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# Synthesis, Characterization, and Reactivity of Rhodium(I) Acetylacetonato Complexes Containing Pyridinecarboxaldimine Ligands

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Addition of *o*-$C_6H_4NCH{=}NAr$ to $Rh(coe)_2(acac)$ (coe = cis-cyclooctene, acac = acetylacetonato) gave several new iminopyridine rhodium(I) complexes of the type $Rh(acac)(\kappa^2$-*o*-$C_6H_4NCH{=}NAr)$ (**1a** Ar = 4-$C_6H_4$-OMe; **1b** Ar = 2,6-$C_6H_3$-$Me_2$; **1c** Ar = 2,6-$C_6H_3$-$Et_2$; **1d** Ar = 2,6-$C_6H_3$-*i*-$Pr_2$). All new rhodium complexes have been characterized by a number of physical methods, including multinuclear NMR spectroscopy and X-ray diffraction studies for **1b** and **1c**. Addition of $CHCl_3$ to **1a** afforded the corresponding rhodium(III) complex *trans*-$Rh(\kappa^2$-*o*-$C_6H_4NCH{=}NAr)(CHCl_2)(Cl)(acac)$ (**2**). Addition of $B_2cat_3$ (cat = 1,2-$O_2C_6H_4$) to **1** gave zwitterionic $Rh(\eta^6$-catBcat$)(\kappa^2$-*o*-$C_6H_4NCH{=}NAr)$ (**3**). The molecular structure of **3b** has been confirmed by a single crystal X-ray diffraction study and shows that the $N_2Rh$ fragment is bound to the catBcat anion via one of the catecholato groups in a $\eta^6$-fashion. These complexes have also been examined for their ability to catalyze the hydroboration of a series of vinylarenes. Reactions using catecholborane and pinacolborane seem to proceed largely through a dehydrogenative borylation mechanism to give a number of boronated products.

## Introduction

The discovery that boron−hydrogen bonds add to unsaturated organic molecules to form a class of compounds known as organoboranes has become a remarkably important synthetic methodology in organic synthesis.[1] Although borane adds readily to alkenes at −80 °C,[2] other hydroborating agents, such as diorganyloxyboranes, are slow to react even at room temperature. For instance, addition of $H_3B{\cdot}THF$ to catechol affords catecholborane (HBcat, cat = 1,2-$O_2C_6H_4$), a relatively stable hydroborating agent which adds to alkenes and alkynes only at elevated temperatures (ca. 100 and 70 °C, respectively).[3,4]

An interesting extension to this chemistry was discovered when transition metals were found to accelerate the addition of B−H bonds to unsaturated organic moieties using polyhedral boranes.[5] Männig and Nöth then demonstrated that rhodium complexes could be used to catalyze the hydroboration of alkenes with HBcat under mild conditions and with selectivities differing from that of the uncatalyzed reaction.[6] Since this remarkable discovery, a considerable amount of research has focused on investigating the mechanism and scope of the catalyzed hydroboration reaction.[7] A number of transition metals have been found to catalyze hydroborations with HBcat; however, reactions using rhodium catalysts are usually the most effective for hydroborations of vinylarenes.[8] The judicious choice of the rhodium complex can be used to effectively generate either the expected linear or the unusual branched hydroboration product (Scheme 1). Unfortunately, these reactions often suffer from poor selectivities or competing pathways (i.e.,

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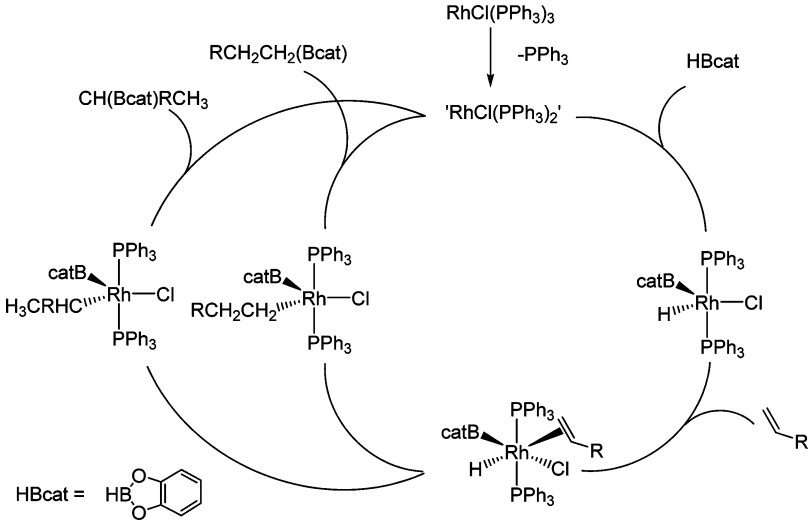
**Scheme 1.** Postulated Mechanism for the $RhCl(PPh_3)_3$ Catalyzed Hydroboration of Alkenes Using Catecholborane (HBcat)




hydrogenation or dehydrogenative borylation[9]) and, as a result, a significant amount of research has focused on designing new catalyst systems.[10] Recently, there has been considerable interest in the use of rhodium complexes containing P,N-bidentate ligands as catalysts for the hydroboration of vinylarenes.[11] Although mixtures of "hydroboration" products were reported in these cases, we have found that reactions using rhodium complexes containing a bulky P,N ligand gave a number of boronated products arising from a competing dehydrogenative borylation pathway. To gain an understanding of the factors that influence selectivities in these reactions we have prepared a series of rhodium(I) complexes containing iminopyridine ligands and examined their ability to catalyze the hydroboration of vinylarenes with HBcat.

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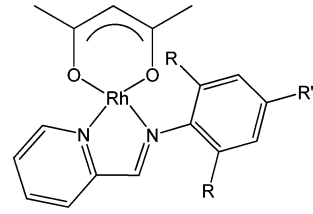
## Results and Discussion

Pyridinecarboxaldimine ligands have been used in conjunction with a variety of metals for a wide range of applications.[12−15] For instance, metal oligonucleotides have recently been prepared using ruthenium complexes containing 2′-iminomethylpyridyl-2′-deoxyuridine.[12a] Likewise, iminopyridines have also been reported to be efficient ligands in the palladium catalyzed cyclization of (Z)-4′-acetoxy-2′-butenyl 2-alkynoates.[14a] These ligands were found to not only inhibit $\beta$-hydride elimination but also stabilize a unique vinylpalladium intermediate. While rhodium complexes containing these ligands are known,[16] to the best of our knowledge, acetylacetonato (acac) compounds have not yet been reported.




**1a**: R = H, R' = OMe
**1b**: R = Me, R' = H
**1c**: R = Et, R' = H
**1d**: R = *i*-Pr, R' = H

**Figure 1.** Iminopyridine rhodium(I) acetylacetonato complexes **1a-d**.

Addition of pyridinecarboxaldimine ligands *o*-$C_6H_4$-NCH═NAr to Rh(coe)$_2$(acac) (coe = cis-cyclooctene) gave iminopyridine rhodium(I) complexes of the type Rh($\kappa^2$-*o*-$C_6H_4$*N*CH═*N*Ar)(acac) (**1**) (Figure 1). All new rhodium complexes have been characterized by a number of physical methods, including multinuclear NMR spectroscopy. A significant downfield shift in the $^1$H NMR is observed for the imine sp$^2$ proton upon coordination to the metal center. For instance, the singlet at $\delta$ 8.61 ppm for the free ligand 4-methoxy-*N*-((pyridin-2-yl)methylene)benzenamine shifts to 8.78 ppm in complex **1a**. This resonance is also observed as a doublet with coupling to rhodium of $J$ = 3.2 Hz. Similar trends are observed for the pyridine hydrogen α to the nitrogen atom as the chemical shift changes from $\delta$ 8.69 ppm to 10.84 ppm (d, $J$ = 5.9 Hz). Significant shifts are also observed in the $^{13}$C{$^1$H} NMR spectra, as the imine carbon for the free ligand is observed at $\delta$ 158.6 pm while that for **1a** is found at 150.2 ppm.

