Notes

Counteranion-Accelerated $Rh^{I}OAc$-Catalyzed Regioselective Hydroboration of Vinylarenes

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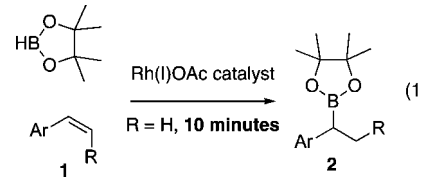
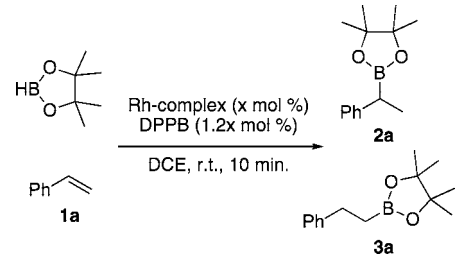
Summary: $Rh^{I}OAc$ shows a remarkably high catalytic activity for the hydroboration of vinylarenes with pinacolborane. The reaction was complete within 10 min to give the Markovnikov product.

The Rh(I)-catalyzed hydroboration of unsaturated bonds, such as in alkenes and alkynes, is an important approach to the synthesis of alcohols, amines, and carboxylic acids.[1] Among the numerous Rh(I)-catalyzed hydroborations, the use of pinacolborane as a borane source is promising as a practical protocol, giving air-stable organoboronate compounds.[2] The typical catalyst for the hydroboration is a cationic Rh(I) complex derived from $[Rh(cod)_2]BF_4$ as a precatalyst, which often shows superior reactivity and regioselectivity.[3] We focus here on the strategy of counteranion-controlled transition-metal catalysis. The present paper describes the drastic acceleration of the hydroboration of vinylarenes in the presence of $Rh^{I}OAc$ catalyst, providing the most powerful and practical approach to date (eq 1).



(1)

Table 1. Screening of Catalyst Precursor



entry	Rh complex (amt (mol % Rh))	yield (%)[a]	**2a/3a**[b]
1	$[RhCl(cod)]_2$ (5.0)	trace[c]	
2	$[Rh(cod)_2]BF_4$ (5.0)	trace[c]	
3[d]	Rh(acac)(cod) (5.0)	trace[c]	
4[e]	$[RhCl(cod)]_2$ (5.0) + AgOAc (6.0)	98	>98/2
5	$[Rh(OAc)(cod)]_2$ (5.0)	98	>98/2
6	$[Rh(OMe)(cod)]_2$ (5.0)	trace[c]	
7[f]	$[Rh(OAc)(cod)]_2$ (1.2)	98	94/6

[a] The yield was determined by the integration ratio of ^1H NMR analysis with 1,1,2,2-tetrachloroethane. [b] The regioselectivity was determined by ^1H NMR analysis. [c] The product was observed by TLC analysis, but there are almost no signals of the products by ^1H NMR analysis. [d] Rh(acac)(cod) was prepared from $[Rh(OMe)(cod)]_2$ and 2,4-pentanedione (acac) in CH_2Cl_2 at room temperature. [e] The mixture of $[RhCl(cod)]_2$ and AgOAc in CH_2Cl_2 was stirred under reflux for 2 h and filtered through a PTFE filter unit (0.2 μm) via syringe. Then the precatalyst solution was dried under vacuo to dryness. [f] Average of four runs.

