A Boron-Substituted Analogue of the Shvo Hydrogenation Catalyst: Catalytic Hydroboration of Aldehydes, Imines, and Ketones

Liza Koren-Selfridge,[†] Hannah N. Londino,[†] Jessica K. Vellucci,[†] Bryan J. Simmons,[‡] Charles P. Casey,[‡] and Timothy B. Clark*,[†]

Department of Chemistry, Western Washington University, Bellingham, Washington 98225-9150, and Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received December 31, 2008

The boron-substituted hydroxycyclopentadienyl ruthenium hydride [2,5-Ph_2-3,4-Tol_2(η^5-C_4COBpin)Ru-$(CO)_2$H] (Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane) **5** was synthesized by the addition of pinacolborane to ruthenium dimer [2,5-Ph_2-3,4-Tol_2(η^5-C_4CO)Ru$(CO)_2]_2$ **4**. Complex **5** reacts with aldehydes both stoichiometrically and catalytically, providing hydroboration products under mild reaction conditions. A Hammett correlation plot of para-substituted benzaldehydes provided a ρ value of +0.91. Catalytic hydroboration of aryl imines provided high yields of the corresponding amines. The hydroboration of aryl ketones, however, required strongly electron-withdrawing substituents to induce hydroboration in reasonable reaction times.

Introduction

Ligand−metal bifunctional catalysis has become a valuable method for the hydrogenation of various organic substrates.[1] The Shvo catalyst [2,3,4,5-Ph_4(η^5-C_4COH)Ru$(CO)_2$H] (RuHOH **1**, Scheme 1) can be used in the hydrogenation of polarized double (C═Y) and triple bonds (C≡Y).[2−5] Mechanistic studies have revealed detailed insights into each elementary step of the catalytic cycle.[6−12] The key mechanistic step involves a unique concerted, outer-sphere reduction in which the substrate does not coordinate to the metal prior to the addition of dihydrogen (step a). The metal-mediated reaction of dihydrogen with a carbonyl compound involves the addition of the metal-based hydride hydrogen (red) to the carbonyl carbon and the addition of the ligand-based acidic hydrogen (blue) to the carbonyl oxygen simultaneously.

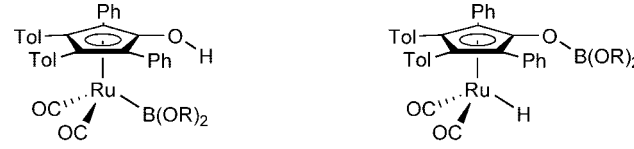


Figure 1. Boron-substituted analogues of the Shvo catalyst.

Our group is interested in exploring the ability of the Shvo catalyst to deliver reagents other than dihydrogen by ligand−metal bifunctional catalysis.[13] We have limited our attention to boron-substituted analogues of the Shvo catalyst, [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)Ru$(CO)_2$**B(OR)$_2$**] (Ru**B(OR)$_2$**OH, **I**, Figure 1) and [2,5-Ph_2-3,4-Tol_2(η^5-C_4CO**B(OR)$_2$**)Ru$(CO)_2$H] (RuHO**B(OR)$_2$**, **II**), due to the synthetic utility of the proposed boron-containing organic products.[14−17] Initial studies have focused on the RuHO**B(OR)$_2$** complex (**II**) to determine the effectiveness of boron as a surrogate for the acidic hydrogen of the Shvo catalyst. We herein report the stoichiometric and catalytic reactivity of [2,5-Ph_2-3,4-Tol_2(η^5-C_4COBpin)Ru$(CO)_2$H](RuHOBpin, Bpin = 4,4,5,5-tetramethyl-1,3,2-dioxaborolane), a boron-substituted analogue of the Shvo catalyst, in the hydroboration of aldehydes and imines.