Complexes **1b** and **1c** have also been characterized by single crystal X-ray diffraction studies, the molecular structures of which are shown in Figures 2 and 3, respectively, and crystallographic data provided in Table 1. Bond distances and angles for the acetylacetonato ligands are similar to those reported previously in related rhodium ethylene[16a,b] and mixed phosphine/CO systems.[16c,d] Likewise, the iminopyridine ligands are well within the expected range for similar rhodium complexes.[17] The metals assume a slightly distorted square planar configuration with Rh−N distances of 1.980(3) (pyridine, **1b**), 1.985(2) (pyridine, **1c**), 1.963(3) (imine, **1b**), and 1.9698(19) (imine, **1c**). As observed previously, the plane of the N-aryl group also lies approximately perpendicular to the metal coordination plane.[18] This conformation places the two ortho groups in positions which will block approach of substrates to the vacant axial sites, which may ultimately affect the regioselectivity of the catalyzed hydroboration reaction.

As with the analogous diphosphine acetylacetonato complexes,[19a] these novel iminopyridine compounds all decompose in chlorinated solvents over time to give a

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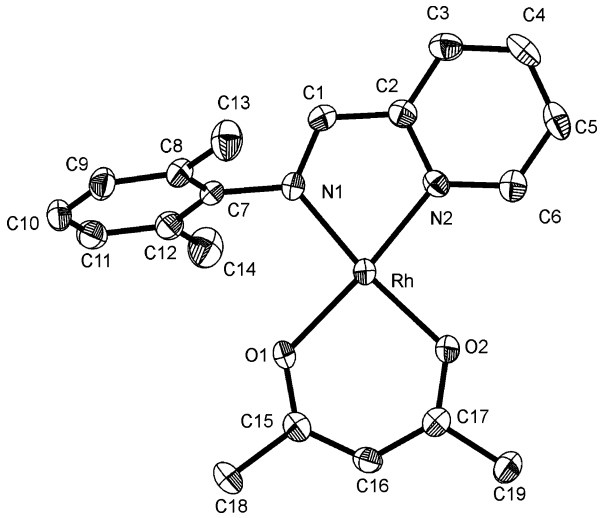


**Figure 2.** Molecular structure of **1b** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−N(1) 1.963(3), Rh−N(2) 1.980(3), Rh−O(1) 2.010(2), Rh−O(2) 2.010(2), N(1)−C(1) 1.298(4), N(2)−C(2) 1.368(4), O(1)−C(15) 1.273(4), O(2)−C(17) 1.280(4); N(1)−Rh−N(2) 79.78(12), N(1)−Rh−O(1) 94.55(11), N(2)−Rh−O(1) 173.60(10), N(1)−Rh−O(2) 172.93(10), N(2)−Rh−O(2) 93.54(11), O(1)−Rh−O(2) 92.24(10), C(1)−N(1)−C(7) 119.0(3), C(1)−N(1)−Rh 116.4(2), C(7)−N(1)−Rh 124.2(2), C(6)−N(2)−C(2) 118.1(3).

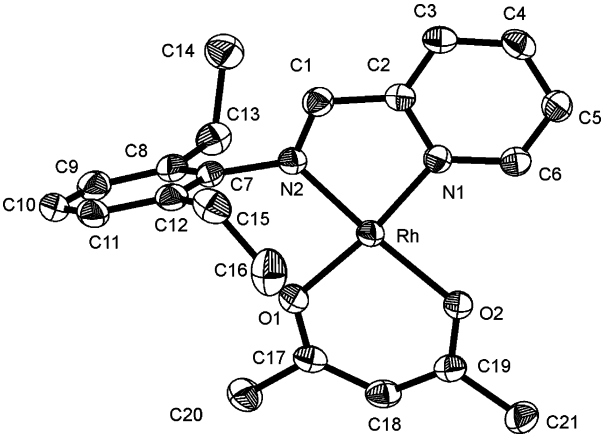


**Figure 3.** Molecular structure of **1c** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−N(2) 1.9698(19), Rh−N(1) 1.985(2), Rh−O(1) 2.0176(18), Rh−O(2) 2.0190(17), N(1)−C(2) 1.377(3), N(2)−C(1) 1.306(3), O(1)−C(17) 1.274(3), O(2)−C(19) 1.288(3); N(2)−Rh−N(1) 79.70(8), N(2)−Rh−O(1) 94.59(7), N(1)−Rh−O(1) 173.33(8), N(2)−Rh−O(2) 172.15(8), N(1)−Rh−O(2) 93.92(7), O(1)−Rh−O(2) 92.05(7), C(6)−N(1)−C(2) 117.3(2), C(6)−N(1)−Rh 127.38(17), C(2)−N(1)−Rh 115.27(16), C(1)−N(2)−C(7) 118.6(2).

mixture of products arising from the oxidative addition of the C−Cl bond. For example, addition of $CHCl_3$ to **1a** afforded the corresponding rhodium(III) complex *trans*-Rh($\kappa^2$-*o*-$C_6H_4$*N*CH=*N*Ar)($CHCl_2$)(Cl)(acac) (**2**) in 81% yield. The ability of rhodium(I) complexes to oxidatively add carbon chlorine bonds is well documented[19] and many of these complexes are active catalyst precursors for the Kharasch reaction.[20] Spectroscopic data for **2** are similar to those for **1a** except a doublet is observed in the $^1$H NMR spectrum for the $CHCl_2$ group at $\delta$ 6.40 ppm with coupling to rhodium at $J_{HRh}$ = 2.7 Hz. Complex **2** has also been characterized by an X-ray diffraction study (Figure 4), showing a *trans* addition of the alkyl chloride. All bond distances and angles are within the range of related complexes.[19] The *trans* addition of alkyl halides to rhodium complexes has been reported previously and is believed to be favored when bulky ligands are coordinated to the metal center.[19a]Such addition reactions are believed to occur via either direct oxidative addition, followed by isomerization, or by a concerted nucleophilic displacement ($S_N2$) pathway.[19g]

Although related phosphinorhodium acetylacetonato complexes are active and selective catalysts for the hydroboration of a wide range of alkenes using HBcat, the catalyst resting state in these systems has been reported to be the zwitterionic complexes Rh($\eta^6$-catBcat)($P_2$), arising from the redistribution

