ORGANOMETALLICS

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pubs.acs.org/Organometallics

POP−Rhodium-Promoted C−H and B−H Bond Activation and C−B Bond Formation

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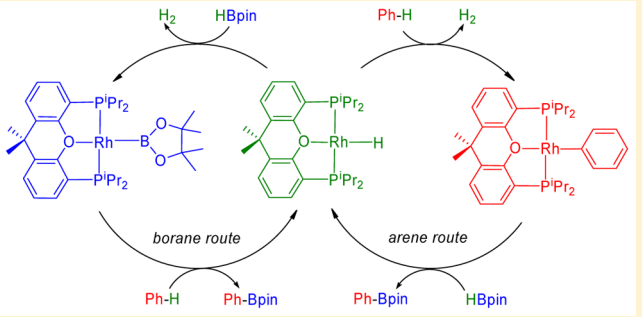
Supporting Information

ABSTRACT: The square-planar monohydride complex RhH{xant(P^iPr_2)$_2$} (**1**; xant(P^iPr_2)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene) activates C−H bonds of arenes. Heating of benzene solutions of **1** at 80 °C affords RhPh{xant(P^iPr_2)$_2$} (**2**). Under the same conditions, toluene gives Rh(*m*-tolyl){xant(P^iPr_2)$_2$} (**3a**) and Rh(*p*-tolyl){xant(P^iPr_2)$_2$} (**3b**) in a 78:22 molar ratio, whereas *m*-xylene leads to Rh(C_6H_3-3,5-Me_2){xant(P^iPr_2)$_2$} (**4**). At room temperature, fluorobenzene and 1,3-difluorobenzene generate Rh(C_6H_4-2-F){xant(P^iPr_2)$_2$} (**5**) and Rh(C_6H_3-2,6-F_2){xant(P^iPr_2)$_2$} (**6**), respectively. Complex **1** also promotes the B−H bond activation of pinacolborane (HBpin) and catecholborane (HBcat). The reactions initially give the *trans*-dihydride derivatives $RhH_2(BR_2)$\{xant(P^iPr_2)$_2$\} (BR_2 = Bpin (**7**), Bcat (**8**)), which lose H_2 to afford the square-planar $Rh(BR_2)$\{xant(P^iPr_2)$_2$\} (BR_2 = Bpin (**9**), Bcat (**10**)). Complex **2** reacts with HBpin to regenerate **1** and to give Ph-Bpin. Similarly, complex **9** regenerates **1** and gives Ph-Bpin by reaction with benzene. In agreement with these transformations, complex **1** catalyzes the direct C−H borylation of arenes. The selectivity of the process appears to be governed by the kinetic of the C−H bond activations of the arenes. Benzylic borylation is not observed for methylbenzenes. The first X-ray structure of a square-planar rhodium−boryl complex is also reported.



INTRODUCTION

C−H bond functionalization reduces the production of toxic byproducts thereby contributing to the growing field of reactions with decreased environmental impact.[1] One of the most efficient reactions is the direct borylation of hydrocarbons, which represents a powerful tool for the functionalization of feedstocks,[2] in combination with cross-coupling methodologies or specific transformations developed for organoboranes.[3]

The borylation of arenes without the need for directing groups is a challenge in the field of C−H bond functionalization because it provides products with complementary regioselectivity, which appears to be determined by steric factors.[4] In this context, significant progress is being made by using iron,[5] cobalt,[6] rhodium,[7] and iridium[8] catalysts with bispinacolborane (B_2pin_2) and pinacolborane (HBpin). The processes take place via stoichiometric reactions involving the sequential cleavage of both C−H[9] and B−H[10] bonds and the formation of B−C and H−H bonds on the metal center of a transition metal complex. Accordingly, the study of these elemental steps is of great interest.

Complexes containing diphosphine pincer ligands show marked abilities to stabilize uncommon species as a consequence of the disposition of their donor ligands.[11] Among the ligands of this type, those based on POP skeletons have a particular interest due to the hemilabile properties of the central oxygen atom. Their reversible κ^3-κ^2 conversion[12] facilitates transformations, which are disfavored with the classical more rigid PNP and PCP systems. With this in mind, we have recently initiated a research program on POP complexes of groups 8 and 9 metals, in the search for new transition metal catalysts.[13] Thus, following the procedure used by Werner to generate $[RhCl(P^iPr_3)_2]_2$,[14] we prepared the square-planar derivative RhCl{xant(P^iPr_2)$_2$} (xant(P^iPr_2)$_2$ = 9,9-dimethyl-4,5-bis(diisopropylphosphino)xanthene).[13e] In agreement with the impact generated by the pincer ligands in homogeneous catalysis,[15] rhodium complexes containing POP ligands had previously shown to be catalysts of interesting organic reactions including the hydroacylation of alkenes and alkynes,[16] the hydroformylation of olefins,[17] the methanol carbonylation,[18] the intramolecular hydroamination of unprotected primary aminoalkenes,[19] or the carbothiolation of alkynes.[20] In parallel with our work, Goldman has observed that the cationic dihydride $[RhH_2$\{xant(P^iPr_2)$_2$\}$]^+$ functions as a modestly active alkane dehydrogenation catalyst,[21] and recently, Manners and Weller have shown that [Rh(xantphos)]$^+$ promotes dehydrocoupling and dehydropolymerization of amine-boranes[22] and the hydroboration of alkenes with amine-boranes.[23]

Received: March 3, 2015

DOI: 10.1021/acs.organomet.5b00176
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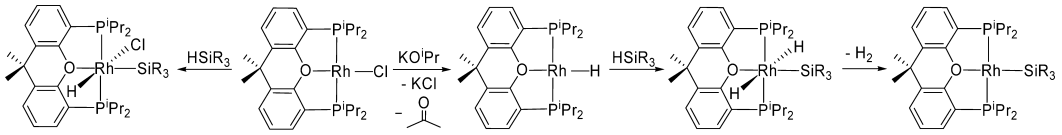
Scheme 1



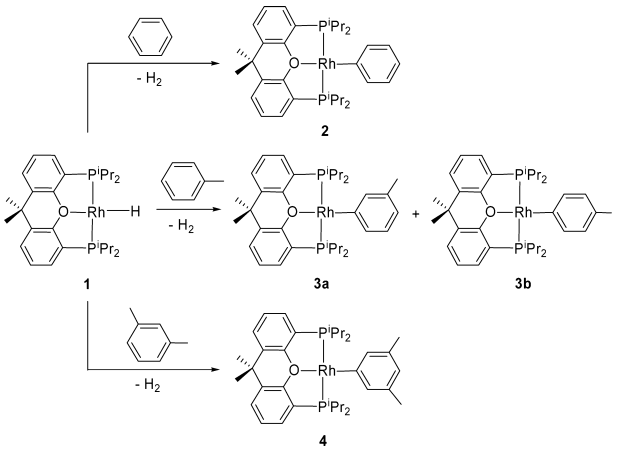
Complex RhCl{xant(P^iPr_2)$_2$} is transformed into the square-planar monohydride RhH{xant(P^iPr_2)$_2$} by reaction with KO^{i}Pr in 2-propanol (Scheme 1).[13e] This compound, which is a notable example of four-coordinate group 8 metal hydride derivative,[24] has been also prepared by Goldman's group[21] by means of a two-step procedure involving the initial oxidative addition of H_2 to the starting chloro-derivative and the subsequent reaction of the resulting rhodium(III)-dihydride with KO^{t}Bu in benzene. The π-basicity of the chloride ligand enhances the nucleophilicity of MX{xant(P^iPr_2)$_2$} (M = Rh, Ir; X = Cl, H) fragments with regard to the hydride.[13e,f] As a result, there is a marked difference in stability between the rhodium(III) species resulting from the oxidative addition processes to the corresponding square-planar complexes. Thus, while the Si−H bond activation of silanes promoted by the chloro complex leads to stable rhodium(III) derivatives, the oxidative addition of the Si−H bond to the monohydride generates dihydride-silyl species, which are unstable and lose H_2 to afford square-planar rhodium(I)-silyl compounds (Scheme 1); that is, the hydride ligand decreases the nucleophilicity of the RhX{xant(P^iPr_2)$_2$} fragment enhancing the lability of the saturated rhodium(III) species. The chloride by hydride replacement should therefore increase the catalytic potentiality of the system. This reason prompted us to select to the monohydride complex RhH{xant(P^iPr_2)$_2$} to investigate the elemental steps involved in the direct C−H borylation of arenes. This paper reports the C−H bond activation of arenes, the B−H bond activation of boranes, and the stoichiometric and catalytic formation of aryl boronate esters promoted by the square-planar rhodium monohydride.

RESULTS AND DISCUSSION

1. C−H Bond Activation Reactions. The square-planar monohydride complex RhH{xant(P^iPr_2)$_2$} (**1**) activates aromatic C−H bonds of benzene, toluene, and *m*-xylene. The reactions lead to aryl−rhodium(I) complexes and release molecular hydrogen. The selectivity of the processes involving the substituted benzenes depends upon the position of the substituents (Scheme 2).

Heating of benzene solutions of **1** at 80 °C for 48 h affords the phenyl derivative RhPh{xant(P^iPr_2)$_2$} (**2**) in a quantitative manner, although it was isolated as a red solid in 33% yield due to its high solubility in the usual organic solvents. Complex **2** was characterized by X-ray diffraction analysis. The structure has two chemically equivalent but crystallographically independent molecules in the asymmetric unit. Figure 1 shows a drawing of one of them. As expected, the Rh{xant(P^iPr_2)$_2$} skeleton is T-shaped, with the metal situated in the common vertex and P(1)−Rh(1)−O(1), P(2)−Rh(1)−O(1), and P(1)−Rh(1)−P(2) angles of 82.15(8)° and 82.35(8)°, 83.38(8)° and 82.62(8)°, and 164.28(5)° and 163.00(4)°, respectively. Thus, the geometry around the rhodium atom is almost square-planar, with the phenyl group trans disposed to the oxygen atom (O(1)−Rh(1)−C(1) = 179.14(14)° and 177.45(14)°). The greatest deviation from the best plane through Rh(1), C(1), P(1), O(1), and P(2) atoms is 0.0716 Å

Scheme 2



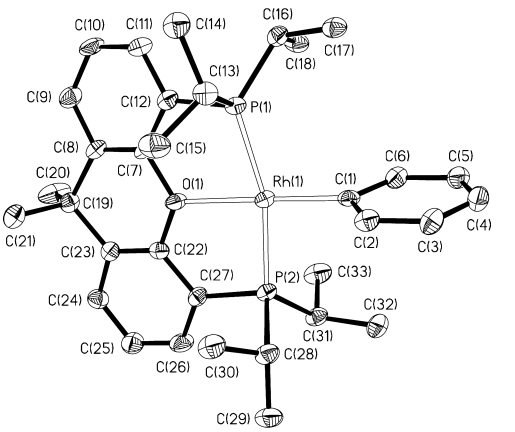


Figure 1. ORTEP diagram of complex **2** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−P(1) = 2.2460(12), 2.2530(12), Rh(1)−P(2) = 2.2293(12), 2.2333(12); Rh(1)−O(1) = 2.214(3), 2.216(3), Rh(1)−C(1) = 1.977(4), 1.979(5); P(1)−Rh(1)−P(2) = 164.28(5), 163.00(4), P(1)−Rh(1)−O(1) = 82.15(8), 82.35(8), P(2)−Rh(1)−O(1) = 83.38(8), 82.62(8), O(1)−Rh(1)−C(1) = 179.14(14), 177.45(14).

in a molecule and 0.0874 Å in the other one and involves to P(2). The metalated aromatic ring lies almost perpendicular to the coordination plane with dihedral angles of 85.93° and 79.45°. The Rh(1)−C(1) bond lengths of 1.977(4) and 1.979(5) Å compare well with those found in the scarcely reported square-planar aryl-rhodium(I) complexes (1.84−2.10 Å).[25] The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **2**, in benzene-d_6, at room temperature are consistent with the structure given in Figure 1. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonance is that corresponding to the phenyl metalated carbon atom, which appears at 162.0 ppm as a double triplet with C−Rh and C−P coupling constants of 41.2 and 12.2 Hz, respectively. In agreement with equivalent P^iPr_2

DOI: 10.1021/acs.organomet.5b00176
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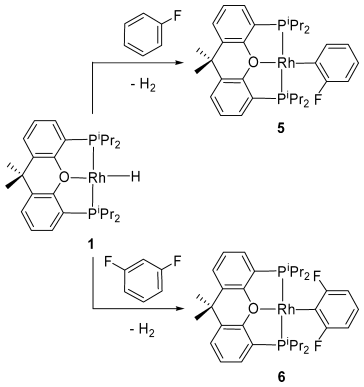
groups, the $^{31}P\{^{1}H\}$ NMR spectrum shows at 36.4 ppm a doublet with a typical P−Rh(I) coupling constant of 177.1 Hz.