Results and Discussion

The initial catalyst screening was investigated to clarify the catalytic activity of the Rh(I) complex for the hydroboration of vinylarenes with pinacolborane (Table 1). The reaction of styrene (**1a**) and pinacolborane (HBpin) (1.2 equiv, commercially available) was examined in the presence of Rh(I) complex and 1,4-bis(diphenylphosphino)butane (DPPB)[4] as a

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(1) (a) Hayashi, T. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Vol. 1. p 349. (b) Hayashi, T.; Matsumoto, Y.; Ito, Y. *J. Am. Chem. Soc.* **1989**, *111*, 3426–3428. (c) Burgess, K.; van der Donk, W. A.; Westcott, S. A.; Marder, T. B.; Baker, R. T.; Calabrese, J. C. *J. Am. Chem. Soc.* **1992**, *114*, 9350–9359. (d) Brown, J. M.; Hulmes, D. E.; Layzell, T. P. *J. Chem. Soc., Chem. Commun.* **1993**, 1673–1674. (e) Togni, A.; Breutel, C.; Schnyder, A.; Spindler, F.; Landert, H.; Tijani, A. *J. Am. Chem. Soc.* **1994**, *116*, 4062–4066. (f) Fernandez, E.; Maeda, K.; Hooper, M. W.; Brown, J. M. *Chem. Eur. J.* **2000**, *6*, 1840–1846. (g) Demay, S.; Volant, F.; Knochel, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1235–1238. (h) Kwong, F. Y.; Yang, Q.; Mak, T. C. W.; Chan, A. S. C.; Chan, K. S. *J. Org. Chem.* **2002**, *67*, 2769–2777. (i) Crudden, C. M.; Edwards, D. *Eur. J. Org. Chem.* **2003**, 4695–4712.

(2) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482–3485.

(3) (a) Westcott, S. A.; Blom, H. P.; Marder, T. B.; Baker, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 8863–8869. (b) Doucet, H.; Fernandez, E.; Layzell, T. P.; Brown, J. M. *Chem. Eur. J.* **1999**, *5*, 1320–1330. (c) Chen, A.; Ren, L.; Crudden, C. M. *J. Org. Chem.* **1999**, *64*, 9704–9710. (d) Murata, M.; Kawakita, K.; Asana, T.; Watanabe, S.; Masuda, Y. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 825–829. (e) Crudden, C. M.; Hleba, Y. B.; Chen, A. C. *J. Am. Chem. Soc.* **2004**, *126*, 9200–9201. (f) Segarra, A. M.; Daura-Oller, E.; Claver, C.; Poblet, J. M.; Bo, C.; Fernández, E. *Chem. Eur. J.* **2004**, *10*, 6456–6467. (g) Moteki, S. A.; Wu, D.; Chandra, K. L.; Reddy, D. S.; Takacs, J. M. *Org. Lett.* **2006**, *8*, 3097–3100. (h) Carroll, A.-M.; O'Sullivan, T. P.; Guiry, P. J. *Adv. Synth. Catal.* **2005**, *347*, 609–631. (i) Edwards, D. R.; Hleba, Y. B.; Lata, C. J.; Calhoun, L. A.; Crudden, C. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 7799–7802.

(4) The screening of ligands clarified the notion that DPPB is suitable for the regioselectivity in the present catalysis. Other ligands diminished the regioselectivity in some cases; see the Supporting Information.