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**Table 1.** Crystallographic Data Collection Parameters for **1b**, **1c**, **2**, and **3b**

| complex | **1b** | **1c** | **2** | **3b** |
|---|---|---|---|---|
| chemical formula | $C_{19}H_{21}N_2O_2Rh$ | $C_{21}H_{25}N_2O_2Rh$ | $C_{23}H_{28}Cl_3N_2O_4Rh$ | $C_{26}H_{22}BN_2O_4Rh$ |
| formula mass | 412.29 | 440.34 | 605.73 | 540.18 |
| crystal dimensions ($mm^3$) | 0.45 × 0.125 × 0.05 | 0.40 × 0.15 × 0.05 | 0.28 × 0.05 × 0.03 | 0.20 × 0.20 × 0.05 |
| crystal system | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | *P*2(1)/*n* | *P*2(1)/*n* | *P*2(1)/*n* | *P*2(1)/*c* |
| *Z* | 4 | 4 | 4 | 4 |
| *a* (Å) | 9.442(6) | 10.8979(13) | 13.268(8) | 11.245(4) |
| *b* (Å) | 7.753(5) | 11.1449(13) | 13.693(8) | 15.187(6) |
| *c* (Å) | 24.080(16) | 16.4137(19) | 14.352(9) | 13.529(5) |
| α (deg) | 90 | 90 | 90 | 90 |
| $\beta$ (deg) | 90.896(11) | 106.008(2) | 104.815(9) | 94.561(6) |
| $\gamma$ (deg) | 90 | 90 | 90 | 90 |
| volume ($Å^3$) | 1763(2) | 1916.2(4) | 2521(3) | 2303.0(15) |
| $D_{calcd}$ (mg $m^{-3}$) | 1.554 | 1.526 | 1.596 | 1.558 |
| *T* (K) | 173(1) | 198(1) | 173(1) | 173(1) |
| radiation | Mo Kα ($\lambda$ = 0.71073Å) | Mo Kα ($\lambda$ = 0.71073Å) | Mo Kα ($\lambda$ = 0.71073Å) | Mo Kα ($\lambda$ = 0.71073Å) |
| $\mu$ ($mm^{-1}$) | 0.982 | 0.908 | 1.028 | 0.778 |
| total reflections collected | 10853 | 12916 | 16705 | 15610 |
| no. of variables | 230 | 239 | 301 | 309 |
| $\theta$ (deg) | 1.69−27.48 | 2.02−27.50 | 1.87−27.50 | 1.82−27.50 |
| GoF on $F^2$ | 1.023 | 1.004 | 1.074 | 1.135 |
| $R_1$[a] [$I > 2\sigma(I)$] | 0.0426 | 0.0284 | 0.0428 | 0.0378 |
| $wR_2$[b] (all data) | 0.1172 | 0.0704 | 0.1101 | 0.1060 |
| largest diff peak and hole (Å) | 0.935, −0.932 | 0.490, −0.375 | 0.802, −0.544 | 1.315, −0.390 |

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[F_o^4])^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0643P)^2]$ (**1b**), $1/[\sigma^2(F_o^2) + (0.032P)^2]$ (**1c**), $1/[\sigma^2(F_o^2) + (0.0342P)^2 + (1.5989P)]$ (**2**), and $1/[\sigma^2(F_o^2) + (0.0388P)^2 + (2.1165P)]$ (**3b**), where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

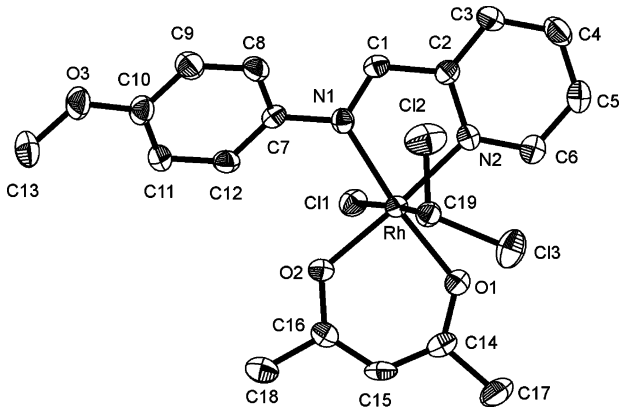


**Figure 4.** Molecular structure of **2·THF** with ellipsoids drawn at 50% probability level. Hydrogen atoms and the solvent molecule omitted for clarity. Selected bond distances (Å) and angles (deg): Rh−O(1) 2.008(3), Rh−O(2) 2.021(3), Rh−N(2) 2.023(4), Rh−N(1) 2.040(4), Rh−C(19) 2.049(4), Rh−Cl(1) 2.4820(18), C(1)−N(1) 1.296(6), C(1)−C(2) 1.454(6), C(2)−N(2) 1.367(6); O(1)−Rh−O(2) 92.51(13), O(2)−Rh−N(2) 174.90(13), O(1)−Rh−N(1) 171.20(14), N(2)−Rh−N(1) 80.34(15), O(1)−Rh−Cl(1) 88.86(9), O(2)−Rh−Cl(1) 89.94(10), N(2)−Rh−Cl(1) 92.61(11), N(1)−Rh−Cl(1) 87.26(10), C(19)−Rh−Cl(1) 176.72(13), Cl(2)−C(19)−Cl(3) 107.1(2).

of substituents on catecholborane (HBcat).[7d] In an elegant study, Marder and co-workers have shown that addition of $B_2cat_3$ to Rh(acac)($P_2$) led to the zwitterionic complexes Rh($\eta^6$-catBcat)($P_2$) in high yields, along with concomitant formation of acacBcat.[21] The diboron species $B_2cat_3$ is generated as a decomposition product in nucleophilic reactions with HBcat or when HBcat is heated at elevated temperatures.[7c,22] In this study we have found that addition of $B_2cat_3$ to **1a-d** gave zwitterionic Rh($\eta^6$-catBcat)($\kappa^2$-*o*-$C_6H_4$*N*CH=*N*Ar) (**3**) in good yields (Scheme 2). The $^{11}$B NMR spectra have a sharp peak at 14 ppm, consistent with the boron atom being four coordinate.[23] The molecular structure of **3b** has been confirmed by a single crystal X-ray diffraction study (Figure 5) and shows that the $N_2$Rh fragment is bound to the catBcat anion via one of the catecholato groups in a $\eta^6$-fashion. As with related systems,[9f−i,24] there appears to be a noticeable slippage of the $N_2$Rh group with respect to the $\pi$-bound arene ring. Interestingly, two bond distances are considerably short (Rh(1)−C(18) 2.198(4), Rh(1)−C(17) 2.254(4) Å), two are average (Rh(1)−C(15) 2.294(4), Rh(1)−C(16) 2.306(4) Å), and the last two are considerably longer with Rh(1)−C(19) and Rh(1)−C(20) bonds at 2.328(4) and 2.355(4) Å, respectively. Although this suggests bonding of the type $\eta^2$:$\eta^2$:$\eta^2$, no such localization within the C−C bond distances of the aromatic ring is observed. The potential surface for such distortions is therefore likely quite shallow and further studies are required to understand the nature of the bonding in these metal aryl spiroboronate esters.