Stirring of toluene solutions of **1** at 80 °C for 24 h produces the quantitative transformation of the starting monohydride into the tolyl derivatives Rh(*m*-tolyl){xant(P^iPr_2)$_2$} (**3a**) and Rh(*p*-tolyl){xant(P^iPr_2)$_2$} (**3b**), which are formed in approximately 78:22 molar ratio. Benzylic bond activation is not observed, despite the fact that products of this type have been observed previously in related reactions using methyl-substituted benzenes.[26] The cleavage of the *meta*- and *para*-CH bonds is preferred with regard to the *ortho*-CH bond rupture from both thermodynamic and kinetic points of view, whereas the *meta*−C-H bond cleavage is the statistically preferred and has been the observed one for the majority of transition metal precursors.[27] Only a few half-sandwich systems favor the formation of the *para* products over the *meta* isomers.[28] The mixture of isomers was isolated as red crystals in 22% yield. The X-ray structure of one of them reveals the cocrystallyzation of **3a** and **3b** in a 71:29 molar ratio (see Supporting Information). Although accurate structural parameters could not be obtained, the data prove the C−H bond activation of both positions of the substrate. The $^{13}C\{^{1}H\}$ NMR spectrum of the *meta* isomer **3a**, in benzene-d_6, at room temperature is consistent with the low symmetry of the tolyl ligand. Thus, it shows five tolyl-resonances, at 140.6, 136.9, 126.0, 125.2, and 119.5 ppm, along with the signal due to the metalated carbon atom, which is observed at 161.6 ppm as a double triplet with C−Rh and C−P coupling constants of 40.5 and 12.6 Hz, respectively. In the $^{31}P\{^{1}H\}$ NMR spectrum, the diphosphine displays a doublet, with a P−Rh coupling constant of 177.8 Hz, at 35.9 ppm. In agreement with its higher symmetry, the *para* isomer **3b** gives rise to three tolyl resonances at 139.5, 126.8, and 125.6 ppm, in the $^{13}C\{^{1}H\}$ NMR spectrum, along with the signal corresponding to the metalated carbon atom which overlaps with that of **3a**. A doublet with a P−Rh coupling constant of 178.2 Hz, at 35.6 ppm, in the $^{31}P\{^{1}H\}$ NMR spectrum is also a characteristic feature of this isomer.

Thermolysis of **1** in *m*-xylene, at 80 °C, for 24 h gives rise to the quantitative formation of the xylenyl derivative Rh(C_6H_3-3,5-Me_2){xant(P^iPr_2)$_2$} (**4**), as a result of the cleavage of the aromatic C−H bond of the substrate equidistant to the methyl substituents. The exclusive formation of **4** agrees well with that observed by Brookhart and Templeton[27a] and Puddephatt[29] about the C−H bond activation of *m*-xylene on platinum(IV) and platinum(II) precursors. Complex **4** was isolated as red crystals in 42% yield. As expected for the positions of the aryl substituents, the $^{13}C\{^{1}H\}$ NMR spectrum of **4**, in benzene-d_6, at room temperature shows three xylenyl resonances, at 138.6, 126.2, and 120.8 ppm, along with a double triplet (J_{C-Rh} = 40.2 Hz, J_{C-P} = 12.4 Hz) at 161.1 ppm assigned to the metalated carbon atom. In accordance with **2** and **3**, the $^{31}P\{^{1}H\}$ NMR spectrum of **4** contains at 35.6 ppm a doublet with a P−Rh coupling constant of 178.3 Hz.

The square-planar monohydride complex **1** also activates a C−H bond of fluorobenzene and 1,3-difluorobenzene[30] at room temperature. The reactions are even faster that those with toluene and *m*-xylene. There are further marked differences in selectivity. In contrast with the methyl counterparts, the activations take place close to the fluorine substituents (Scheme 3). Stirring of **1** in fluorobenzene for 3 h gives rise to the quantitative formation of Rh(C_6H_4-2-F){xant(P^iPr_2)$_2$} (**5**), as a result of the cleavage of the C−H bond of the solvent disposed

Scheme 3



in *ortho* position with regard to the substituent, whereas complex **1** rapidly evolves into Rh(C_6H_3-2,6-F_2){xant(P^iPr_2)$_2$} (**6**) in 1,3-difluorobenzene, as a consequence of the cleavage of the C−H bond of the arene situated between the fluorine atoms (i.e., *ortho* to both substituents). The reason for the observed selectivity appears to be thermodynamic in origin. In this context, it should be noted that the M-C bond energy increases with the *ortho*-fluorine substitution, becoming between 2 and 3 times higher than the C−H bond energy depending upon the metal fragment.[31] The *ortho*-fluorine effect has been explained in terms of an increase of the ionic component of the M−C bond through inductive effect of the *ortho*-fluorine atom.[9d] The reactivity of **1** toward fluorobenzene and 1,3-difluorobenzene agrees well with that recently reported by Braun for $RhH(PEt_3)_3$,[32] containing monodentated phosphines instead of a POP pincer. However, it is in contrast with the behavior observed for the saturated compounds $OsTp\{\kappa^1\text{-}C[NC_5H_3Me]\}(\eta^2\text{-}CH_2{=}CH_2)_2$[33] and $[OsTp(CH_2CH_2P^iPr_3)(\eta^2\text{-}CH_2{=}CH_2)_2]BF_4$[34] (Tp = hydridotris(pyrazolyl)borate), which activate fluorobenzene, 1,3-difluorobenzene, and substituted 1,3-chlorobenzenes, via σ-bond metathesis, to afford products resulting from the cleavage of the C−H bond more distant from the substituents.

Complexes **5** and **6** were isolated as orange solids in 91% and 73% yield, respectively, and characterized by X-ray diffraction analysis. The structures prove the *ortho*-activation of the substrates. Figure 2 shows a drawing of **5**. Like for **2**, the coordination geometry around the rhodium atom is almost square-planar with the diphosphine coordinated in a *mer*-fashion (P(1)−Rh(1)−O(1) = P(1A)-Rh(1)−O(1) = 82.73(2), P(1)−Rh(1)−P(1A) = 161.13(4)°) and the aryl group *trans* disposed to the oxygen atom (C(1)−Rh(1)−O = 179.90(14)°). The Rh(1)−C(1) bond length of 1.994(4) Å is statistically identical with those of **2**. The $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of this compound, in benzene-d_6, at room temperature are consistent with the structure shown in Figure 2. Thus, as expected, the $^{13}C\{^{1}H\}$ NMR spectrum shows six resonances between 168 and 111 ppm for the inequivalent carbon atoms of the metalated ring, whereas the $^{31}P\{^{1}H\}$ NMR spectrum contains at 40.0 ppm a double doublet (J_{P-Rh} = 167.6 Hz, J_{P-F} = 4.2 Hz) for the equivalent P^iPr_2 groups of the diphosphine. The structure of **6** (Figure 3) resembles those of **2** and **5** with P(1)−Rh(1)−O = P(1A)-Rh(1)-O, P(1)−Rh-P(1A) and C(1)−Rh(1)−O angles of 82.782(10)°, 161.611(18)° and 179.45(6)°, respectively. The Rh(1)−C(1) distance of 1.9898(19) Å is statistically identical with those of both **2** and **5**. Although the resonance corresponding to the

DOI: 10.1021/acs.organomet.5b00176
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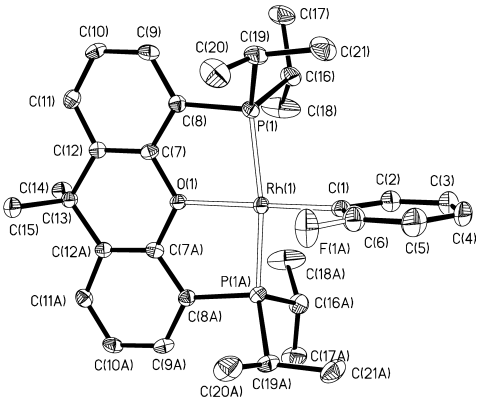


Figure 2. ORTEP diagram of complex **5** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−P(1) = 2.2520(8), Rh(1)−O(1) = 2.193(3), Rh(1)−C(1) = 1.994(4); P(1)−Rh(1)−P(1A) = 161.13(4), P(1)−Rh(1)−O(1) = 82.73(2), P(1A)−Rh(1)−O(1) = 82.73(2), O(1)−Rh(1)−C(1) = 179.90(14).

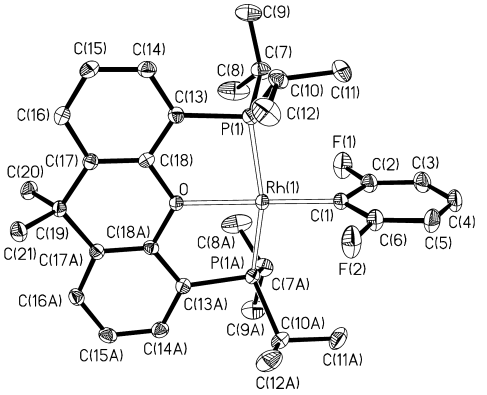


Figure 3. ORTEP diagram of complex **6** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh(1)−P(1) = 2.2521(3), Rh(1)−O = 2.1850(13), Rh(1)−C(1) = 1.9898(19); P(1)−Rh(1)−P(1A) = 161.611(18), P(1)−Rh(1)−O(1) = 82.782(10), P(1A)−Rh(1)−O(1) = 82.781(10), O(1)−Rh(1)−C(1) = 179.45(6).

metalated aryl carbon atom is missing in the $^{13}C\{^1H\}$ NMR spectrum, it reflects the symmetry of the coordinated aryl group, showing one C−F resonance at 167.4 ppm and two C−H resonances at 121.6 and 108.5 ppm. The $^{31}P\{^1H\}$ NMR spectrum contains at 43.0 ppm a double triplet with P−Rh and P−F coupling constants of 159.8 and 3.7 Hz, respectively.

2. B−H Bond Activation Reactions. In agreement with the marked diagonal relationship between boron and silicon, which is also evident in the chemistry of the platinum group metals,[35] complex **1** reacts with pinacolborane (HBpin) and catecholborane (HBcat) to afford boryl derivatives (Scheme 4), which are diagonal counterparts of the silyl complexes shown in Scheme 1.