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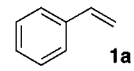
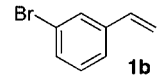
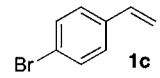
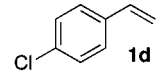
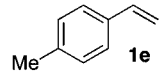
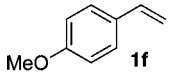
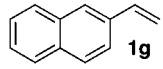
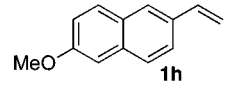
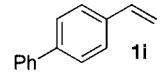
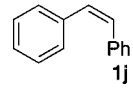
ligand (1.2 equiv to Rh(I) center) in 1,2-dichloroethane (DCE) (1 M) at room temperature for *10 min*. The employment of $[RhCl(cod)]_2$ (5.0 mol % Rh) provided a trace amount of the desired products **2a**/**3a** (entry 1). Accordingly, the reaction in the presence of $[Rh(cod)_2]BF_4$ (5.0 mol % Rh) also gave a trace amount of the corresponding products (entry 2).[5] The reaction in the presence of Rh(acac)(cod) (5.0 mol %), which is known as a effective precatalyst for diboration reactions, did not promote the reaction (entry 3).[6] In contrast, the catalyst prepared from $[RhCl(cod)]_2$ (5.0 mol % Rh) and AgOAc (6.0 mol %) surprisingly facilitated the reaction to give the branched product **2a** in almost quantitative yield (entry 4). Under the present conditions, impurities such as Ag(I) analogues totally terminated the reaction. The isolated $[Rh(OAc)(cod)]_2$[7] (5.0 mol % Rh) was also an efficient precatalyst for the present reaction and furnished comparable results (entry 5), while the precatalyst $[Rh(OMe)(cod)]_2$ (5.0 mol % Rh) gave a trace amount of the corresponding products (entry 6). These results imply the specific nature of Rh^IOAc catalyst for the rapid hydroboration of styrene.[8] The reaction in the presence of a one-fourth amount of catalyst loading using $[Rh(OAc)(cod)]_2$ (1.2 mol % Rh) was complete within 10 min to furnish the branched product **2a** in excellent yield with high regioselectivity (entry 7).[9] In general, the formation of Rh^IH and AcOBpin via reductive elimination or transmetalation provides the reduction product.[10] In addition, Rh^IH causes the generation of a Rh−Bpin intermediate, which participates in the oxidative borylation of styrene and reduction of styrene to give styrylboronate and ethylbenzene. Further reduction of styrylboronate gave the linear boronate compound **3a**. The change in the electronic nature of Rh(I) also causes the diminished regioselectivity. Accordingly, the present reaction should be completed rapidly before Rh^IH is generated. Because the reaction in the presence of more basic Rh^IOMe catalyst, affording Rh^IH and MeOBpin rapidly, did not provide a high catalytic activity, as shown in entry 6, the present catalysis could be considered as due to the specific nature of Rh^IOAc.[11]

The regioselective hydroborations of various functionalized vinylarenes under optimum reaction conditions are shown in Table 2. All of these reactions were carried out in the presence of $[Rh(OAc)(cod)]_2$ (5.0 mol % Rh) and DPPB (6.0 mol %) in dimethyl sulfoxide (DMSO) (1 M) for 10 min. It is noteworthy that the reaction in the presence of cationic $[Rh(cod)_2]BF_4$ (5.0 mol %) and DPPB (6.0 mol %) instead of Rh^IOAc catalyst in DMSO (1 M) afforded a trace amount of products **2a** and **3a** after 10 min; thus, the specific solvent effect could be excluded for the acceleration of the reaction drastically.[12] The reaction of styrene (**1a**) under Rh^IOAc catalysis gave the product **2a** in 98% NMR yield and 81% isolated yield regioselectively (entry 1). The halogen-substituted vinylarenes were compatible with the reaction conditions, and the desired products were obtained without decreasing the yield and regioselectivity; the reaction of 3-bromostyrene (**1b**) and 4-bromostyrene (**1c**) afforded the products **2b**,**c** in 94% NMR and 72% isolated yield and 93% NMR and 73% isolated yield, respectively (entries 2 and 3). The reaction of 4-chlorostyrene (**1d**) furnished the product **2d** in 97% NMR and 79% isolated yield (entry 4). The electron-donating group on the benzene ring did not diminish the yield and regioselectivity. The reaction of 4-vinyltoluene (**1e**) regioselectively provided the product **2e** in 95% NMR and 78% isolated yield (entry 5). The reaction of 4-vinylanisole (**1f**) gave