To compare complexes **1a-d** against other rhodium catalysts, we have examined their ability to catalyze the hydroboration of a series of vinylarenes (i.e., 4-vinylanisole, 2-vinylnaphthalene, perfluorostyrene, etc.) using multinuclear NMR spectroscopy.[7c−e] Reactions were conducted at room

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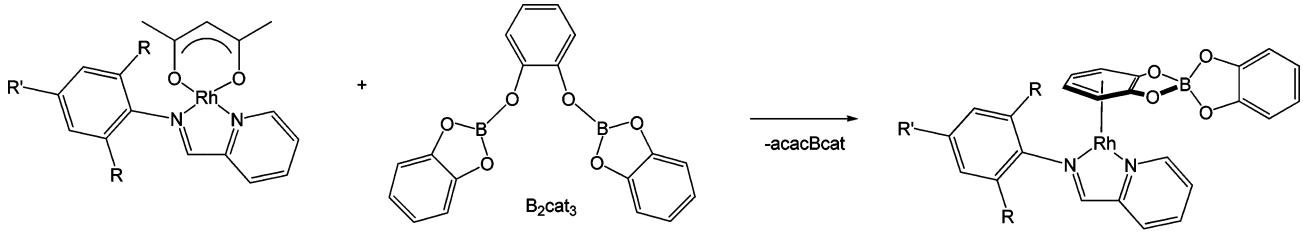
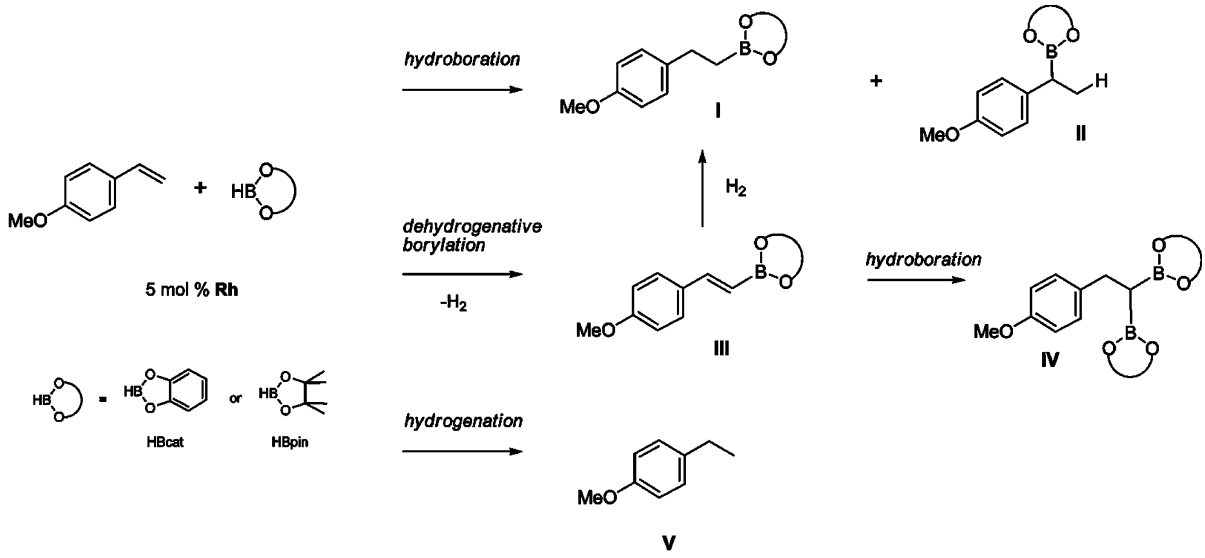
**Scheme 2.** Synthesis of Rhodium(I) Arylspiroboronate Ester Complexes




**1a**: R = H, R' = OMe
**1b**: R = Me, R' = H
**1c**: R = Et, R' = H
**1d**: R = i-Pr, R' = H

**3a**: R = H, R' = OMe
**3b**: R = Me, R' = H
**3c**: R = Et, R' = H
**3d**: R = i-Pr, R' = H

**Scheme 3.** Rhodium Pyridinecarboxaldimine Catalyzed Hydroboration of 4-Vinylanisole[a]




| Entry | Reagent | Catalyst | Borane | I | II | III | IV | V |
|---|---|---|---|---|---|---|---|---|
| 1 | R = OMe | **1a** | HBcat | 50 | 5 | 5 | 5 | 35 |
| 2 | R = OMe | **1b** | HBcat | 20 | 15 | 10 | 35 | 20 |
| 3 | R = OMe | **1c** | HBcat | 40 | 5 | 10 | 15 | 30 |
| 4 | R = OMe | **1d** | HBcat | 20 | 15 | 10 | 30 | 25 |
| 5 | R = F | **1a** | HBcat | 35 | 10 | 5 | 10 | 40 |
| 6 | R = F | **1b** | HBcat | 10 | 40 | 10 | 25 | 15 |
| 7 | R = F | **1c** | HBcat | 20 | 20 | 10 | 20 | 30 |
| 8 | R = F | **1d** | HBcat | 10 | 25 | 20 | 25 | 20 |
| 9 | R = F | **1d** | HBpin | 15 | 0 | 15 | 0 | 70 |
| 10 | R = OMe | **1d** | HBpin | 15 | 0 | 25 | 0 | 60 |

[a] All reactions were conducted in $C_6D_6$ at RT (conversion 100%, TON = 20) and product ratios were determined by $^1H$ NMR spectroscopy and confirmed by GC/MS.

temperature using 5 mol% of catalyst and a slight excess of borane to ensure complete conversion of the starting vinylarene. Unfortunately, reactions using HBcat with catalytic amounts of complexes **1a-d** all gave complex product distributions arising from a competing dehydrogenative borylation reaction. For instance, addition of HBcat to 4-vinylanisole (Scheme 3) using a catalytic amount of **1d** (5 mol%, TON = 20) gave a mixture of hydroboration products **I** and **II**, along with products derived from the initial formation of *trans*-4-$MeOC_6H_4CH{=}CHBcat$ (**III**). It is possible that the traditional hydroboration product **I** may also be generated by a rhodium catalyzed hydrogenation of the vinyl boronate ester, as dihydrogen is liberated as a side product in the dehydrogenative borylation reaction. The bisborated product **IV** presumably arises from a subsequent hydroboration of the vinyl boronate ester **III**. Similar product distributions were observed in reactions using other vinylarenes and in reactions run in other solvents, such as THF-