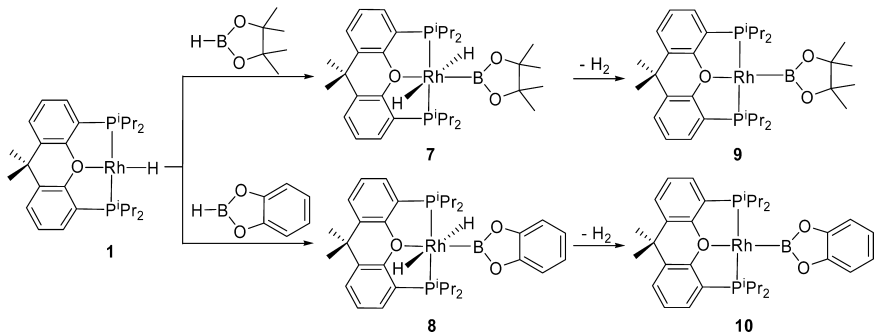
The addition of 1.0 equiv of the boron hydrides, at −15 °C, to toluene solutions of **1** gives rise to the immediate and quantitative formation of the *trans*-dihydride-rhodium(III) compounds $RhH_2(BR_2)\{xant(P^iPr_2)_2\}$ (BR_2 = Bpin (**7**), Bcat (**8**)), in a diastereoselective process with specific B−H orientation.[36] The oxidative addition takes place along the O−Rh−H axis with the boron atom directed toward the hydride ligand. The mutually *trans* disposition of the hydride ligands is strongly supported by the ^1H NMR spectra of these complexes, which show only one high field resonance. It appears at about −6.0 ppm as a double triplet with H−Rh ad H−P coupling constants of about 23 Hz and between 16 and 13 Hz, respectively. In accordance with the single character of the Rh−B bonds, the $^{11}B\{^1H\}$ NMR spectra contain a broad resonance at 33.3 ppm for **7** and at 34.7 ppm for **8**. The equivalent P^iPr_2 groups display, at 68.3 ppm for **7** and 63.8 ppm for **8**, a doublet with a P−Rh coupling constant of about 130 Hz in the $^{31}P\{^1H\}$ NMR spectra.

The high *trans* influence of the hydride ligand[37] makes unstable the *trans*-dihydride complexes **7** and **8**. Thus, At room temperature, in solution, they lose molecular hydrogen to afford the boryl derivatives $Rh(BR_2)\{xant(P^iPr_2)_2\}$ (BR_2 = Bpin (**9**), Bcat (**10**)), which were isolated as red solids in 93% (**9**) and 70% (**10**) yield. The *trans* disposition of the hydride ligands prevents the three-centered transition state for the hydrogen reductive elimination. However, the previously mentioned hemilability of the phosphine oxygen atom makes feasible the *trans*−*cis*-isomerization, which allows the formation of a transitory dihydrogen intermediate as a previous step to the hydrogen release.

Complex **9**, plus HBpin, is also formed in a quantitative manner by reaction of compound **1** with one equivalent of B_2pin_2.

Complex **9** has been characterized by X-ray diffraction analysis. In this context, it should be noted that boryl complexes of rhodium(I) are very rare,[38] in particular four-coordinate species. As far as we know only the compounds $Rh(BR_2)(PEt_3)_3$ (BR_2 = Bpin, Bcat, $BO_2C_5H_{10}$)[24f,39] and $Rh(BR_2)(PPh_3)_3$[40] have been previously characterized, but not by X-ray diffraction analysis. Figure 4 shows a drawing of the molecule. The coordination geometry around the rhodium

Scheme 4



DOI: 10.1021/acs.organomet.5b00176
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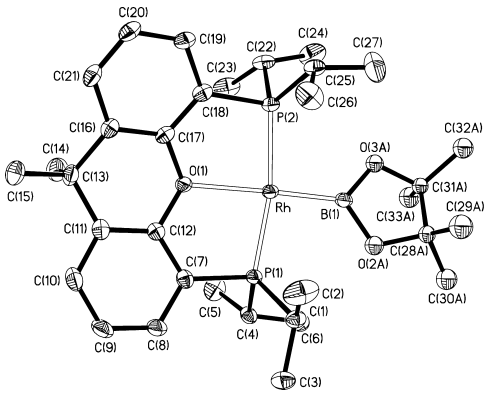


Figure 4. ORTEP diagram of complex **9** (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−P(1) = 2.2255(9), Rh−P(2) = 2.2432(9), Rh(1)−O(1) = 2.268(2), Rh−B(1) = 1.981(4); P(1)−Rh(1)−P(2) = 161.98(3), P(1)−Rh−O(1) = 83.07(6), P(2)−Rh−O(1) = 82.98(6), O(1)−Rh(1)−C(1) = 177.22(14).

atom is almost square-planar with the diphosphine coordinated in the expected pincer fashion (P(1)−Rh−O(1) = 83.07(6)°, P(2)−Rh-O(1) = 82.98(6)°, and P(1)−Rh-P(2) = 161.98(3)°) and the boryl group *trans* disposed to the oxygen atom of the diphosphine (B(1)−Rh−O(1) = 177.22(14)°). The Rh−B(1) bond length is 1.981(4) Å. The $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of **9** and **10** are consistent with the reduction of the metal center as a result of the release of molecular hydrogen from **7** and **8**. Thus, the $^{11}B\{^1H\}$ NMR spectra contain broad resonances, at 42 (**9**) and 49 (**10**) ppm, which are shifted 9 and 14 ppm toward lower field with regard to the respective signals corresponding to the rhodium(III) dihydride precursors. The $^{31}P\{^1H\}$ NMR spectra show, at 51.9 (**9**) and 55.1 (**10**) ppm, doublets with P−Rh coupling constants of 176.0 and 165.3 Hz, respectively, which are between 46 and 35 Hz higher that these of **7** and **8**.

3. Stoichiometric Formation of Ph−Bpin. The addition of 1.0 equiv of B_2pin_2 to toluene solutions of the phenyl complex **2**, at 60 °C, leads to Ph−Bpin and the boryl derivative **9**. The formation of these compounds is strongly supported by the $^{11}B\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra of the mixtures generated during the first 24 h of reaction (Figure 5). In benzene, the boryl complex **9** affords Ph−Bpin and the monohydride **1**, which regenerates the phenyl derivative **2** and releases molecular hydrogen in accordance with Scheme 2. These elemental reactions can be combined in a cycle (Scheme 5) for the RhH{xant(P^iPr_2)$_2$}-promoted borylation of benzene with B_2pin_2, according to eq 1, where the aryl complex **2** and the boryl derivative **9** are implied as intermediates.

The phenyl complex **2** also reacts with HBpin, in toluene, at 55 °C. The reaction gives Ph−Bpin and the monohydride **1**. This transformation, which is faster than the reaction between **2** and B_2pin_2, and the C−H bond activation of benzene promoted by **1** to afford **2** form an alternative cycle (A in Scheme 6), in this case, for the RhH{xant(P^iPr_2)$_2$}-promoted borylation of benzene with HBpin according to the mass balance shown in eq 2. Because complex **1** reacts with HBpin to afford molecular hydrogen and the boryl derivative **9** (Scheme 4) and the latter gives Ph−Bpin and regenerates **1**, in benzene, the reaction shown in eq 2 can also take place via the cycle B of Scheme 6. In other words, Scheme 6 suggests that the RhH{xant(P^iPr_2)$_2$}-promoted borylation of arenes with HBpin to give aryl-Bpin

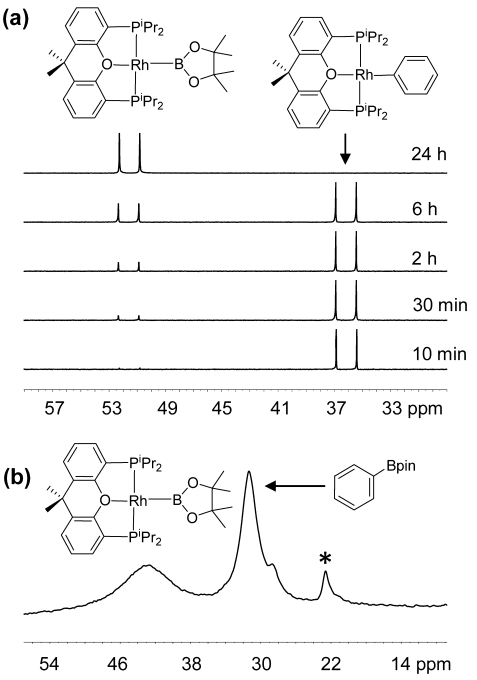
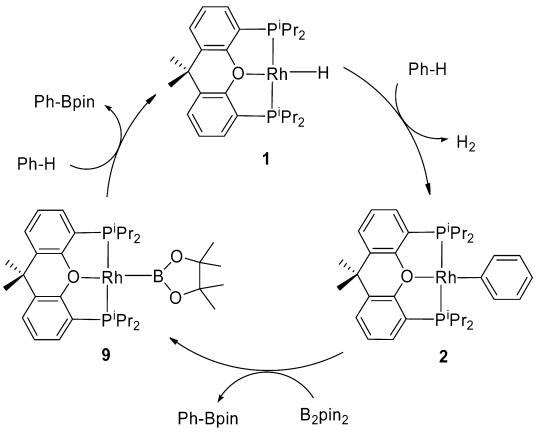


Figure 5. (a) Stacked $^{31}P\{^1H\}$ NMR spectra showing the transformation of RhPh{xant(P^iPr_2)$_2$} (**2**) into Rh(Bpin){xant(P^iPr_2)$_2$} (**9**) by reaction with B_2pin_2 (toluene, 60 °C). (b) $^{11}B\{^1H\}$ NMR spectrum of the reaction after 24 h at 60 °C. * B_2pin_3 (decomposition product).

Scheme 5



and molecular hydrogen could go through two routes; arene and borane. The first of them, *the arene route*, should involve the initial C−H bond activation of the arene followed by the reaction of the resulting aryl complex with the boron-hydride, while the second one, *the borane route*, could proceed through the initial H−B bond activation of the borane followed by the reaction of the resulting boryl intermediate with the arene.

$$2\text{Ph-H} + B_2pin_2 \rightarrow 2\text{Ph-B pin} + H_2 \quad (1)$$

$$\text{Ph-H} + \text{HBpin} \rightarrow \text{Ph-Bpin} + H_2 \quad (2)$$

4. Catalytic Borylation of Arenes. As expected from the reactions summarized in Schemes 5 and 6, the monohydride complex **1** is an efficient catalyst for the borylation of benzene with both B_2pin_2 and HBpin. The reactions were performed in the arene as solvent, at 110 °C, and using a Rh/B molar ratio of

DOI: 10.1021/acs.organomet.5b00176
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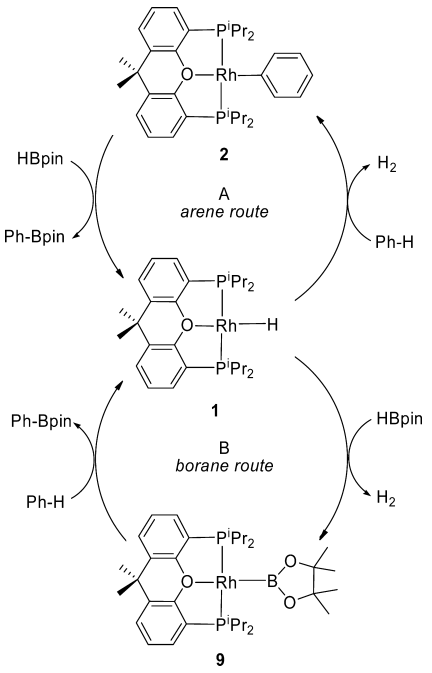
Scheme 6

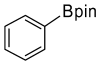
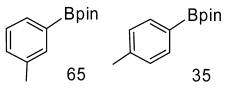
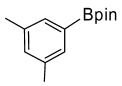
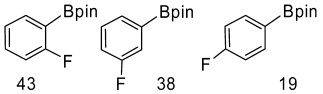
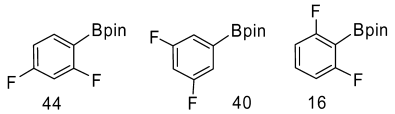
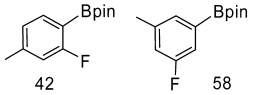
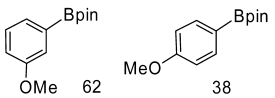


1:25. After 24 h, under these conditions, the borylation with B_2pin_2 (eq 1) affords Ph−Bpin with an isolated yield of 68%, whereas starting from HBpin (eq 2), the borylation product was isolated in 66% yield. The addition, to the catalytic solution, of 1.0 equiv of cyclohexene as hydrogen acceptor per equiv of boron increases the yield of the reactions up to 89% in the first case and up to 95% in the second case. Because the borylation with HBpin, in the presence of cyclohexene, appears to be more efficient than that with B_2pin_2, we explored the scope of this arene functionalization under these conditions. Table 1 collects the arenes investigated and the obtained results.