Table 2. Rh^IOAc-Catalyzed Rapid Hydroboration of Vinylarenes[a]

entry	vinylarene	yield (%)[b, c]
1	 **1a**	**2a**, 98 (81)
2	 **1b**	**2b**, 94 (72)
3	 **1c**	**2c**, 93 (73)
4	 **1d**	**2d**, 97 (79)
5	 **1e**	**2e**, 95 (78)
6	 **1f**	**2f**, 96 (78)
7	 **1g**	**2g**, 88 (81)[d]
8	 **1h**	**2h**, 93 (78)
9	 **1i**	**2i**, 95 (78)
10[e]	 **1j**	**2j**, 75 (53)

[a] The reaction of vinylarene and pinacolborane (1.2 equiv) was conducted in the presence of $[Rh(OAc)(cod)]_2$ (5.0 mol % Rh) and DPPB (6.0 mol %) in DMSO (1 M) at room temperature for 10 min. [b] The yield was determined by the integration ratio of ^1H NMR with 1,1,2,2-tetrachloroethane. The regioselectivity **2**/**3** of all the products was >98/2. [c] The isolated yield is described in parentheses. [d] The reaction in dried and freshly distilled DMSO gave similar results. [e] The reaction was carried out for 5 h at room temperature.

(5) The commercially available pinacolborane, which might contain $BH_3 \cdot SMe_2$, from Wako Pure Chemical Industries was further treated with pinacol and distilled under vacuum for purification by literature methods. Both the purified pinacolborane and the commercially available pinacolborane gave the same results. Therefore, the commercially available pinacolborane from Wako Pure Chemical Industries was used in the present reaction. The contamination of $BH_3 \cdot SMe_2$ in pinacolborane was suggested by: Shimada, S.; Batsanov, A. S.; Howard, J. A. K.; Marder, T. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2168–2171.

(6) (a) Dai, C.; Robins, E. G.; Scott, A. J.; Clegg, W.; Yufit, D. S.; Howard, J. A. K.; Marder, T. B. *Chem. Commun.* **1998**, 1983–1984. (b) Trudeau, S.; Morgan, J. B.; Shrestha, M.; Morken, J. P. *J. Org. Chem.* **2005**, *70*, 9538–9544.

(7) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88–90.

(8) The use of catecholborane (HBcat) under the same reaction conditions as entry 5, Table 1 gave a mixture of 1-phenylethanol and 2-phenylethanol in 82% yield with 93/7 ratio after the oxidation of the crude boronate compounds. The preceding reports detailed the difference between HBpin and HBcat; see ref 3i and: Lam, W. H.; Shimada, S.; Batsanov, A. S.; Lin, Z.; Marder, T. B.; Cowan, J. A.; Howard, J. A. K.; Mason, S. A.; McIntyre, G. J. *Organometallics* **2003**, *22*, 4557–4568. A mechanistic investigation will be carried out in due course in future studies.

(9) The reaction in the presence of low catalyst loading should be conducted under precisely dehydrated conditions; the decomposition of HBpin with H_2O causes decreasing regioselectivity.

(10) (a) Westcott, S.; Marder, T. B.; Baker, R. T. *Organometallics* **1993**, *12*, 975–979. (b) Brown, J. M.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **1994**, *116*, 866–878.

(11) Other counteranions, such as pivalate and benzoate, gave similar results.

(12) The reaction in DMSO as a solvent gave better results in some cases. The details are described in the Supporting Information.