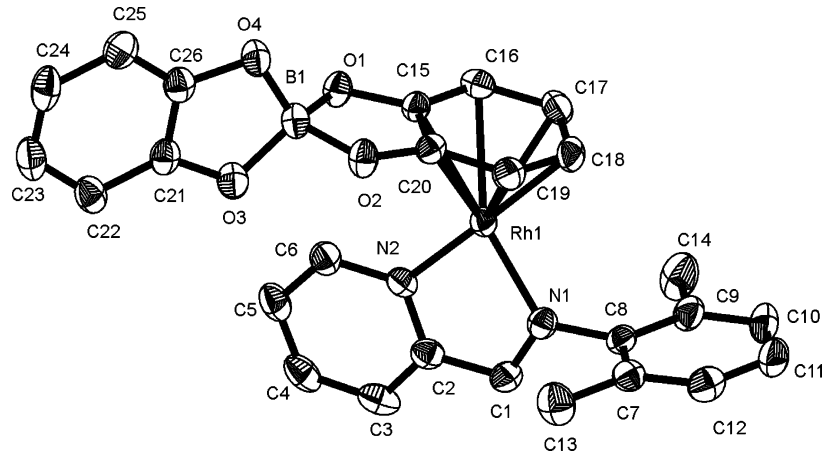



**Figure 5.** Molecular structure of **3b** with ellipsoids drawn at 50% probability level. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (deg): Rh(1)−N(1) 1.986(3), Rh(1)−N(2) 2.002(3), Rh(1)−C(18) 2.198(4), Rh(1)−C(17) 2.254(4), Rh(1)−C(15) 2.294(4), Rh(1)−C(16) 2.306(4), Rh(1)−C(19) 2.328(4), Rh(1)−C(20) 2.355(4), O(1)−B(1) 1.505(5), O(2)−B(1) 1.507(5), O(3)−B(1) 1.478(5), O(4)−B(1) 1.463(5), N(1)−C(1) 1.317(5), N(2)−C(2) 1.361(5), C(15)−C(16) 1.405(5), C(15)−C(20) 1.429(5), C(16)−C(17) 1.412(6), C(17)−C(18) 1.408(6), C(18)−C(19) 1.425(5), C(19)−C(20) 1.395(5); N(1)−Rh(1)−N(2) 78.39(13), O(4)−B(1)−O(3) 106.4(3), O(4)−B(1)−O(1) 113.8(3), O(3)−B(1)−O(1) 111.7(3), O(4)−B(1)−O(2) 110.0(3), O(3)−B(1)−O(2) 111.5(3), O(1)−B(1)−O(2) 103.4(3).

$d_8$. A small amount of borane degradation[7d] to give $B_2cat_3$ and $H_2$ was also observed, further complicating product distributions.

Reactions using pinacolborane (HBpin, pin = 1,2-$O_2C_2Me_4$), another common reagent in metal catalyzed hydroboration reactions,[25] also gave complicated product distributions. Although none of the internal hydroboration product **II** was observed in reactions using HBpin, this is not unusual as hydroborations using this less reactive borane predominantly give the corresponding linear product. A notable exception to this observed selectivity is when cationic rhodium[25s] or iridium[25c] complexes are used to catalyze this reaction. Likewise, changing the catalyst precursor to the less bulky **1a** did not improve selectivities. Reactions using the zwitterionic species **3** gave product distributions similar to those using the acetylacetonato precursors. The fate of the catalyst precursors upon completion of these reactions appears to be the zwitterionic complexes **3a-d**, where the coordinated imine fragment has not been reduced by either the borane or the liberated dihydrogen. Unfortunately, all attempts to improve selectivities by optimizing catalyst conditions (lowering reaction temperatures, changing order of substrate addition, rate of substrate addition, etc.) proved unsuccessful.

In summary, we have prepared four novel rhodium(I) acetylacetonato complexes containing bidentate *o*-$C_6H_4NCH$═NAr ligands. These complexes react with $B_2cat_3$ to give the corresponding zwitterions of the type Rh($\eta^6$-catBcat)($\kappa^2$-*o*-$C_6H_4$*N*CH═*N*Ar) (**3**) in moderate to good yields. Unlike the bisphosphine analogs, hydroborations of vinylarenes using complexes with nitrogen containing ligands give complex product distributions arising from competing dehydrogenative borylation reactions and borane degradation.

## Experimental Section

Reagents and solvents were purchased from Aldrich Chemicals and used as received. Rh(acac)(coe)$_2$,[26] $B_2cat_3$,[27] and iminopyridines[12] were synthesized as previously reported. NMR spectra were recorded on a JEOL JNM-GSX270 FT NMR ($^1$H 270 MHz; $^{11}$B 87 MHz;$^{13}$C 68 MHz) spectrometer. Chemical shifts ($\delta$) are reported in ppm [relative to residual solvent peaks ($^1$H and $^{13}$C) or external $BF_3\cdot OEt_2$ ($^{11}$B)] and coupling constants ($J$) in Hz. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), septet (sept), multiplet (m), broad (br), and overlapping (ov). Decomposition points were determined using a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed

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by Guelph Chemical Laboratories (Guelph, ON). All reactions were performed under an atmosphere of dinitrogen.

**Synthesis of 1a.** To a 5 mL tetrahydrofuran (THF) solution of Rh(acac)(coe)$_2$ (250 mg, 0.59 mmol) was added a 3 mL THF solution of 4-methoxy-*N*-((pyridin-2-yl)methylene)benzenamine (128 mg, 0.60 mmol). The reaction mixture was heated at reflux for 18 h at which point solvent was removed under vacuum. The resulting oily solid was washed with hexane (2 × 3 mL) and **1a** was collected as a dark purple solid by suction filtration. Yield: 225 mg (92%), mp 264−268 °C (decomp.). NMR spectroscopic data (in $C_6D_6$): $^1$H $\delta$: 10.84 (d, $J$ = 5.9 Hz, 1H, Ar), 8.78 (d, $J_{HRh}$ = 3.2 Hz, 1H, C(*H*)N), 8.08 (d, $J$ = 8.7 Hz, 2H, Ar), 7.21 (ov ddd, $J$ = 7.2, 7.2, 1.0 Hz, 1H, Ar), 7.05 (ddd, $J$ = 7.2, 5.9, 1.0 Hz, 1H, Ar), 6.92 (d, $J$ = 8.7 Hz, 2H, Ar), 6.67 (d, $J$ = 7.2 Hz, 1H, Ar), 5.06 (s, 1H, C(*H*)═C), 3.39 (s, 3H, OC$H_3$), 1.99 (s, 3H, acac-C$H_3$), 1.84 (s, 3H, acac-C$H_3$); $^{13}$C{$^1$H} $\delta$: 184.0 (*C*(O)), 182.7 (*C*(O)), 159.5, 158.2 (d, $J_{CRh}$ = 2.0 Hz), 151.1, 150.2, 147.2, 129.8, 126.3, 124.7, 124.1, 113.5, 99.7 (*C*(H)═C), 54.8 (O*C*H$_3$), 27.1 (acac-*C*H$_3$), 27.0 (acac-*C*H$_3$). Anal. Calcd for $C_{18}H_{19}N_2O_3Rh$ (414.29) (%): C 52.18, H 4.63, N 6.76; found: C 51.88, H 4.61, N 6.56.

**Synthesis of 1b.** To a 5 mL toluene solution of Rh(acac)(coe)$_2$ (300 mg, 0.71 mmol) was added a 3 mL toluene solution of 2,6-dimethyl-*N*-((pyridin-2-yl)methylene)benzenamine (155 mg, 0.74 mmol). The reaction mixture was heated at reflux for 18 h at which point solvent was removed under vacuum. The resulting oily solid was washed with hexane (2 × 3 mL) and **1b** was collected as a dark purple solid by suction filtration. Yield: 200 mg (68%), mp 218−222 °C (decomp.). NMR spectroscopic data (in $C_6D_6$): $^1$H $\delta$: 10.81 (d, $J$ = 5.7 Hz, 1H, Ar), 8.38 (d, $J_{HRh}$ = 4.2 Hz, 1H, C(*H*)N), 7.29−7.16 (ov m, 4H, Ar), 7.06 (ddd, $J$ = 7.9, 5.7, 1.5 Hz, 1H, Ar), 6.64 (d, $J$ = 7.9 Hz, 1H, Ar), 4.93 (s, 1H, C(*H*)═C), 2.42 (s, 6H, Ar−C$H_3$), 1.95 (s, 3H, acac-C$H_3$), 1.65 (s, 3H, acac-C$H_3$); $^{13}$C{$^1$H} $\delta$: 184.6 (*C*(O)), 182.5 (*C*(O)), 157.7 (d, $J_{CRh}$ = 4.1 Hz), 153.3, 152.8, 150.6, 131.9, 130.1, 127.8, 125.9, 125.4, 123.9, 99.6 (d, $J_{CRh}$ = 2.7 Hz, *C*(H)═C), 27.0 (acac-*C*H$_3$), 18.6 (Ar-*C*H$_3$). Anal. Calcd for $C_{19}H_{21}N_2O_2Rh$ (412.32) (%): C 55.35, H 5.14, N 6.80; found: C 54.92, H 4.99, N 6.40.