Complex **1** is efficient not only for the benzene borylation (run 1) but also for the borylation of methyl substituted benzenes (runs 2 and 3). In contrast to the related precursor $RhCl(P^iPr_3)_2(N_2)$,[41] containing the monodentated triisopropylphosphine, the formation of benzylboronate esters is not observed in our case. This is consistent with the rigidity and robustness of **1**, imposed by the POP diphosphine, which prevents the formation of η^3-benzyl intermediates, the key species in the benzylic borylation. Toluene (run 2) is quantitatively transformed into the *meta*- and *para*-tolylboronate esters in a 65:35 molar ratio after 48 h. This isomers ratio agrees well with that observed for the stoichiometric C−H bond activation of the substrate, according to Scheme 2. This suggests that under the reaction conditions employed, toluene as solvent and 110 °C, the arene is the main route (A in Scheme 6) for the catalysis and that the reactions of the tolyl complexes **3a** and **3b** with HBpin are fast. Therefore, the selectivity of the process is determined by the kinetic of the toluene C−H bond activations. Also in agreement with Scheme 3, *m*-xylene (run 3) is quantitatively borylated in position *meta* with regard to both substituents.

The borylation of fluoroarenes is more complex. Fluorobenzene (run 4) and 1,3-difluorobenzene (run 5) yield mixtures of the three possible isomers, in contrast to the selectivity observed for the C−H bond activation reactions of

Table 1. Borylation of Arenes Catalyzed by RhH{xant(P^{i}Pr$_2$)$_2$} (1)[a]

Run	Arenes	Products [b]	Time (h)	Yield (%) [c]
1			24	100 (95)
2		 65 35	48	100 (98)
3			48	100 (99)
4		 43 38 19	24	100 (99)
5		 44 40 16	24	100 (99)
6		 42 58	24	74 (73)
7		 OMe 62 MeO 38	24	67 (65)

[a]4 mol % **1**, 2.06 mmol HBpin, 2.00 mmol cyclohexene, 5 mL of arene, 110 °C. [b]The numbers indicate the ratio of products. [c]Isolated yields are reported in parentheses.

DOI: 10.1021/acs.organomet.5b00176
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the arenes (Scheme 3). It should be even noted that, for 1,3-difluorobenzene, the borylation at the C−H bond position between both fluorine substituents is the less favored. These results are consistent with those obtained for methylbenzenes, because they also suggest that the selectivity of the catalysis is governed by the kinetic of the C−H bond activations of the arene. The borylation of 3-fluorotoluene (run 6) appears to be run by the methyl susbtituent, which keeps the boryl fragment away from it.

Anisole (run 7) shows a similar behavior to toluene, suggesting that the oxygen atom of the ether does not play any significant role in the selectivity of the process.

■ CONCLUDING REMARKS

This study reveals that the square-planar monohydride complex RhH{xant(P^iPr_2)$_2$} promotes the C−H bond activation of arenes, the B−H bond activation of pinacolborane and catecholborane, and the stoichiometric and catalytic borylation of arenes.

The C−H bond activation products depend upon the substituents of the arene. Methyl groups keep the metal fragment away from them, whereas the metal fragment moves toward the fluorine substituents. Thus, the observed selectivity suggests that the activation is thermodynamically controlled.

The B−H bond activation of the boranes is a diastereoselective process with specific B−H bond orientation. The oxidative addition takes place along the O−Rh−H axis of the monohydride, with the boron atom toward the hydride, and selectively leads to *trans*-dihydride-boryl-rhodium(III) intermediates, which lose molecular hydrogen to afford rare square-planar rhodium(I) boryl derivatives. The X-ray characterization of one of them allows us to report the first structure of a compound of this type.

The stoichiometric borylation of arenes with pinacolborane can be performed by means of two pathways, arene and borane routes. The first of them involves the initial C−H bond activation of the arene followed by the reaction of the resulting aryl intermediate with the borane, while the borane route involves the initial B−H bond activation of the borane and the subsequent reaction of the resulting boryl intermediate with the arene. In spite of this, the comparison between the selectivities observed in the stoichiometric arene C−H bond activation and the catalytic arene borylation suggests that, under the experimental conditions employed for the catalysis, the arene route is the main pathway to the formation of the borylation products and that the selectivity of the process is governed by the kinetic of the C−H bond activation of the arenes.

In conclusion, the characteristic of rigidity and robustness provided by the POP diphosphine 9,9-dimethyl-4,5-bis-(diisopropylphosphino)xanthene, along with the hemilability of its oxygen atom, give to the square-planar monohydride RhH{xant(P^iPr_2)$_2$} the capacity of promoting the arene borylation, of serving as model to study the stoichiometric steps of the process, and to be the starting material to isolate the key intermediates.

■ 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 all the arenes were dried and distilled under argon. Pinacolborane and B_2pin_2 were purchased from commercial sources and used without further purification. Catecholborane was purchased from commercial sources and distilled in a Kugelrohr distillation over. ^{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), 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). RhH{xant(P^iPr_2)$_2$} (**1**) was prepared by the published method.[13e]

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with Benzene: Preparation of RhPh{xant(P^iPr_2)$_2$} (2). Complex **1** (200 mg, 0.37 mmol) was dissolved in benzene (5 mL), and the resulting mixture was stirred during 48 h at 80 °C. After this time, it was concentrated to dryness to afford a red residue. Addition of pentane (5 mL) afforded a red solid, which was further washed with pentane (6 × 1 mL), and lastly, it was dried in vacuo. Yield: 82 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. Anal. Calcd for $C_{33}H_{45}OP_2Rh$: C, 63.66; H, 7.28. Found: C, 64.03; H, 7.47. HRMS (electrospray, m/z): calcd for $C_{33}H_{45}OP_2Rh$ $[M]^+$, 622.1995; found, 622.2037. IR (cm^{-1}): ν(C═C) 1559 (w), ν(C−O−C) 1099 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.06 (d, J_{H-H} = 7.2, 2H, *o*-CH Ph), 7.27 (m, 2H, C*H*-arom POP), 7.21 (t, J_{H-H} = 7.2, 1H, *m*-CH Ph), 7.04 (dd, J_{H-H} = 7.7, J_{H-H} = 1.6, 2H, C*H*-arom POP), 6.97 (t, J_{H-H} = 7.2, 1H, *p*-CH Ph), 6.86 (t, J_{H-H} = 7.5, 2H, C*H*-arom POP), 2.40 (m, 4H, PC*H*$(CH_3)_2$), 1.24 (s, 6H, CH_3), 1.23 (dvt, J_{H-H} = 7.2, N = 15.7, 12H, PCH$(CH_3)_2$), 1.18 (dvt, J_{H-H} = 7.0, N = 13.3, 12H, PCH$(CH_3)_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 162.0 (dt, J_{C-Rh} = 41.2, J_{C-P} = 12.2, Rh−C), 156.2 (dvt, J_{C-Rh} = 0.9, N = 16.0, Carom POP), 139.9 (t, J_{C-P} = 3.1, *o*-CH Ph), 131.3 (s, CH arom POP), 130.7 (vt, N = 6, Carom POP) 127.7 (s, CH-arom POP), 126.0 (vt, N = 21.7, Carom POP), 125.6 (dt, J_{C-Rh} = 2.3, J_{C-P} = 1.0, *m*-CH Ph), 124.0 (vt, N = 4.0, CH-arom POP), 118.4 (t, J_{C-P} = 1.6, *p*-CH Ph), 34.1 (s, $C(CH_3)_2$), 33.0 (s, $C(CH_3)_2$), 25.3 (dvt, J_{C-Rh} = 2.9, N = 17.5, PCH$(CH_3)_2$), 19.4 (vt, N = 8.4, PCH$(CH_3)_2$), 18.7 (vt, N = 3.0, PCH$(CH_3)_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 36.4 (d, J_{P-Rh} = 177.1).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with Toluene: Preparation of Rh(*m*-tolyl){xant(P^iPr_2)$_2$} (3a) and Rh(*p*-tolyl){xant(P^iPr_2)$_2$} (3b). Complex **1** (200 mg, 0.37 mmol) was dissolved in toluene (5 mL), and the resulting mixture was stirred during 24 h at 80 °C. After this time, it was concentrated to dryness to afford a red residue. Addition of pentane (5 mL) afforded a red solid, which was further washed with pentane (15 × 1 mL), and lastly, it was dried in vacuo. Yield: 52 mg (22%). ^{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 mixture in pentane. ^{1}H and ^{31}P{^{1}H} NMR spectra show a mixture of **3a** and **3b** in a ratio of 78:22. Anal. Calcd for $C_{34}H_{47}OP_2Rh$: C, 64.15; H, 7.44. Found: C, 63.80;

DOI: 10.1021/acs.organomet.5b00176
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H, 7.08. IR (cm^{-1}): ν(C═C) 1556 (w), ν(C−O−C) 1098 (m).

Spectroscopic data for Rh(*m*-tolyl){xant(P^iPr_2)$_2$} (**3a**): ^{1}H NMR (500.13 MHz, C_6D_6, 298 K): δ 7.94 (s, 1H, *o*−C*H* Ph), 7.88 (d, 1H, J_{H-H} = 7.3, *o*−C*H* Ph), 7.29 (m, 2H, C*H*-arom POP), 7.16 (t, J_{H-H} = 7.3, 1H, *m*−C*H* Ph), 7.05 (dd, J_{H-H} = 6.5, J_{H-H} = 1.5, 2H, C*H*-arom POP), 6.86 (t, J_{H-H} = 7.5, 2H, C*H*-arom POP), 6.78 (d, J_{H-H} = 7.3, 1H, *p*−C*H* Ph), 2.46 (s, 3H, CH_3Ph), 2.42 (m, 4H, PC*H*(CH$_3$)$_2$), 1.26 (dvt, J_{H-H} = 7.0, *N* = 16.1, 12H, PCH(CH_3)$_2$), 1.24 (s, 6H, CH_3), 1.20 (dvt, J_{H-H} = 6.8, *N* = 13.7, 12H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 161.6 (dt, J_{C-Rh} = 40.5, J_{C-P} = 12.6, Rh−C), 156.2 (vt, *N* = 16.3, C*arom* POP), 140.6 (t, J_{C-P} = 2.9, *o*-CH Ph), 136.9 (t, J_{C-P} = 2.9, *o*-CH Ph), 131.3 (s, C*H* arom POP), 130.8 (vt, *N* = 5.4, C*arom* POP), 128.0 (overlapping with C_6D_6, C*arom* POP), 127.6 (s, C*H*-arom POP), 126.0 (t, J_{C-P} = 7.1, *m*-C Ph), 125.2 (s, *m*-CH Ph), 124.0 (s, C*H*-arom POP), 119.5 (s, *p*-CH Ph), 34.1 (s, *C*(CH$_3$)$_2$), 33.0 (s, C(*C*H$_3$)$_2$), 25.3 (dvt, J_{C-Rh} = 2.8, *N* = 17.4, PCH(CH$_3$)$_2$), 22.4 (s, Ph-*C*H$_3$), 19.5 (vt, *N* = 8.5, PCH-(CH$_3$)$_2$), 18.7 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 35.9 (d, J_{P-Rh} = 177.8).