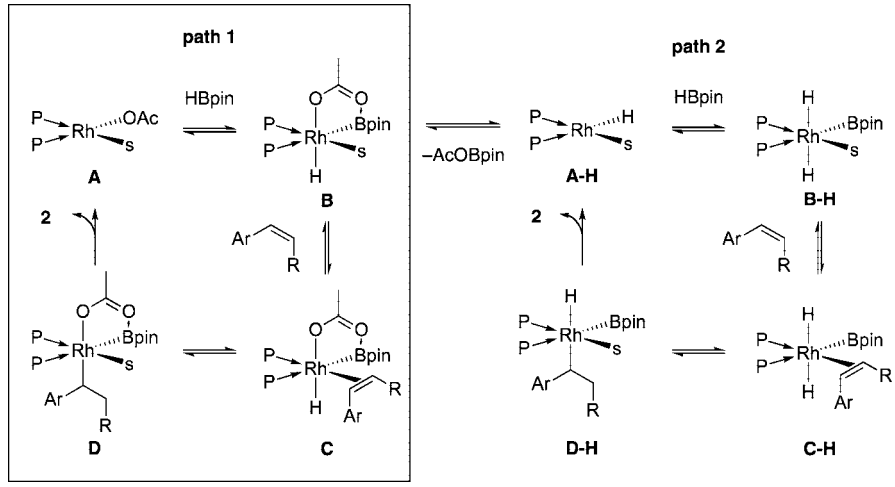


Figure 1. Proposed mechanism of $Rh^{I}OAc$ catalysis.

a comparable yield of product **2f** regioselectively (entry 6). In the case of 2-vinylnaphthalene (**1g**), the product **2g** was obtained in 88% NMR and 81% isolated yield along with the formation of 2-ethylnaphthalene in less than 10% yield as a byproduct (entry 7). The generation of 2-ethylnaphthalene via reduction was not suppressed even in dried and freshly distilled DMSO. Thus, the generation of $Rh^{I}H$ would be the major factor for the reduction and was dependent on the substrate. The reaction of 6-methoxy-2-vinylnaphthalene (**1h**) suppressed the reduction to afford the product **2h** in 93% NMR and 78% isolated yield (entry 8). The reaction of 4-vinylbiphenyl (**1i**) gave the product **2i** in sufficient yield regioselectively (entry 9). The reaction of the disubstituted olefin *cis*-stilbene (**1j**) proceeded at room temperature to afford the product in 75% NMR and 53% isolated yield; the reduction of *cis*-stilbene could not be suppressed (entry 10).[13] The preceding result requires 80 °C for 3 days using $Rh^{I}BF_4$ catalyst;[3i] therefore the present complex shows the most enhanced catalytic activity to date.

The proposed mechanism is outlined in Figure 1 (s = solvent).[14] There are two pathways considered that would explain the influence of counteranion. The reaction starts from the $Rh^{I}OAc$−phosphine complex **A**. The oxidative addition of HBpin to complex **A** generates the Rh(III) complex **B**, followed by the coordination of vinylarene via complex **C** inducing the insertion into the Rh−H bond to give **D**. Then the reductive elimination provides the product **2** and regenerates complex **A** (path 1). The counteranion generally affects the electronic nature of the Rh complex; it is unclear whether the electronic nature of Rh−OAc shows a specific acceleration effect or not because Rh−BF_4, Rh−Cl, and even Rh−OMe and Rh−acac complexes did not accelerate the present reaction. Another influence could be considered as the coordination of the counteranion OAc to the boron of complex **B**. Such a coordination might inhibit the back-donation from the Rh(III) d orbital to the vacant p orbital of boron, which would make the Rh−B bond stronger according to the literature.[15] Therefore, a coordinative counteranion on the Rh(III) center might change the intrinsic nature of the Rh−B bond.[16] A simple coordination effect could also be considered without an inhibition of back-donation. In addition, an Rh(I) dimer complex could not be ruled out; however, the lack of acceleration in the presence of more basic $[Rh(OMe)(cod)]_2$ indicates that the formation of a dimer complex is not essential. On the other hand, path 2 gives another possibility. A neutral to basic counteranion bearing an oxygen atom often accelerates the transmetalation with organoboronic acid derivatives;[17] accordingly, the catalytic cycle begins with the formation of complex **A-H** (OAc counteranion free complex). The oxidative addition of HBpin proceeds to give **B-H**, and the insertion of vinylarene generates **D-H**. The following reductive elimination gives the product **2** and regenerates the complex **A-H**. It is clearly notable that the reductive elimination to generate $Rh^{I}H$ could not be important for the high catalytic performance, because the reaction in the presence of more basic $Rh^{I}OMe$ did not show a high catalytic activity at all as compared to $Rh^{I}OAc$ (Table 1, entry 6).[18] The generation of the complex **A-H** causes the reduction and/or oxidative borylation to give ethylarene and/or alkenylboronate.[10] The reduction of alkenylboronate gives the linear boronate **3**, which could be considered as one of the causes for the lower regioselectivity. Thus, the reductive elimination from complex **B** to form the complex **A-H** might be competitive with the insertion of styrene into complex **B** to form complex **D**. Rapid hydroboration using $Rh^{I}OAc$ is thus essential before an $Rh^{I}H$ species such as complex **A-H** participates in the reaction. Although the coordination of a counteranion on boron is unclear now, path 1 in the presence of $Rh^{I}OAc$ during the course of the catalytic cycle seems favorable in accelerating the present reaction efficiently.