**Synthesis of 1c.** To a 5 mL toluene solution of Rh(acac)(coe)$_2$ (300 mg, 0.71 mmol) was added a 3 mL toluene solution of 2,6-diethyl-*N*-((pyridin-2-yl)methylene)benzenamine (177 mg, 0.74 mmol). The reaction mixture was heated at reflux for 18 h at which point solvent was removed under vacuum. The resulting oily solid was washed with hexane (2 × 3 mL) and **1c** was collected as a dark purple solid by suction filtration. Yield: 250 mg (80%), mp 208−210 °C (decomp.). NMR spectroscopic data (in $C_6D_6$): $^1$H $\delta$: 10.81 (d, $J$ = 5.7 Hz, 1H, Ar), 8.54 (d, $J_{HRh}$ = 4.2 Hz, 1H, C(*H*)N), 7.36 (2nd order ov dd, $J$ = 6.7, 6.7 Hz, 1H, Ar), 7.26−7.15 (ov m, 3H, Ar), 7.06 (ddd, $J$ = 7.9, 5.7, 1.5 Hz, 1H, Ar), 6.65 (d, $J$ = 7.9 Hz, 1H, Ar), 4.92 (s, 1H, C(*H*)═C), 3.04 (q, $J$ = 7.7 Hz, 1H, C*H*HCH$_3$), 2.98 (q, $J$ = 7.7 Hz, 1H, C*H*HCH$_3$), 2.91 (q, $J$ = 7.7 Hz, 1H, CH*H*CH$_3$), 2.85 (q, $J$ = 7.7 Hz, 1H, CH*H*CH$_3$), 1.94 (s, 3H, acac-C$H_3$), 1.65 (s, 3H, acac-C$H_3$), 1.20 (t, $J$ = 7.7 Hz, 6H, CH$_2$C$H_3$); $^{13}$C{$^1$H} $\delta$: 184.4 (*C*(O)), 182.5 (*C*(O)), 157.5 (d, $J_{CRh}$ = 4.1 Hz), 153.8, 151.5, 150.6, 137.7, 130.2, 126.3, 125.8, 125.6, 123.9, 99.6 (d, $J_{CRh}$= 2.3 Hz, *C*(H)═C), 27.0 (acac-*C*H$_3$), 24.7 (*C*H$_2$CH$_3$), 15.0 (CH$_2$*C*H$_3$). Anal. Calcd for $C_{21}H_{25}N_2O_2Rh$ (440.38) (%): C 57.28, H 5.72, N 6.36; found: C 57.47, H 5.79, N 5.90.

**Synthesis of 1d.** To a 5 mL toluene solution of Rh(acac)(coe)$_2$ (300 mg, 0.71 mmol) was added a 3 mL toluene solution of 2,6-diisopropyl-*N*-((pyridin-2-yl)methylene)benzenamine (198 mg, 0.74 mmol). The reaction mixture was heated at reflux for 18 h at which point solvent was removed under vacuum. The resulting oily solid was washed with hexane (2 × 3 mL) and **1d** was collected as a dark purple solid by suction filtration. Yield: 265 mg (80%), mp 261−263 °C (decomp.). NMR spectroscopic data (in $C_6D_6$): $^1$H $\delta$: 10.81 (d, $J$ = 5.7 Hz, 1H, Ar), 8.76 (d, $J_{HRh}$ = 4.2 Hz, 1H, C(*H*)N), 7.41 (2nd order ov dd, $J$ = 6.6, 6.6 Hz, 1H, Ar), 7.33 (2nd order dd, $J$ = 6.6, 2.0 Hz, 2H, Ar), 7.15 (ov ddd, $J$ = 7.9, 7.9, 1.5 Hz, 1H, Ar), 7.05 (ddd, $J$ = 7.9, 5.7, 1.5 Hz, 1H, Ar), 6.64 (d, $J$ = 7.9 Hz, 1H, Ar), 4.93 (s, 1H, C(*H*)═C), 3.80 (sept, $J$ = 6.7 Hz, 2H, C*H*(CH$_3$)$_2$), 1.92 (s, 3H, acac-C$H_3$), 1.68 (s, 3H, acac-C$H_3$), 1.44 (d, $J$ = 6.7 Hz, 6H, CH(C$H_3$)$_2$), 1.10 (d, $J$ = 6.7 Hz, 6H, CH(C$H_3$)$_2$); $^{13}$C{$^1$H} $\delta$: 184.2 (*C*(O)), 182.5 (*C*(O)), 157.3 (d, $J_{CRh}$ = 2.6 Hz), 153.2, 150.5, 149.7, 142.3, 130.2, 126.7, 125.6, 123.7, 122.7, 99.7 (*C*(H)═C), 27.9 (acac-*C*H$_3$), 26.9 (*C*H(CH$_3$)$_2$), 26.8 (*C*H(CH$_3$)$_2$), 24.2 (CH(*C*H$_3$)$_2$), 23.9 (CH(*C*H$_3$)$_2$). Anal. Calcd for $C_{23}H_{29}N_2O_2Rh$ (468.44) (%): C 58.97, H 6.25, N 5.98; found: C 59.39, H 6.11, N 5.63.

**Synthesis of 2.** To a 3 mL toluene solution of Rh(acac)(coe)$_2$ (200 mg, 0.47 mmol) was added a 1 mL toluene solution of 4-methoxy-*N*-((pyridin-2-yl)methylene)benzenamine (100 mg, 0.47 mmol). The reaction mixture was heated at reflux for 18 h then allowed to cool to room temperature (RT). Dry $CHCl_3$ (1 mL) was added and the reaction allowed to proceed for 18 h. The resulting orange precipitate was collected by suction filtration and recrystallized from THF (10 mL) stored at −30 °C for 3 days. The resulting orange precipitate was collected by suction filtration and dried under vacuum. Yield: 205 mg (81%), mp 218−222 °C (decomp.). NMR spectroscopic data (in $CDCl_3$): $^1$H $\delta$: 9.18 (d, $J$ = 5.2 Hz, 1H, Ar), 8.39 (d, $J_{HRh}$ = 2.7 Hz, 1H, C(*H*)N), 8.01−7.92 (ov m, 2H, Ar), 7.67−7.62 (ov m, 3H, Ar), 6.91 (d, $J$ = 8.9 Hz, 2H, Ar), 6.40 (d, $J_{HRh}$ = 2.7 Hz, 1H, Rh−C*H*Cl$_2$), 5.47 (s, 1H, C(*H*)═C), 3.85 (s, 3H, OC$H_3$), 2.18 (s, 3H, acac-C$H_3$), 2.03 (s, 3H, acac-C$H_3$); $^{13}$C{$^1$H} $\delta$: 187.4 (*C*(O)), 186.6 (*C*(O)), 163.6, 160.8, 156.2, 150.1, 139.7, 138.3, 127.6, 126.7, 125.9, 113.7, 100.5 (*C*(H)═C), 72.5 (d, $J_{CRh}$ = 37.4 Hz, Rh−*C*HCl$_2$), 55.6 (OCH$_3$), 27.2 (acac-*C*H$_3$), 27.1 (acac-*C*H$_3$). Anal. Calcd for $C_{19}H_{20}Cl_3N_2O_3Rh \cdot C_4H_8O$ (605.93) (%): C 45.59, H 4.67, N 4.62; found: C 46.18, H 4.63, N 4.66.