Spectroscopic data for Rh(*p*-tolyl){xant(P^iPr_2)$_2$} (**3b**): ^{1}H NMR (500.13 MHz, C_6D_6, 298 K): δ 7.96 (dd, J_{H-H} = 8.0, J_{H-Rh} = 2.3, 2H, *o*−C*H* Ph), 7.24 (m, 2H, C*H*-arom POP), 7.09 (d, J_{H-H} = 7.7, 2H, *m*−C*H* Ph), 7.05 (d, J_{H-H} = 6.5, 2H, C*H*-arom POP), 6.85 (t, J_{H-H} = 7.5, 2H, C*H*-arom POP), 2.42 (m, 4H, PC*H*(CH$_3$)$_2$), 2.38 (s, 3H, CH_3Ph), 1.27 (dvt, J_{H-H} = 7.7, *N* = 18.2, 12H, PCH(CH_3)$_2$), 1.24 (s, 6H, CH_3), 1.20 (dvt, J_{H-H} = 7.0, *N* = 14.1, 12H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 161.6 (dt, J_{C-Rh} = 40.5, J_{C-P} = 12.6, Rh−C), 156.7 (vt, *N* = 25.8, C*arom* POP), 139.5 (t, J_{C-P} = 2.9, *o*-CH Ph), 131.0 (s, C*H* arom POP), 130.7 (vt, *N* = 5.4, C*arom* POP), 128.0 (overlapping with C_6D_6, C*arom* POP), 127.4 (s, C*H*-arom POP), 126.8 (s, *m*-CH Ph), 125.6 (t, J_{C-P} = 7.2, *p*-C Ph), 124.0 (s, C*H*-arom POP), 34.1 (s, *C*(CH$_3$)$_2$), 33.0 (s, C(*C*H$_3$)$_2$), 24.5 (dvt, J_{C-Rh}= 3.6, *N* = 18.0, P*C*H(CH$_3$)$_2$), 21.5 (s, Ph-*C*H$_3$), 19.4 (vt, *N* = 8.6, PCH(*C*H$_3$)$_2$), 18.0 (s, PCH(*C*H$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 35.6 (d, J_{P-Rh} = 178.2).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with *m*-Xylene: Preparation of Rh(C_6H_3-3,5-Me_2){xant(P^iPr_2)$_2$} (4). Complex **1** (200 mg, 0.37 mmol) was dissolved in *m*-xylene (5 mL), and the resulting mixture was stirred during 24 h at 80 °C. After this time, it was concentrated to dryness to afford a red residue. Addition of pentane (5 mL) afforded a red solid, which was further washed with pentane (8 × 1 mL), and lastly, it was dried in vacuo. Yield: 102.3 mg (42%). Anal. Calcd for $C_{35}H_{49}OP_2Rh$: C, 64.61; H, 7.65. Found: C, 64.30; H, 7.35. IR (cm^{-1}): ν(C═C) 1556 (w), ν(C−O−C) 1099 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.73 (s, 2H, *o*−C*H* Ph), 7.29 (m, 2H, C*H*-arom POP), 7.05 (dd, J_{H-H} = 7.7, J_{H-H} = 1.6, 2H, C*H*-arom POP), 6.86 (t, J_{H-H} = 7.7, 2H, C*H*-arom POP), 6.55 (s, 1H, *p*−C*H* Ph), 2.45 (s, 6H, CH_3Ph), 2.42 (m, 4H, PC*H*(CH$_3$)$_2$), 1.24 (s, 6H, CH_3), 1.28 (dvt, J_{H-H} = 7.2, *N* = 16.0, 12H, PCH(CH_3)$_2$), 1.20 (dvt, J_{H-H} = 7.1, *N* = 13.2, 12H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 161.1 (dt, J_{C-Rh} = 40.2, J_{C-P} = 12.4, Rh−C), 156.3 (vt, *N* = 15.9, C*arom* POP), 138.6 (t, J_{C-P} = 2.8, *o*-CH Ph), 131.3 (s, C*H* arom POP), 130.8 (vt, *N* = 5.2, C*arom* POP), 128.0 (overlapping with C_6D_6, C*arom* POP), 127.4 (s, C*H*-arom POP), 126.2 (td, J_{C-P} = 7.2, J_{C-Rh} = 1.6, *m*-C Ph), 123.9 (s, C*H*-arom POP), 120.8 (s, *p*-CH Ph), 34.5 (s, *C*(CH$_3$)$_2$), 32.9 (s, C(*C*H$_3$)$_2$), 25.5 (dvt, J_{C-Rh} = 3.0, *N* = 17.2, PCH(CH$_3$)$_2$), 19.5 (vt, *N* = 8.5, PCH(*C*H$_3$)$_2$), 18.7 (s, PCH(*C*H$_3$)$_2$), 14.3 (s, Ph-*C*H$_3$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 35.6 (d, J_{P-Rh} = 178.3).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with Fluorobenzene: Preparation of Rh(C_6H_4-2-F){xant(P^iPr_2)$_2$} (5). Complex **1** (200 mg, 0.366 mmol) was dissolved in fluorobenzene (2 mL), and the resulting mixture was stirred at room temperature for 3 h. After this time, the solvent was removed under vacuum, affording a orange residue. Addition of pentane (2 mL) afforded an orange solid, which was further washed with pentane (2 × 1 mL), and lastly, it was dried in vacuo. Yield: 210.2 mg (91%). Anal. Calcd for $C_{33}H_{44}FOP_2Rh{\cdot}C_5H_{12}$: C, 61.88; H, 6.92. Found: C, 61.30; H, 6.65. IR (cm^{-1}): ν(C═C) 1573 (w), ν(C−O−C) 1101 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 8.08 (m, 1H, CH C_6H_4-2-F), 7.24 (m, 2H, C*H*-arom POP), 7.05 (dd, J_{H-H} = 7.9, J_{H-H} = 1.5, 2H, C*H*-arom POP), 7.03−6.91 (m, 3H, CH C_6H_4-2-F), 6.85 (t, J_{H-H} = 7.5, 2H, C*H*-arom POP), 2.38 (m, 4H, PC*H*(CH$_3$)$_2$), 1.35−1.10 (m, 30H, C(CH_3)$_2$ + PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 167.4 (ddt, J_{C-F} = 222.8, J_{C-Rh} = 2.5, J_{C-P} = 2.5, *C*-F C_6H_4F), 156.4 (vt, *N* = 15.8, *C*-arom POP), 143.1 (ddt, J_{C-Rh} = 44.3, J_{C-F} = 42.6, J_{C-P} = 13.5, Rh-*C* C_6H_4F), 141.5 (dt, J_{C-F} = 21.4, J_{C-P} = 2.6, *C*H C_6H_4F), 131.2 (s, C*H*-arom POP), 130.8 (vt, *N* = 5.5, *C*-arom POP), 127.9 (s, C*H*-arom POP), 125.7 (dvt, J_{C-Rh} = 1.8, *N* = 14.6, *C*-arom POP), 124.1 (vt, *N* = 4.0, C*H*-arom POP), 122.0 (m, *C*H C_6H_4F), 120.1 (dt, J_{C-F} = 7.1, J_{C-P} = 1.5, *C*H C_6H_4F), 111.9 (ddt, J_{C-F} = 30.6, J_{C-Rh} = 1.3, J_{C-P} = 1.3, *C*H C_6H_4F), 34.0 (s, *C*(CH$_3$)$_2$), 33.5, 32.6 (both br, C(*C*H$_3$)$_2$), 26.5, 25.0 (both br, PCH-(CH$_3$)$_2$), 19.3 (vt, *N* = 8.4, 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 40.0 (dd, J_{P-Rh} = 167.6, J_{P-F} = 4.2). ^{19}F{^{1}H} NMR (282.33 MHz, C_6D_6, 298 K): δ −85.4 (dt, J_{F-Rh} = 19.8, J_{F-P} = 4.1).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with 1,3-Difluorobenzene: Preparation of Rh(C_6H_3-2,6-F_2){xant(P^iPr_2)$_2$} (6). Complex **1** (200 mg, 0.366 mmol) was dissolved in 1,3-difluorobenzene (5 mL), and the resulting mixture was stirred at room temperature for 5 min, getting a reddish solution. After this time, the solvent was removed under vacuum, affording a red residue. Addition of pentane (3 mL) afforded an orange solid, which was further washed with pentane (2 × 1 mL), and lastly, it was dried in vacuo. Yield: 175.2 mg (73%). Anal. Calcd for $C_{33}H_{43}F_2OP_2Rh{\cdot}C_5H_{12}$: C, 62.29; H, 7.56. Found: C, 62.01; H, 7.74. IR (cm^{-1}): ν(C═C) 1573 (w), ν(C−O−C) 1036 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.21 (m, 2H, C*H*-arom POP), 7.08 (d, J_{H-H} = 7.1, 2H, C*H*-arom POP), 6.78−6.68 (m, 5H, C*H*-arom POP + $C_6H_3F_2$), 2.36 (m, 4H, PC*H*(CH$_3$)$_2$), 1.30−1.10 (m, 30H, C(CH_3)$_2$ + PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (75.47 MHz, C_6D_6, 298 K): δ 167.4 (ddt, J_{C-F} = 224.4, J_{C-Rh} = 24.2, J_{C-P} = 2.4, *C*-F $C_6H_3F_2$), 156.4 (vt, *N* = 16.4, *C*-arom POP), 131.1 (s, C*H*-arom POP), 130.7 (vt, *N* = 5.6, *C*-arom POP), 128.0 (s, C*H*-arom POP, inferred from the HSQC spectrum), 125.4 (dvt, J_{C-Rh} = 1.9, *N* = 15.2, *C*-arom POP), 124.2 (vt, *N* = 3.9, C*H*-arom POP), 121.6 (t, J_{C-F} = 8.2, *C*H $C_6H_3F_2$), 108.5 (d, J_{C-F} = 31.2, *C*H $C_6H_3F_2$), 33.9 (s, *C*(CH$_3$)$_2$), 33.2 (s, C(*C*H$_3$)$_2$), 26.0 (dvt, J_{C-Rh} = 2.7, *N* = 18.7, PCH(CH$_3$)$_2$), 19.1 (vt, *N* = 8.3, PCH(*C*H$_3$)$_2$), 18.4 (s, PCH(*C*H$_3$)$_2$), the signal for the Rh−C atom was not observed. ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 43.0 (dt, J_{P-Rh} = 159.8, J_{P-F} = 3.6). ^{19}F{^{1}H} NMR (282.33 MHz, C_6D_6, 298 K): δ −80.8 (dt, J_{F-Rh} = 22.1, J_{F-P} = 3.7).