Conclusions

We found a dramatic influence of a counteranion on the Rh(I) center for regioselective hydroboration. The present catalysis realized the completion of the hydroboration of vinylarenes with

(13) The reaction of a 1,1-disubstituted ethylene, such as α-methylstyrene, gave a mixture of regioisomers. We have not examined the reaction of trisubstituted ethylenes due to insufficient regioselectivity.

(14) The ^{11}B and ^{31}P NMR experiments were examined; however, the precise characterization of the Rh(III) intermediate is difficult. Details of the NMR experiments are described in the Supporting Information. Further investigation is ongoing to clarify Rh(III) intermediates.

(15) Irvine, G. J.; Lesley, M. J. G.; Marder, T. B.; Norman, N. C.; Rice, C. R.; Robins, E. G.; Roper, W. R.; Whittell, G. R.; Wright, L. J. *Chem. Rev.* **1998**, *98*, 2685–2722.

(16) One reviewer suggested the possibility of active catalyst as the borate−Rh(I) complex according to ref 6a for $Rh^{I}acac$ and B_2cat_3. It is notable that hydroboration in the presence of $Rh^{I}acac$ did not promote the reaction at all (entry 3, Table 1). In addition, the distilled HBpin can promote the present reaction. The generation of a borate−Rh(I) complex does not seem to be essential.

(17) Yamamoto, Y.; Kirai, N.; Harada, Y *Chem. Commun.* **2008**, 2010–2012, and references cited therein.

(18) Hayashi et al. reported that rapid transmetalation proceeds using $Rh^{I}OR$ and $PhB(OH)_2$: Hayashi, T.; Takahashi, M.; Takaya, Y.; Ogasawara, M. *J. Am. Chem. Soc.* **2002**, *124*, 5052–5058.

pinacolborane within 10 min to give the branched products exclusively. The high catalytic performance can be attributed to the OAc counteranion of the Rh(III) intermediate. These findings provide a powerful and practical hydroboration approach to obtain organoboronate compounds. We expect that the present dramatic influence could play a role in the discussion to clarify the exact mechanism of Rh(I)-catalyzed hydroboration, which is a maker of much debate. Further studies to reveal the mechanism and the application of a counteranion-controlled strategy are ongoing in our laboratory.

Experimental Section

General Considerations. Anhydrous 1,2-dichloroethane (DCE) and dimethyl sulfoxide (DMSO) are commercially available. They were dried over molecular sieves 4A (MS 4A) before use. DMSO was dried over CaH_2 and distilled under vacuum. Pinacolborane was commercially available from Wako Pure Chemical Industries and used as received or after purification according to the literature.[5] All reactions were examined under an Ar atmosphere. IR spectra were recorded with a Horiba FT730 spectrophotometer. NMR spectra were measured with a JEOL AL-400 spectrometer, using tetramethylsilane as an internal reference, $BF_3 \cdot OEt_2$ as an external reference, and $CDCl_3$ as the solvent. Mass spectra were measured with a JEOL JMS-SX102A instrument.