**Synthesis of 3a.** To a 5 mL toluene solution of **1a** (150 mg, 0.36 mmol) was added a 5 mL toluene suspension of $B_2cat_3$ (125 mg, 0.36 mmol). The reaction was allowed to proceed for 18 h at which point a dark precipitate was collected by suction filtration. The solid was washed with THF (1 × 2 mL) and dried under vacuum. Yield: 175 mg (92%), mp 192 °C (decomp.). NMR spectroscopic data (in $CDCl_3$): $^1$H $\delta$: 9.37 (d, $J$ = 5.9 Hz, 1H, Ar), 7.81 (d, $J_{HRh}$ = 4.9 Hz, 1H, C(*H*)N), 7.77 (d, $J$ = 7.2 Hz, 1H, Ar), 7.62 (ov dd, $J$ = 7.2, 7.2 Hz, 1H, Ar), 7.27−7.12 (ov m, 3H, Ar), 6.90 (d, $J$ = 8.9 Hz, 2H, Ar), 6.82−6.69 (ov m, 4H, catechol), 6.49 (ov m, 2H, catechol), 5.01 (dd, $J$ = 4.5, 2.7 Hz, 2H, $\eta^6$-C$_6H_4$O$_2$), 3.84 (s, 3H, OC$H_3$); $^{11}$B $\delta$: 14.1 (sharp). Anal. Calcd for $C_{25}H_{20}N_2BO_5Rh \cdot C_4H_8O$ (614.30) (%): C 57.06, H 3.84, N 5.33; found: C 56.75, H 4.13, N 4.87.

**Synthesis of 3b.** To a 5 mL toluene solution of **1b** (175 mg, 0.42 mmol) was added a 5 mL toluene suspension of $B_2cat_3$ (147 mg, 0.42 mmol). The reaction was allowed to proceed for 18 h at which point a dark precipitate was collected by suction filtration. Yield: 180 mg (79%), mp 266−269 °C (decomp.). NMR spectroscopic data (in $CDCl_3$): $^1$H $\delta$: 9.48 (d, $J$ = 6.2 Hz, 1H, Ar), 7.78 (2nd order d, $J$ = 7.4 Hz, 1H, Ar), 7.68 (ov ddd, $J$ = 7.4, 7.4, 1.5 Hz, 1H, Ar), 7.64 (d, $J_{HRh}$ = 5.4 Hz, 1H, C(*H*)N), 7.28 (ddd, $J$ = 7.4, 6.2, 1.5 Hz, 1H, Ar), 7.14−7.11 (ov m, 3H, Ar), 6.80−6.72 (m, 4H, catechol), 6.61 (2nd order ddd, $J$ = 4.2, 2.4, 1.2 Hz, 2H, $\eta^6$-C$_6H_4$O$_2$), 4.54 (dd, $J$ = 4.2, 2.5 Hz, 2H, $\eta^6$-C$_6H_4$O$_2$), 2.17 (s, 6H, C$H_3$); $^{11}$B $\delta$: 13.9 (sharp); $^{13}$C{$^1$H} $\delta$: 152.9, 151.9, 151.0, 150.8, 148.3, 132.0, 131.5, 129.1, 128.5, 127.1, 126.5, 122.0, 118.9

(d, $J_{CRh}$ = 13.3 Hz, $\eta^6$-$C_6H_4O_2$), 109.5 (d, $J_{CRh}$ = 15.4 Hz, $\eta^6$-$C_6H_4O_2$), 86.7 (*C*(H)═C), 81.8 (d, $J_{CRh}$ = 7.2 Hz, $\eta^6$-$C_6H_4O_2$), 17.5 ($CH_3$). Anal. Calcd for $C_{26}H_{22}N_2BO_4Rh$ (540.21) (%): C 57.80, H 4.11, N 5.19; found: C 57.82, H 4.21, N 4.88.

**Synthesis of 3c.** To a 5 mL toluene solution of **1c** (200 mg, 0.45 mmol) was added a 5 mL toluene suspension of $B_2cat_3$ (157 mg, 0.45 mmol). The reaction was allowed to proceed for 18 h at which point a dark precipitate was collected by suction filtration. Yield: 190 mg (74%), mp 243−245 °C (decomp.). NMR spectroscopic data (in $CDCl_3$): $^1$H $\delta$: 9.48 (d, $J$ = 5.9 Hz, 1H, Ar), 7.78 (2nd order d, $J$ = 7.9 Hz, 1H, Ar), 7.71−7.64 (ov m, 2H, Ar and C(*H*)N), 7.31−7.23 (ov m, 2H, Ar), 7.18−7.15 (ov m, 2H, Ar), 6.83−6.70 (ov m, 4H, catechol), 6.58 (app t, $J$ = 2.7 Hz, 2H, $\eta^6$-$C_6H_4O_2$), 4.51 (dd, $J$ = 4.2, 2.5 Hz, 2H, $\eta^6$-$C_6H_4O_2$), 2.57 (q, $J$ = 7.4 Hz, 4H, $CH_2CH_3$, 4H), 1.14 (t, $J$ = 7.4 Hz, 6H, $CH_2CH_3$); $^{11}$B $\delta$: 13.8 (sharp); $^{13}$C{$^1$H} $\delta$: 151.8, 151.3, 151.0, 150.5 (d, $J_{CRh}$ = 2.0 Hz), 148.8, 135.1, 132.1, 131.4, 127.5, 126.5, 126.4, 122.1, 119.0 (d, $J_{CRh}$ = 11.8 Hz, $\eta^6$-$C_6H_4O_2$), 109.5 (d, $J_{CRh}$ = 14.3 Hz, $\eta^6$-$C_6H_4O_2$), 86.8 (d, $J_{CRh}$ = 3.7 Hz, *C*(H)═C), 81.9 (d, $J_{CRh}$ = 7.2 Hz, $\eta^6$-$C_6H_4O_2$), 23.6 ($CH_2CH_3$), 15.3 ($CH_2CH_3$). Anal. Calcd for $C_{28}H_{26}N_2BO_4Rh$ (568.27) (%): C 59.18, H 4.62, N 4.93; found: C 58.91, H 4.73, N 4.80.

