refinement fixing the RhH bond length to 1.59 Å (CCDC) was used. The fluorine atoms of the CF_3 group of complex **9** were observed disordered. This group was defined with three moieties, complementary occupancy factors, isotropic atoms, and restrained geometry. Complex **9** crystallizes with a half molecule of pentane that was refined isotropically with restrained geometry. For all structures the highest electronic residuals were observed in the close proximity of the metal centers and make no chemical sense.

Crystal data for 4. $C_{33}H_{53}BClO_3P_2Rh$, M_W 708.86, colorless, irregular prism (0.16 × 0.14 × 0.06 mm), monoclinic, space group $P2_1/c$, a = 19.0180(17) Å, b = 9.5701(9) Å, c = 19.2725(18) Å, β = 92.9000(10)°, V = 3503.2(6) Å^3, Z = 4, D_{calc} = 1.344 g cm^{-3}, F(000) = 1488, T = 100(2) K, μ = 0.686 mm^{-1}. There were 31 398 measured reflections (2θ: 2−57°, ω scans 0.3°), 8330 unique (R_{int} = 0.0563); minimum/maximum transmission factors 0.826/0.939. Final agreement factors were R1 = 0.0403 (5830 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.0851; data/restraints/parameters 8330/1/387; GOF = 0.928. Largest peak and hole 1.243 and −1.029 e/Å^3.

Crystal data for 8. $C_{40}H_{57}BNO_3P_2Rh$, M_W 775.53, red, irregular block (0.14 × 0.12 × 0.10 mm), monoclinic, space group $P2_1/c$, a = 15.5616(17) Å, b = 27.648(3) Å, c = 18.575(2) Å, β = 101.299(2)°, V = 7836.9(15) Å^3, Z = 8, D_{calc} = 1.315 g cm^{-3}, F(000) = 3264, T = 100(2) K, μ = 0.554 mm^{-1}. There were 59 149 measured reflections (2θ: 2−51°, ω scans 0.3°), 14 598 unique (R_{int} = 0.1576); minimum/maximum transmission factors 0.740/0.951. Final agreement factors were R1 = 0.0653 (8141 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.1260; data/restraints/parameters 14 598/0/893; GOF = 0.996. Largest peak and hole 0.608 and −0.754 e/Å^3.

Crystal data for 9. $C_{41}H_{56}BF_3NO_3P_2Rh{\cdot}0.5C_5H_{12}$, M_W 879.60, red, irregular block (0.18 × 0.13 × 0.12 mm), monoclinic, space group $C2/c$, a = 30.455(2) Å, b = 14.1380(11) Å, c = 21.0720(16) Å, β = 90.7240(10)°, V = 9072.3(12) Å^3, Z = 8, D_{calc} = 1.288 g cm^{-3}, F(000) = 3688, T = 100(2) K, μ 0.496 mm^{-1}. There were 35 340 measured reflections (2θ: 3−51°, ω scans 0.3°), 8450 unique (R_{int} = 0.0832); minimum/maximum transmission factors 0.828/0.947. Final agreement factors were R1 = 0.0790 (5810 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.1582; data/restraints/parameters 8450/26/504; GOF = 1.139. Largest peak and hole 1.174 and −1.041 e/Å^3.

Crystal Data for 10. $C_{34}H_{44}F_3OP_2Rh$, M_W 690.54, red, prism (0.23 × 0.16 × 0.12 mm), orthorhombic, space group $Pmn2_1$, a = 15.142(3) Å, b = 7.5379(15) Å, c = 14.685(3) Å, V = 1676.2(6) Å^3, Z = 2, D_{calc} = 1.368 g cm^{-3}, F(000) = 716, T = 100(2) K, μ 0.646 mm^{-1}. There were 16 918 measured reflections (2θ: 4−60°, ω scans 0.3°), 3935 unique (R_{int} = 0.0418); minimum/maximum transmission factors 0.764/0.921. Flack parameter = 0.05(4). Final agreement factors were R1 = 0.0412 (3436 observed reflections, $I > 2\sigma(I)$) and wR2 = 0.1047; data/restraints/parameters 3935/1/208; GOF = 1.008. Largest peak and hole 1.000 and −0.555 e/Å^3.

■ ASSOCIATED CONTENT

Supporting Information

CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **4**, **8**, **9**, and **10**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07357.

Positional and displacement parameters, crystallographic data, and bond lengths and angles for **10** (CIF)
Positional and displacement parameters, crystallographic data, and bond lengths and angles for **9** (CIF)
Positional and displacement parameters, crystallographic data, and bond lengths and angles for **8** (CIF)
Positional and displacement parameters, crystallographic data, and bond lengths and angles for **4** (CIF)
NMR spectra of complexes **4** and **7**−**10** and IR spectrum of polymeric boryl isocyanide (PDF)

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Notes

The authors declare no competing financial interest.

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