Typical Experimental Procedure. A mixture of $[Rh(OAc)(cod)]_2$ (13.5 mg, 0.025 mmol, 2.5 mol %) and DPPB (25.6 mg, 0.06 mmol, 6 mol %) was stirred in dichloromethane (1 mL) at room temperature for 30 min. The volatiles were removed under vacuum to dryness. Then DCE (1 mL) or DMSO (1 mL) was added. To the catalyst solution were added styrene (104 mg, 1.0 mmol) and pinacolborane (154 mg, 1.2 mmol) at room temperature. After it was stirred at room temperature for 10 min, the reaction mixture was filtered through a pad of silica gel to remove catalyst with ether eluent (50 mL) and concentrated to dryness. The ^{1}H NMR analysis with 1,1,2,2-tetrachloroethane suggested the yield to be 98% and the branched/linear ratio to be >98/2. Purification by silica gel column chromatography (5% EtOAc in hexane eluent) gave the product **2a** in 81% yield (188 mg, 0.81 mmol) as a colorless oil. The products **2a**,**c**−**h** are known compounds, and their spectral and analytical data matched the results in the literature.[3] The physical properties of the new compounds **2b**,**i**,**j** are described below.

Pinacol[1-(*m*-bromophenyl)ethyl]boronate (2b). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (m, 1H), 7.25 (m, 1H), 7.13 (m, 2H), 2.40 (q, J = 7.6 Hz, 1H), 1.31 (d, J = 7.6 Hz, 3H), 1.21 (s, 6H), 1.20 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.4, 130.7, 129.8, 128.2, 126.5, 122.3, 83.4, 24.57, 24.55, 16.8; one signal is broad and is not specified. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.2. IR (neat, cm^{-1}): 2977, 1563, 1324, 1143. HRMS (FAB, positive): m/z calcd for $C_{14}H_{20}BBrO_2$ 311.0740, found 311.0817.

Pinacol[1-(*p*-biphenyl)ethyl]boronate (2i). White solid, mp = 60 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (m, 2H), 7.50 (m, 2H), 7.41 (m, 2H), 7.30 (m, 3H), 2.48 (q, J = 7.6 Hz, 1H), 1.37 (d, J = 7.6 Hz, 3H), 1.23 (s, 6H), 1.21 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.1, 141.2, 137.9, 128.6, 128.1, 127.0, 126.9, 126.8, 83.3, 24.62, 24.59, 17.1; one signal is broad and is not specified. ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.3. IR (neat, cm^{-1}): 2977, 1461, 1349, 1139. HRMS (FAB, positive): m/z calcd for $C_{20}H_{25}BO_2$ 308.1948, found 308.1978.

Pinacol(1,2-diphenylethyl)boronate (2j). Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.32−7.07 (m, 10H), 3.45 (dd, J = 13.6, 9.6 Hz, 1H), 2.96 (dd, J = 13.6, 6.8 Hz, 1H), 2.68 (dd, J = 9.6, 6.8 Hz, 1H), 1.10 (s, 6H), 1.09 (s, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 142.5, 141.7, 128.8, 128.4, 128.3, 128.0, 125.7, 125.3, 83.3, 38.8, 24.54, 24.47; one signal is broad and is not specified. ^{11}B NMR ($CDCl_3$, 128 MHz) δ 33.1. IR (neat, cm^{-1}): 2883, 1495, 1327, 1142. HRMS (FAB, positive): m/z calcd for $C_{20}H_{25}BO_2$ 308.1948, found 309.2013.

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Supporting Information Available: Figures and tables giving details of the screening of ligands and solvents, NMR experiments on Rh complexes, and ^{1}H NMR, ^{13}C NMR, and ^{11}B NMR spectra for compounds **2b**,**i**,**j**. This material is available free of charge via the Internet at http://pubs.acs.org.

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