**Synthesis of 3d.** To a 5 mL toluene solution of **1d** (200 mg, 0.43 mmol) was added a 5 mL toluene suspension of $B_2cat_3$ (148 mg, 0.43 mmol). The reaction was allowed to proceed for 18 h at which point a dark precipitate was collected by suction filtration. Yield: 150 mg (59%), mp 251−254 °C (decomp.). NMR spectroscopic data (in $CDCl_3$): $^1$H $\delta$: 9.50 (d, $J$ = 6.2 Hz, 1H, Ar), 7.79 (2nd order d, $J$ = 7.4 Hz, 1H, Ar), 7.69 (ddd, $J$ = 7.4, 6.2, 1.2 Hz, 1H, Ar), 7.62 (d, $J$ = 5.2 Hz, 1H, C(*H*)N), 7.34−7.27 (ov m, 2H, Ar), 7.2 (2nd order dd, $J$ = 6.9, 1.5 Hz, 2H, Ar), 6.84−6.78 (ov m, 2H, catechol), 6.75−6.68 (ov m, 2H, catechol), 6.61 (ddd, $J$ = 4.4, 2.4, 1.0 Hz, 2H, $\eta^6$-$C_6H_4O_2$), 4.60 (2nd order dd, $J$ = 4.2, 2.5 Hz, 2H, $\eta^6$-$C_6H_4O_2$), 3.11 (sept, $J$ = 6.9 Hz, 2H, $CH(CH_3)_2$), 1.30 (d, $J$ = 6.9 Hz, 6H, $CH(CH_3)_2$), 1.03 (d, $J$ = 6.9 Hz, 6H, $CH(CH_3)_2$); $^{11}$B $\delta$: 13.9 (sharp); $^{13}$C{$^1$H} $\delta$: 151.8, 151.0, 150.3 (d, $J_{CRh}$ = 3 Hz), 149.8, 149.0, 140.2, 132.1, 131.6, 127.9, 126.5, 123.6, 122.2, 119.0 (d, $J_{CRh}$ = 14.3 Hz, $\eta^6$-$C_6H_4O_2$), 109.5 (d, $J_{CRh}$ = 17.4 Hz, $\eta^6$-$C_6H_4O_2$), 86.6 (d, $J_{CRh}$ = 3.6 Hz, *C*(H)═C), 81.6 (d, $J_{CRh}$ = 7.2 Hz, $\eta^6$-$C_6H_4O_2$), 27.5, 26.2, 22.9. Anal. Calcd for $C_{30}H_{30}N_2BO_4Rh$ (596.33) (%): C 60.42, H 5.08, N 4.70; found: C 60.50, H 5.24, N 4.68.

**General Procedure for the Catalyzed Hydroboration of Vinylarenes.** The appropriate borane (1.2 equiv) in 0.5 mL of $C_6D_6$, was added to a 0.5 mL $C_6D_6$ solution of **1** or **3** and the vinylarene. Reactions were allowed to proceed for 18 h and then monitored by multinuclear NMR spectroscopy.[7c−e]

Selected NMR spectroscopic data for 4-$MeOC_6H_4CH_2CH_2$(Bcat), **I**: 2.79 (t, $J$ = 7.9 Hz, $CH_2CH_2$(Bcat)), 1.42 (t, $J$ = 7.9 Hz, $CH_2CH_2$(Bcat)); 4-$MeOC_6H_4CH$(Bcat)$CH_3$, **II**: 2.74 (q, $J$ = 7.7 Hz, $CH$(Bcat)$CH_3$), 1.48 (d, $J$ = 7.7 Hz, CH(Bcat)$CH_3$); 4-$MeOC_6H_4CH$═CH(Bcat), **III**: 7.82 (d, $J$ = 18.3 Hz, $CH$ = CH(Bcat)), 6.34 (d, $J$ = 18.3 Hz, CH═$CH$(Bcat)); 4-$MeOC_6H_4CH_2CH$(Bcat)$_2$, **IV**: 3.36 (d, $J$ = 8.2 Hz, $CH_2CH$(Bcat)$_2$), 2.11 (t, $J$ = 8.2 Hz, $CH_2CH$(Bcat)$_2$); 4-$MeOC_6H_4CH_2CH_3$, **V**: 2.45 (q, $J$ = 7.7 Hz, $CH_2CH_3$), 1.10 (t, $J$ = 7.7 Hz, $CH_2CH_3$).

Selected NMR spectroscopic data for 4-$FC_6H_4CH_2CH_2$(Bcat), **I**: 2.64 (t, $J$ = 8.2 Hz, $CH_2CH_2$(Bcat)), 1.28 (t, $J$ = 8.2 Hz, $CH_2CH_2$(Bcat)); 4-$FC_6H_4CH$(Bcat)$CH_3$, **II**: 2.60 (q, $J$ = 7.7 Hz, $CH$(Bcat)$CH_3$), 1.36 (d, $J$ = 7.7 Hz, CH(Bcat)$CH_3$); 4-$FC_6H_4CH$═CH(Bcat), **III**: 7.62 (d, $J$ = 18.3 Hz, $CH$ = CH(Bcat)), 6.23 (d, $J$ = 18.3 Hz, CH═$CH$(Bcat)); 4-$FC_6H_4CH_2CH$(Bcat)$_2$, **IV**: 3.22 (d, $J$ = 8.2 Hz, $CH_2CH$(Bcat)$_2$), 1.99 (t, $J$ = 8.2 Hz, $CH_2CH$(Bcat)$_2$); 4-$FC_6H_4CH_2CH_3$, **V**: 2.28 (q, $J$ = 7.7 Hz, $CH_2CH_3$), 0.97 (t, $J$ = 7.7 Hz, $CH_2CH_3$).

Selected NMR spectroscopic data for 4-$MeOC_6H_4CH_2CH_2$(Bpin), **I**: 2.85 (t, $J$ = 7.9 Hz, $CH_2CH_2$(Bpin)), 1.10 (t, $J$ = 7.9 Hz, $CH_2CH_2$(Bpin)); 4-$MeOC_6H_4CH$═CH(Bpin), **III**: 7.76 (d, $J$ = 18.3 Hz, $CH$ = CH(Bpin)), 6.35 (d, $J$ = 18.3 Hz, CH═$CH$(Bpin)).

Selected NMR spectroscopic data for 4-$FC_6H_4CH_2CH_2$(Bpin), **I**: 2.69 (t, $J$ = 8.1 Hz, $CH_2CH_2$(Bpin)), 1.10 (t, $J$ = 8.1 Hz, $CH_2CH_2$(Bpin)); 4-$FC_6H_4CH$═CH(Bpin), **III**: 7.90 (d, $J$ = 18.0 Hz, $CH$ = CH(Bpin)), 6.23 (d, $J$ = 18.0 Hz, CH═$CH$(Bpin)).

**X-ray Crystallography.** Crystals of **1b** and **1c** were grown from saturated hexane solutions at −25 °C, **2** from THF, and **3b** from nitromethane at −25 °C. Single crystals were coated with Paratone-N oil, mounted using a glass fiber, and frozen in the cold stream of the goniometer. A hemisphere of data were collected on a Bruker AXS P4/SMART 1000 diffractometer using $\omega$ and $\theta$ scans with a scan width of 0.3° and 20 s (**1b**) and 30 s (**1c**, **2**, and **3b**) exposure times. The detector distance was 5 cm. Crystals of **1b** were twinned, and the orientation matrix for two components determined (RLATT, GEMINI).[28a] The data were reduced (SAINT) and corrected for absorption (SADABS).[29a] The structures were solved by direct methods and refined by full-matrix least-squares on $F^2$(SHELXTL) (**1c**, **2**, and **3a**) or on all but partially overlapping data (**1b**). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions and refined using a riding model. CCDC 684246−684249 contain the supplementary crystallographic data for this paper.

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**Supporting Information Available:** X-ray crystallographic files in CIF format for complexes **1b**, **1c**, **2**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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