DOI: 10.1021/acs.organomet.5b00176
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Reaction of RhH{xant(P^iPr_2)$_2$} (1) with Pinacolborane at Low Temperature: Spectroscopic Detection of RhH_2(Bpin){xant(P^iPr_2)$_2$} (7). A screw-top NMR tube containing a solution of **1** (23.2 mg, 0.04 mmol) in toluene-d_8 (0.4 mL) and cooled at 195 K was treated with HBpin (6.2 μL, 0.04 mmol). Immediately the NMR tube was introduced in a NMR probe precooled at 258 K. The immediate and quantitative conversion to **7** was observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies (in solution at this temperature **9** was observed as a minor product with time). ^{1}H NMR (400.13 MHz, C_7D_8, 258 K): δ 7.21 (m, 2H, C*H*-arom POP), 6.97 (dd, J_{H-H} = 7.5, J_{H-H} = 1.3, 2H, C*H*-arom POP), 6.89 (t, J_{H-H} = 7.5, 2H, C*H*-arom POP), 2.61 (m, 4H, PC*H*(CH_3)$_2$), 1.56 (dvt, J_{H-H} = 7.8, *N* = 15.9, 12H, PCH(CH_3)$_2$), 1.23 (s, 12H, CH_3 Bpin), 1.22 (dvt, J_{H-H} = 7.3, *N* = 14.2, 12H, PCH(CH_3)$_2$), 1.16 (s, 6H, CH_3), −5.94 (dt, J_{H-Rh} = 23.4, J_{H-P} = 15.9, 2H, RhH_2). ^{13}C{^{1}H} NMR (75.47 MHz, C_7D_8, 258 K): δ 155.7 (vt, *N* = 12.4, *C*-arom POP), 132.3 (vt, *N* = 4.5, *C*-arom POP), 130.2 (s, *C*H-arom POP), 126.3 (vt, *N* = 23.0, *C*-arom POP), 126.1 (s, *C*H-arom POP), 123.7 (vt, *N* = 4.2, *C*H-arom POP), 80.7 (s, C Bpin), 34.8 (s, *C*(CH_3)$_2$), 29.7 (s, C(CH_3)$_2$), 26.6 (vt, *N* = 24.0, PCH(CH_3)$_2$), 25.1 (s, CH_3 Bpin), 20.1 (vt, *N* = 8.3, PCH(CH_3)$_2$), 19.0 (s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, C_7D_8, 258 K): δ 68.3 (d, J_{P-Rh} = 131.0). ^{11}B{^{1}H} NMR (128.38 MHz, C_7D_8, 258 K): δ 33.3 (br).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with Catecholborane at Low Temperature: Spectroscopic Detection of RhH_2(Bcat){xant(P^iPr_2)$_2$} (8). A screw-top NMR tube containing a solution of **1** (23.0 mg, 0.04 mmol) in toluene-d_8 (0.4 mL) and cooled at 195 K was treated with HBcat (4.5 μL, 0.04 mmol). Immediately the NMR tube was introduced in a NMR probe precooled at 258 K. The immediate and quantitative conversion to **8** was observed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopies (in solution at this temperature **10** was observed as a minor product with time). ^{1}H NMR (400.13 MHz, C_7D_8, 258 K): δ 7.11 (m, 2H, C*H*-arom POP), 7.06 (m, 2H, Bcat), 6.98 (m, 2H, C*H*-arom POP), 6.89 (t, J_{H-H} = 7.5, 2H, C*H*-arom POP), 6.85 (m, 2H, Bcat), 2.67 (m, 4H, PC*H*(CH_3)$_2$), 1.42 (dvt, J_{H-H} = 7.9, *N* = 16.1, 12H, PCH(CH_3)$_2$), 1.17 (s, 6H, CH_3), 1.13 (dvt, J_{H-H} = 6.8, *N* = 13.9, 12H, PCH(CH_3)$_2$), −6.04 (dt, J_{H-Rh} = 23.9, J_{H-P} = 13.5, 2H, RhH_2). ^{13}C{^{1}H} NMR (100.62 MHz, C_7D_8, 258 K): δ 156.6 (vt, *N* = 12.3, *C*arom POP), 151.7 (s, *C*-O Bcat), 133.4 (vt, *N* = 4.7, *C*arom POP), 130.0 (s, *C*H-arom POP), 125.9 (s, *C*H-arom POP), 123.7 (br, *C*H-arom POP), 120.2, 110.2 (both s, *C*H Bcat), 35.1 (s, *C*(CH_3)$_2$), 28.3 (s, C(CH_3)$_2$), 25.7 (vt, *N* = 24.5, PC*H*(CH_3)$_2$), 19.4 (vt, *N* = 8.1, PCH(CH_3)$_2$), 18.4 (s, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (161.98 MHz, C_7D_8, 258 K): δ 63.8 (d, J_{P-Rh} = 132.0). ^{11}B{^{1}H} NMR (128.8 MHz, C_7D_8, 258 K): δ 34.7 (br).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with Pinacolborane at Room Temperature: Preparation of Rh(Bpin){xant-(P^iPr_2)$_2$} (9). HBpin (110 μL, 0.76 mmol) was added to a solution of **1** (400 mg, 0.73 mmol) in pentane (10 mL). After stirring for 3 min, a dark red solution is obtained. This solution was evaporated to dryness to afford a red residue, which was further washed with pentane (3 × 3 mL) and dried in vacuo. Yield: 458.2 mg (93%). Anal. Calcd for $C_{33}H_{52}BO_3P_2Rh$: C, 58.94; H, 7.79. Found: C, 58.90; H, 8.20. HRMS (electrospray, *m*/*z*): calcd for $C_{33}H_{53}BO_3P_2Rh$ [M + H]$^+$ 673.2618; found, 673.2629. IR (cm^{-1}): ν(C−O−C) 1102 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.36 (m, 2H, CH-arom POP), 7.10 (dd, J_{H-H} = 7.7, J_{H-H} = 1.6, 2H, CH-arom POP), 6.91 (t, J_{H-H} = 7.7, 2H, CH-arom POP), 2.47 (m, 2H, PC*H*(CH_3)$_2$), 1.59 (dvt, J_{H-H} = 7.1, *N* = 16.5, 12H, PCH(CH_3)$_2$), 1.38 (s, 12H, CH_3 Bpin), 1.28 (s, 6H, CH_3), 1.20 (dvt, J_{H-H} = 7.1, *N* = 14.2, 12H, PCH(CH_3)$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 155.5 (dvt, J_{C-Rh} = 0.9, *N* = 16.3, C-arom POP), 131.2 (s, CH-arom POP), 131.1 (vt, *N* = 5.2, C-arom POP), 127.7 (vt, *N* = 25.0, C-arom POP), 127.2 (s, CH-arom POP), 124.0 (vt, *N* = 3.7, CH-arom POP), 79.5 (d, J_{C-Rh} = 1.4, C Bpin), 34.4 (s, *C*(CH_3)$_2$), 32.2 (s, C(*C*H$_3$)$_2$), 27.6 (dvt, J_{C-Rh} = 3.8, *N* = 19.3, PCH(CH_3)$_2$), 26.5 (s, CH_3 Bpin), 20.8 (dvt, J_{C-Rh} = 0.8, *N* = 10.5, PCH(CH_3)$_2$), 19.8 (dvt, J_{C-Rh} = 2.1, *N* = 3.6, PCH(CH_3)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 51.9 (d, J_{P-Rh} = 176.0). ^{11}B NMR (96.29 MHz, C_6D_6, 298 K): δ 41.9 (br).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with Catecholborane at Room Temperature: Preparation of Rh(Bcat){xant-(P^iPr_2)$_2$} (10). HBcat (11.5 μL, 0.11 mmol) was added to a solution of **1** (59.0 mg, 0.11 mmol) in toluene (3 mL) cooled at 195 K. After stirring for 5 min at this temperature, it was slowly heated at room temperature, affording a dark red solution. This solution was evaporated to dryness to afford a red residue. Addition of pentane afforded a red solid that was washed with pentane (2 × 0.5 mL) and dried in vacuo. Yield: 50 mg (70%). Anal. Calcd for $C_{33}H_{44}BO_3P_2Rh$: C, 59.66; H, 6.68. Found: C, 59.90; H, 6.20. HRMS (electrospray, *m*/*z*): calcd. for $C_{33}H_{44}BO_3P_2Rh$ [M]$^+$: 661.2601; found: 661.2612. IR (cm^{-1}): ν(C−O−C) 1102 (m). ^{1}H NMR (300.13 MHz, C_6D_6, 298 K): δ 7.32 (m, 2H, Bcat), 7.22 (m, 2H, CH-arom POP), 7.09 (dd, J_{H-H} = 7.7, J_{H-H} = 1.4, 2H, CH-arom POP), 6.92−6.85 (m, 4H, 2H CH-arom POP + 2H Bcat), 2.35 (m, 2H, PC*H*(CH_3)$_2$), 1.33 (dvt, J_{H-H} = 7.5, *N* = 16.9, 12H, PCH(C*H*$_3$)$_2$), 1.27 (s, 6H, CH_3), 1.10 (dvt, J_{H-H} = 7.1, *N* = 14.3, 12H, PCH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (100.62 MHz, C_6D_6, 298 K): δ 155.7 (vt, *N* = 12.3, Carom POP), 151.6 (s, *C*-O Bcat), 131.3 (s, *C*H-arom POP), 131.2 (vt, *N* = 5.4, Carom POP), 127.6 (s, *C*H-arom POP), 128.3 (vt, *N* = 25.0, C-arom POP), 124.2 (vt, *N* = 3.9, *C*H-arom POP), 120.3, 110.5 (both s, *C*H Bcat), 34.5 (s, *C*(CH_3)$_2$), 32.2 (s, C(*C*H$_3$)$_2$), 26.7 (dvt, J_{C-Rh} = 3.7, *N* = 21.2, PCH(CH_3)$_2$), 20.3 (dvt, J_{C-Rh} = 1.0, *N* = 9.9, PCH(CH_3)$_2$), 19.3 (vt, *N* = 4.2, PCH(C*H*$_3$)$_2$). ^{31}P{^{1}H} NMR (121.49 MHz, C_6D_6, 298 K): δ 55.1 (d, J_{P-Rh} = 165.3). ^{11}B{^{1}H} NMR (96.29 MHz, C_6D_6, 298 K): δ 48.7 (br).

Reaction of RhH{xant(P^iPr_2)$_2$} (1) with Bis(pinacolato)-diboron. A solution of **1** (20 mg, 0.036 mmol) in C_6D_6 (0.5 mL) in an NMR tube was treated with the stoichiometric amount of B_2pin_2 (9.3 mg, 0.036 mmol) at room temperature. ^{1}H, ^{31}P{^{1}H} and ^{11}B NMR spectroscopies show the quantitative and immediate formation of Rh(Bpin){xant(P^iPr_2)$_2$} (**9**) and HBpin.

Reaction of RhPh{xant(P^iPr_2)$_2$} (2) with Bis-(pinacolato)diboron. A solution of **2** (20 mg, 0.032 mmol) in toluene (0.5 mL) in an NMR tube was treated with the stoichiometric amount of B_2pin_2 (8.1 mg, 0.032 mmol), and the resulting solution was heated at 60 °C in an oil bath. The reaction was periodically checked by ^{31}P{^{1}H} NMR spectroscopy. After 24 h, the ^{31}P{^{1}H} NMR spectrum shows the quantitative conversion of **2** and the formation of Rh(Bpin)-{xant(P^iPr_2)$_2$} (**9**). In addition to the formation of **9** (br, δ 42.9), the ^{11}B{^{1}H} NMR spectrum shows the formation of Ph-Bpin (br, δ 31.4)

Reaction of RhPh{xant(P^iPr_2)$_2$} (2) with HBpin. A solution of **2** (21.4 mg, 0.034 mmol) in toluene (0.5 mL) in an NMR tube was treated with HBpin (5.0 μL, 0.034 mmol),

DOI: 10.1021/acs.organomet.5b00176
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and the resulting solution was heated at 55 °C in an oil bath. The NMR tube was periodically checked by $^{31}P\{^{1}H\}$ NMR spectroscopy.

Reaction of Rh(Bpin){xant(P^{i}Pr$_2$)$_2$} (9) with Benzene. A solution of **9** (20 mg, 0.030 mmol) in benzene (0.5 mL) in an NMR tube was heated at 65 °C in an oil bath. The NMR tube was periodically checked by $^{31}P\{^{1}H\}$ NMR spectroscopy. After 2.5 h the $^{31}P\{^{1}H\}$ NMR spectrum shows signals corresponding to Rh(Bpin){xant(P^{i}Pr$_2$)$_2$} (**9**), RhH{xant(P^{i}Pr$_2$)$_2$} (**1**) and Rh(C$_6$H$_5$){xant(P^{i}Pr$_2$)$_2$} (**2**) in a ratio of 28:28:44, together with a small signal of an unidentified species.

Borylation of Benzene with B$_2$pin$_2$ Catalyzed by RhH{xant(P^{i}Pr$_2$)$_2$} (1). In an argon-filled glovebox, an Ace pressure tube was charged with **1** (43.7 mg, 0.08 mmol), B$_2$pin$_2$ (254 mg, 1 mmol), and 5 mL of benzene. The resulting mixture was stirred at 110 °C for 24 h. After this time, the arene was evaporated under reduced pressure to afford a crude reaction mixture. After purification of the crude reaction mixture by flash chromatography over silica gel using diethyl ether as the eluyent, phenylboronic acid pinacol ester was isolated in a 68% yield.

Borylation of Benzene with HBpin Catalyzed by RhH{xant(P^{i}Pr$_2$)$_2$} (1). This reaction was performed analogously as described for the borylation of benzene with B$_2$pin$_2$, starting from **1** (43.7 mg, 0.08 mmol), HBpin (300 μL, 2.06 mmol), and 5 mL of benzene. Isolated yield: 66%.

Borylation of Benzene with B$_2$pin$_2$ Catalyzed by RhH{xant(P^{i}Pr$_2$)$_2$} (1) in the presence of cyclohexene. This reaction was performed analogously as described for the borylation of benzene with B$_2$pin$_2$, adding cyclohexene (200 μL, 2.00 mmol). Isolated yield: 89%.

Borylation of Benzene with HBpin Catalyzed by RhH{xant(P^{i}Pr$_2$)$_2$} (1) in the Presence of Cyclohexene. This reaction was performed analogously as described for the borylation of benzene with HBpin, adding cyclohexene (200 μL, 2.00 mmol). Isolated yield: 95%.

General Procedure for the Borylation Reactions. In an argon-filled glovebox an Ace pressure tube was charged with RhH{xant(P^{i}Pr$_2$)$_2$} (43.7 mg, 0.08 mmol), HBpin (300 μL, 2.06 mmol), cyclohexene (200 μL, 2.00 mmol), and 5 mL of the arene. The resulting mixture was stirred at 110 °C for 24 or 48 h. After this time the arene was evaporated under reduced pressure to afford a crude reaction mixture. The yield of the borylation reaction was determined by ^{1}H NMR spectroscopy by dissolving the crude reaction mixture in CDCl$_3$ and adding 50 μL of 1,2-dichloroethane, which was used as internal standard. In order to ensure accurate integration of the signals, the spectra were recorded using eight scans and a 5 s delay. The isolated yields were calculated after purification of the crude reaction mixture by flash chromatography over silica gel using diethyl ether as the eluent and by evaporation to dryness.

Borylation of Benzene: Preparation of Phenylboronic Acid Pinacol Ester (Run 1). The reaction was performed using the general procedure. The title compound was obtained in 100% yield (isolated 95%) after 24 h. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.78 (m, 1H, CH), 7.37 (m, 1H, CH), 7.30 (m, 1H, CH), 1.27 (s, 12H, CH$_3$). $^{13}C\{^{1}H\}$-APT NMR (100.5 MHz, CDCl$_3$, 298 K): δ 134.8 (s, CH), 131.2 (s, CH), 127.7 (s, CH), 83.7 (s, C), 24.9 (s, CH$_3$). ^{1}H and $^{13}C\{^{1}H\}$ NMR data agree with previously reported data.[42]

Borylation of Toluene: Preparation of 3- and 4-Methylphenyl Boronic Acid Pinacol Ester (Run 2). The reaction was performed using the general procedure. The borylation product was obtained in 100% yield (isolated 98%) after 48 h as a mixture of two isomers in a ratio 65 (*meta*): 35 (*para*).

NMR data for 3-methylphenyl boronic acid pinacol ester: ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.63 (d, J_{H-H} = 0.8, 1H, CH), 7.60 (t, J_{H-H} = 4.6, 1H, CH), 7.25 (dd, J_{H-H} = 5.0, J_{H-H} = 1.1, 1H, CH), 7.25 (dd, J_{H-H} = 5.0, J_{H-H} = 1.1, 1H, CH), 2.34 (s, 3H, CH$_3$), 1.33 (s, 12H, CH$_3$). $^{13}C\{^{1}H\}$-APT NMR (100.5 MHz, CDCl$_3$, 298 K): δ 137.2 (s, *C*-CH$_3$), 135.5 (s, CH), 132.2 (s, CH), 131.9 (s, CH), 127.8 (s, CH), 83.8 (s, C), 25.0 (s, CH$_3$), 21.4 (s, CH$_3$). ^{1}H and $^{13}C\{^{1}H\}$ NMR data agree with previously reported data.[42]

NMR data for 4-methylphenyl boronic acid pinacol ester: ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.70 (d, J_{H-H} = 7.9, 2H, CH), 7.17 (d, J_{H-H} = 7.5, 2H, CH), 2.35 (s, 3H, CH$_3$), 1.32 (s, 12H, CH$_3$). $^{13}C\{^{1}H\}$-APT NMR (100.5 MHz, CDCl$_3$, 298 K): δ 141.5 (s, *C*-CH$_3$), 134.9 (s, CH), 128.6 (s, CH), 83.7 (s, C), 25.0 (s, CH$_3$), 21.8 (s, CH$_3$). ^{1}H and $^{13}C\{^{1}H\}$ NMR data agree with previously reported data.[42]

Borylation of 1,3-Dimethylbenzene: Preparation of 3,5-Dimethylphenylboronic Acid Pinacol Ester (Run 3). The reaction was performed using the general procedure. The title compound was obtained in 100% yield (isolated 99%) after 48 h. ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.44 (s, 2H, CH), 7.10 (s, 1H, CH), 2.32 (s, 6H, CH$_3$), 1.34 (s, 12H, CH$_3$). $^{13}C\{^{1}H\}$-APT NMR (100.5 MHz, CDCl$_3$, 298 K): δ 137.3 (s, C), 133.1 (s, CH), 132.5 (s, CH), 83.8 (s, C), 25.0 (s, CH$_3$), 21.3 (s, CH$_3$). ^{1}H and $^{13}C\{^{1}H\}$ NMR data agree with previously reported data.[43]

Borylation of Fluorobenzene: Preparation of 2-, 3- and 4-Fluorophenyl Boronic Acid Pinacol Ester (Run 4). The reaction was performed using the general procedure. The borylation product was obtained in 100% yield (isolated 99%) after 24 h as a mixture of the three possible isomers in a ratio of 43 (*ortho*): 38 (*meta*): 19 (*para*).

NMR data for 2-fluorophenyl boronic acid pinacol ester: ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.77 (dd, J_{H-F} = 6.1, J_{H-H} = 7.7, J_{H-H} = 1.9, 1H, CH), 7.40 (dddd, J_{H-F} = 6.0, J_{H-H} = 8.3, J_{H-H} = 7.3, J_{H-H} = 1.9, 1H, CH), 7.11 (m, 1H, CH), 7.01 (ddd, J_{H-F} = 9.0, J_{H-H} = 8.3, J_{H-H} = 0.9, 1H, CH), 1.35 (s, 12H, CH$_3$). $^{13}C\{^{1}H\}$-APT NMR (100.5 MHz, CDCl$_3$, 298 K): δ 167.2 (d, J_{C-F} = 249.4, C−F), 136.9 (d, J_{C-F} = 7.9, CH), 133.3 (d, J_{C-F} = 8.7, CH), 123.6 (d, J_{C-F} = 3.3, CH), 114.8 (d, J_{C-F} = 20.1, CH), 83.8 (s, C), 24.8 (s, CH$_3$). ^{19}F NMR (376.49 MHz, CDCl$_3$, 298 K): δ −102.3 (dtd, J_{F-H} = 9.0, J_{F-H} = 5.8, J_{F-H} = 2.5). ^{1}H NMR data agree with previously reported data.[44]

NMR data for 3-fluorophenyl boronic acid pinacol ester: ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.59 (d, J_{H-F} = 7.3, 1H, CH), 7.51 (dd, J_{H-H} = 9.1, J_{H-F} = 2.5, 2H, CH), 7.32 (ddd, J_{H-H} = 8.2, J_{H-H} = 7.3, J_{H-F} = 5.4, 1H, CH), 7.13 (m, 1H, CH), 1.32 (s, 12H, CH$_3$). $^{13}C\{^{1}H\}$-APT NMR (100.5 MHz, CDCl$_3$, 298 K): δ 162.6 (d, J_{C-F} = 256.5, *C*-F), 130.4 (d, J_{C-F} = 3.0, CH), 129.5 (d, J_{C-F} = 7.1, CH), 121.0 (d, J_{C-F} = 19.2, CH), 118.1 (d, J_{C-F} = 21.1, CH), 83.8 (s, C), 24.8 (s, CH$_3$). ^{19}F NMR (376.49 MHz, CDCl$_3$, 298 K): δ −114.00 (td, J_{F-H} = 9.0, J_{F-H} = 5.4). ^{1}H and $^{13}C\{^{1}H\}$ NMR data agree with previously reported data.[45]

NMR data for 4-fluorophenyl boronic acid pinacol ester: ^{1}H NMR (400 MHz, CDCl$_3$, 298 K): δ 7.82 (dd, J_{H-F} = 6.3, J_{H-H} = 8.4, 1H, CH), 7.04 (dd, J_{H-F} = 6.7, J_{H-H} = 8.5, 1H, CH), 1.33 (s, 6H, CH$_3$). $^{13}C\{^{1}H\}$-APT NMR (100.5 MHz, CDCl$_3$, 298 K): δ 165.1 (d, J_{C-F} = 260.4, *C*-F), 137.1 (d, J_{C-F} = 8.1, CH), 115.2 (d, J_{C-F} = 23.8, CH), 83.8 (s, C), 24.8 (s, CH$_3$). ^{19}F

DOI: 10.1021/acs.organomet.5b00176
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NMR (376.49 MHz, $CDCl_3$, 298 K): δ −108.2 (tt, J_{F-H} = 9.0, J_{F-H} = 6.2). ^1H and $^{13}C\{^1H\}$ NMR data agree with previously reported data.[46]

Borylation of 1,3-Difluorobenzene: Preparation of 2,4-, 3,5- and 2,6-Difluoro-Phenylboronic Acid Pinacol Ester (Run 5). The reaction was performed using the general procedure. The borylation product was obtained in 100% yield (isolated 99%) after 24 h as a mixture of 2,4-difluoro-phenylboronic acid pinacol ester, 3,5-difluoro-phenylboronic acid pinacol ester, and 2,6-difluoro-phenylboronic acid pinacol ester in a ratio of 44:40:16.

NMR data for 2,4-difluoro-phenylboronic acid pinacol ester: ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.62 (dt, J_{H-F} = 8.4, J_{H-H} = 7.1, 1H, CH), 6.75 (m, 1H, CH), 6.64 (td, J_{H-F} = 9.4, J_{H-H} = 2.3, 1H, CH), 1.29 (s, 12H, CH_3). $^{13}C\{^1H\}$-APT NMR (100.5 MHz, $CDCl_3$, 298 K): δ 168.0 (dd, J_{C-F} = 234.7, J_{C-F} = 12.2, *C*-F), 165.5 (dd, J_{C-F} = 233.5, J_{C-F} = 12.1, *C*-F), 138.3 (t, J_{C-F} = 10.0, *C*H), 111.1 (dd, J_{C-F} = 20.1, J_{C-F} = 3.6, CH), 103.6 (dd, J_{C-F} = 27.9, J_{C-F} = 24.3, CH), 84.0 (s, C), 24.8 (s, CH_3). $^{19}F\{^1H\}$ NMR (376.49 MHz, $CDCl_3$, 298 K): δ −105.2 (d, J_{F-F} = 10.8), −98.8 (d, J_{F-F} = 10.8). ^1H and $^{13}C\{^1H\}$ NMR data agree with previously reported data.[47]

NMR data for 3,5-difluoro-phenylboronic acid pinacol ester: ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.25 (m, 2H, CH), 6.85 (m, 1H, CH), 1.30 (s, 12H, CH_3). $^{13}C\{^1H\}$-APT NMR (100.5 MHz, $CDCl_3$, 298 K): δ 162.8 (dd, J_{C-F} = 249.7, J_{C-F} = 11.0, *C*-F), 116.8 (m, CH), 106.5 (t, J_{C-F} = 25.1, *C*H), 84.5 (s, C), 24.8 (s, *C*H_3). $^{19}F\{^1H\}$ NMR (376.49 MHz, $CDCl_3$, 298 K): δ −110.7 (s). ^1H and $^{13}C\{^1H\}$ NMR data agree with previously reported data.[47]

NMR data for 2,6-difluoro-phenylboronic acid pinacol ester: ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.30 (m, 1H, CH), 6.82 (m, 2H, CH), 1.34 (s, 12H, CH_3). $^{13}C\{^1H\}$-APT NMR (100.5 MHz, $CDCl_3$, 298 K): δ 166.6 (dd, J_{C-F} = 250.5, J_{C-F} = 12.8, *C*-F), 133.1 (t, J_{C-F} = 10.6, *C*H), 111.0 (m, CH), 84.2 (s, C), 24.7 (s, *C*H_3). $^{19}F\{^1H\}$ NMR (376.49 MHz, $CDCl_3$, 298 K): δ −100.5 (s). ^1H and $^{13}C\{^1H\}$ NMR data agree with previously reported data.[47]

Borylation of 1-Fluoro-3-methylbenzene: Preparation of 3-Fluoro-5-methylphenylboronic Acid Pinacol Ester and 2-Fluoro-4-methylphenylboronic Acid Pinacol Ester (Run 6). The reaction was performed using the general procedure. The borylation product was obtained in 74% yield (isolated 73%) after 24 h as a mixture of 3-fluoro-5-methylphenylboronic acid pinacol ester and 2-fluoro-4-methylphenylboronic acid pinacol ester in a ratio of 58:42.

NMR data for 3-fluoro-5-methylphenylboronic acid pinacol ester. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.37 (s, 1H, CH), 7.26 (dd, J_{H-F} = 8.8, J_{H-H} = 2.5, 1H, CH), 6.92 (m, 1H, CH), 2.32 (s, 3H, CH_3), 1.32 (s, 12H, CH_3). $^{13}C\{^1H\}$-APT NMR (100.5 MHz, $CDCl_3$, 298 K): δ 162.7(d, J_{C-F} = 246.0, *C*-F), 139.9 (d, J_{C-F} = 7.0, *C*-CH_3), 131.1 (d, J_{C-F} = 2.5, CH), 118.9 (d, J_{C-F} = 20.9, CH), 117.9 (d, J_{C-F} = 19.3, CH), 84.1 (s, C), 24.9 (s, CH_3), 21.1 (d, J_{C-F} = 1.7, CH_3).^{19}F NMR (376.49 MHz, $CDCl_3$, 298 K): δ −115.2 (t, J_{F-H} = 9.3).

NMR data for 2-fluoro-4-methylphenylboronic acid pinacol ester. ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.59 (dd, J_{H-F} = 7.6, J_{H-H} = 7.6, 1H, CH), 6.91 (m, 1H, CH), 6.82 (d, J_{H-F} = 10.3, 1H, CH), 2.32 (s, 3H, CH_3), 1.33 (s, 12H, CH_3). $^{13}C\{^1H\}$-APT NMR (100.5 MHz, $CDCl_3$, 298 K): δ 167.5 (d, J_{C-F} = 250.5, *C*-F), 144.5 (d, J_{C-F} = 8.7, *C*-CH_3), 136.7 (d, J_{C-F} = 8.6, CH), 124.6 (d, J_{C-F} = 2.7, CH), 115.9 (d, J_{C-F} = 23.7, CH), 83.8 (s, C), 24.9 (s, CH_3), 21.5 (d, J_{C-F} = 1.7, CH_3). ^{19}F NMR (376.49 MHz, $CDCl_3$, 298 K): δ −103.7 (dd, J_{F-H} = 10.3, J_{F-H} = 6.5). ^1H, $^{13}C\{^1H\}$ and ^{19}F NMR data agree with previously reported data.[48]

Borylation of Anisole: Preparation of 3- and 4-Methoxyphenyl Boronic Acid Pinacol Ester (Run 7). The reaction was performed using the general procedure. The borylation product was obtained in 67% yield (isolated 65%) after 24 h as a mixture of two isomers in a ratio of 62 (*meta*): 38 (*para*).

NMR data for 3-methoxyphenyl boronic acid pinacol ester: ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.38 (dt, J_{H-H} = 7.3, J_{H-H} = 1.0, 1H, CH), 7.30 (dd, J_{H-H} = 2.8, J_{H-H} = 1.0, 1H, CH), 7.24 (dd, J_{H-H} = 8.2, J_{H-H} = 7.3, 1H, CH), 6.96 (ddd, J_{H-H} = 8.2, J_{H-H} = 2.8, J_{H-H} = 1.1, 1H, CH), 3.83 (s, 3H, OCH_3), 1.29 (s, 12H, CH_3). $^{13}C\{^1H\}$-APT NMR (100.5 MHz, $CDCl_3$, 298 K): δ 159.0 (s, *C*-OCH_3), 128.8 (s, CH), 127.1 (s, CH), 118.8 (s, CH), 117.7(s, CH), 83.7 (s, C), 55.3 (s, OCH_3), 24.9 (s, CH_3). ^1H and $^{13}C\{^1H\}$ NMR data agree with previously reported data.[5]

NMR data for 4-methoxyphenyl boronic acid pinacol ester: ^1H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.72 (d, J_{H-H} = 8.6, 2H, CH), 6.85 (d, J_{H-H} = 8.6, 2H, CH), 3.70 (s, 3H, OCH_3), 1.28 (s, 12H, CH_3). $^{13}C\{^1H\}$-APT NMR (100.5 MHz, $CDCl_3$, 298 K): δ 162.1 (s, *C*-OCH_3), 136.4 (s, CH), 113.2 (s, CH), 83.5 (s, C), 54.9 (s, OCH_3), 24.9 (s, CH_3). ^1H and $^{13}C\{^1H\}$ NMR data agree with previously reported data.[42]

Structural Analysis of Complexes 2, 3, 5, 6, and 9. Crystals suitable for the X-ray diffraction were obtained by slow evaporation of pentane (**2**, **3**, **9**) or by diffusion of pentane into solutions of **5** and **6** in benzene. X-ray data were collected on a Bruker Smart APEX difractometer equipped with a normal focus, 2.4 kW sealed tube source (Mo radiation, λ = 0.71073 Å) operating at 50 kV and 30 (**6**) or 40 (**2**, **3**, **5**, **9**) mA. Data were collected over the complete sphere by a combination of four sets. Each frame exposure time was 10 s (**2**, **6**), 20 s (**3**), 30 s (**5**, **9**) covering 0.3° in ω. Data were corrected for absorption by using a multiscan method applied with the SADABS program.[49] 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.[50] 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. Complexes **3a** and **3b** cocrystallize (**3**) in a ratio of 71.3:28.7. The atoms of the tolyl groups were refined with restrained geometry and thermal parameters. The fluorine atom of **5** is disordered (50/50) between the atoms C(2) and C(6) of the aryl moiety. The boryl ligand of **9** is disordered between two orientations (0.8/0.2) by a 68° rotation around the Rh−B bond. The disordered groups were refined with two moieties, complementary occupancy factors, and isotropic thermal parameters. Complexes **5** and **6** crystallize with two molecules of benzene each, one of them disordered. These disordered solvent molecules were 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 **2**: $C_{33}H_{45}OP_2Rh$, M_W 622.54, red, prism (0.22 × 0.12 × 0.09), triclinic, space group *P*-1, *a*: 12.2682(9) Å, *b*: 13.4969(10) Å, *c*: 19.9489(15) Å, α = 91.5600(10)°, β = 107.3610(10)°, γ = 104.3260(10)°, *V* = 3036.4(4) Å^3, *Z* = 2, D_{calc}: 1.362 g cm^{-3}, *F*(000): 1304, *T* = 100(2) K, μ 0.692

DOI: 10.1021/acs.organomet.5b00176
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mm^{-1}. 28048 measured reflections (2θ: 2−57°, ω scans 0.3°), 13 844 unique (R_{int} = 0.0512); minimum/maximum transmission factors 0.733/0.862. Final agreement factors were R^1 = 0.0593 (9942 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1146; data/restraints/parameters 13 844/0/687; GoF = 1.072. Largest peak and hole 1.063 and −1.405 e/Å^3.

Crystal data for **3**: $C_{34}H_{47}OP_2Rh$, M_W 636.57, red, prism (0.30 × 0.21 × 0.13), orthorhombic, space group *Pbca*, *a*: 14.8931(19) Å, *b*: 20.025(3)Å, *c*: 21.472(3) Å, V = 6403.8(14) Å^3, Z = 8, D_{calc}: 1.321 g cm^{-3}, $F(000)$: 267, T = 100(2) K, μ 0.657 mm^{-1}. 49325 measured reflections (2θ: 3−60°, ω scans 0.3°), 9226 unique (R_{int} = 0.0701); minimum/maximum transmission factors 0.708/0.900. Final agreement factors were R^1 = 0.0398 (5052 observed reflections, $I > 2\ \sigma(I)$) and wR^2 = 0.0948; data/restraints/parameters 9226/5/326; GoF = 0.861. Largest peak and hole 1.078 and −0.959 e/Å^3.

Crystal data for **5**: $C_{33}H_{44}FOP_2Rh{\cdot}2C_6H_6$, M_W 796.75, orange, irregular block (0.13 × 0.12 × 0.10), monoclinic, space group *P*2(1)/*m*, *a*: 11.8790(17) Å, *b*: 14.547(2) Å, *c*: 12.9966(18) Å, β = 114.323(2)°, V = 2046.6(5) Å^3, Z = 2, D_{calc}: 1.293 g cm^{-3}, $F(000)$: 836, T = 100(2) K, μ 0.532 mm^{-1}. 22891 measured reflections (2θ: 3−57°, ω scans 0.3°), 5112 unique (R_{int} = 0.0387); minimum/maximum transmission factors 0.738/0.862. Final agreement factors were R^1 = 0.0463 (4595 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.1179; data/restraints/parameters 5112/0/250; GoF = 1.048. Largest peak and hole 2.248 and −0.814 e/Å^3.

Crystal data for **6**: $C_{33}H_{53}F_2OP_2Rh{\cdot}2C_6H_6$, M_W 814.74, orange, irregular block (0.24 × 0.20 × 0.16), monoclinic, space group *P*2(1)/*m*, *a*: 11.8677(4) Å, *b*: 14.5318(5) Å, *c*: 13.0100(5) Å, β = 114.51°, V = 2041.44(13) Å^3, Z = 2, D_{calc}: 1.325 g cm^{-3}, $F(000)$: 852, T = 100(2) K, μ 0.539 mm^{-1}. 24908 measured reflections (2θ: 3−57°, ω scans 0.3°), 5113 unique (R_{int} = 0.0249); minimum/maximum transmission factors 0.822/0.922. Final agreement factors were R^1 = 0.0230 (4726 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0578; data/restraints/parameters 5113/60/290; GoF = 1.025. Largest peak and hole 0.605 and −0.329 e/Å^3.

Crystal data for **9**: $C_{33}H_{52}BO_3P_2Rh$, M_W 672.41, red, irregular block (0.12 × 0.08 × 0.07), monoclinic, space group *P*2(1)/*n*, *a*: 9.6438(4) Å, *b*: 18.7522(8) Å, *c*: 18.5770(8) Å, β = 96.2620(10)°, V = 3339.5(2)Å^3, Z = 4, D_{calc}: 1.337 g cm^{-3}, $F(000)$: 1416, T = 100(2) K, μ 0.638 mm^{-1}. 38723 measured reflections (2θ: 3−57°, ω scans 0.3°), 8089 unique (R_{int} = 0.0603); minimum/maximum transmission factors 0.843/0.957. Final agreement factors were R^1 = 0.0543 (6758 observed reflections, $I > 2\sigma(I)$) and wR^2 = 0.0930; data/restraints/parameters 8089/0/371; GoF = 1.173. Largest peak and hole 0.774 and −0.688 e/Å^3.

■ ASSOCIATED CONTENT

Supporting Information

Molecular diagram of cocrystallized **3a** and **3b**, NMR spectra of complexes **7** and **8** and of all borylated arenes. CIF files giving positional and displacement parameters, crystallographic data, and bond lengths and angles of compounds **2**, **3**, **5**, **6**, and **9**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00176.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the MINECO of Spain (Projects CTQ2014-52799-P and CTQ2014-51912-REDC), the Diputación General de Aragón (E-35), FEDER, and the European Social Fund is acknowledged. We are very grateful to Dr. Enrique Oñate for collecting the X-ray diffraction data.

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DOI: 10.1021/acs.organomet.5b00176
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