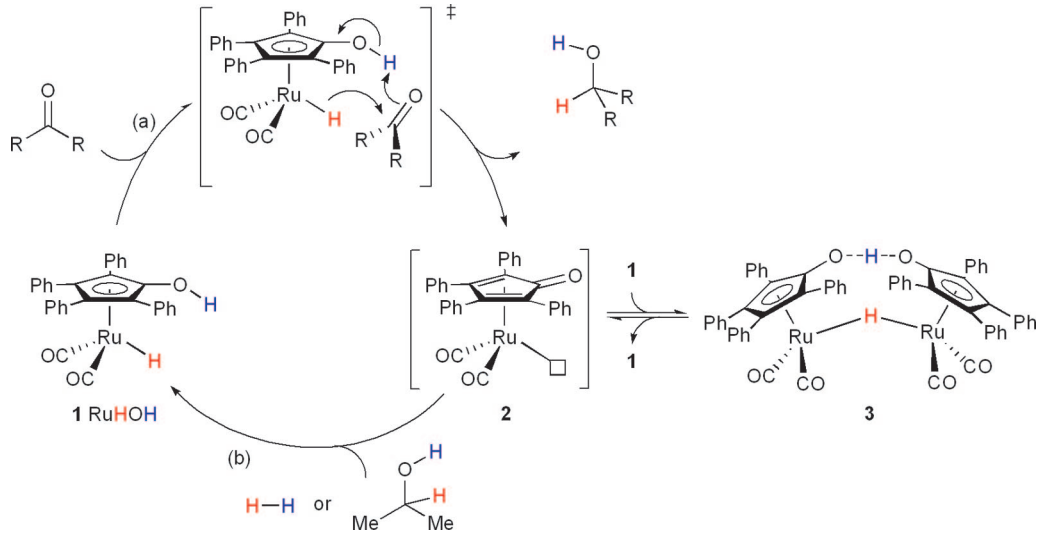
The desired boron-substituted analogue of the Shvo catalyst (complex **II**, Figure 1) requires a balance between a complex that has sufficient Lewis acidity to promote hydroboration and one that is stable toward hydrolysis or thermal decomposition. Pinacolato-substituted boronate ester (Bpin) is known to be

* To whom correspondence should be addressed. E-mail: clark@chem.wwu.edu.
[†] Western Washington University.
[‡] University of Wisconsin—Madison.

(1) For reviews of ligand−metal bifunctional catalysis, see: (a) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40–73. (b) Noyori, R.; Kitamura, M.; Ohkuma, T. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5356–5362. (c) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201–2237. (d) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393–406.
(2) Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics* **1985**, *4*, 1459–1461.
(3) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 7400–7402.
(4) Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885–3891.
(5) Menashe, N.; Salant, E.; Shvo, Y. *J. Organomet. Chem.* **1996**, *514*, 97–102.
(6) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090–1100.
(7) Casey, C. P.; Bikzhanova, G. A.; Cui, Q.; Guzei, I. A. *J. Am. Chem. Soc.* **2005**, *127*, 14062–14071.
(8) Casey, C. P.; Johnson, J. B. *J. Am. Chem. Soc.* **2005**, *127*, 1883–1894.
(9) Casey, C. P.; Johnson, J. B.; Singer, S. W.; Cui, Q. *J. Am. Chem. Soc.* **2005**, *127*, 3100–3109.
(10) Samec, J. S. M.; Éll, A. H.; Åberg, J. B.; Privalov, T.; Eriksson, L.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2006**, *128*, 14293–14305.
(11) Casey, C. P.; Clark, T. B.; Guzei, I. A. *J. Am. Chem. Soc.* **2007**, *129*, 11821–11827.
(12) Casey, C. P.; Beetner, S. E.; Johnson, J. B. *J. Am. Chem. Soc.* **2008**, *130*, 2285–2295.
(13) For examples of additional ligand−metal bifunctional catalysts that employ functional groups other than hydrogen, see: (a) Watanabe, M.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc.* **2003**, *125*, 7508–7509. (b) Watanabe, M.; Ikagawa, A.; Wang, H.; Murata, K.; Ikariya, T. *J. Am. Chem. Soc.* **2004**, *126*, 11148–11149. (c) Shibasaki, M.; Yoshikawa, N. *Chem. Rev.* **2002**, *102*, 2187–2209. (d) Shibasaki, M.; Matsunaga, S. *Chem. Soc. Rev.* **2006**, *35*, 269–279.
(14) Matteson, D. S. *Chem. Rev.* **1989**, *89*, 1535–1551.
(15) Matteson, D. S. *Tetrahedron* **1998**, *54*, 10555–10607.
(16) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457–2483.
(17) Takagi, J.; Takahashi, K.; Ishiyama, T.; Miyaura, N. *J. Am. Chem. Soc.* **2002**, *124*, 8001–8006.

10.1021/om801228m CCC: $40.75
Publication on Web 03/19/2009

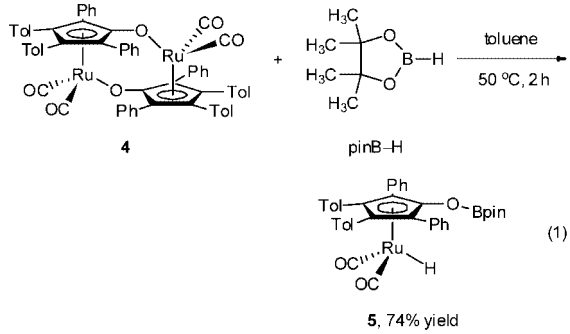
Scheme 1. Catalytic Cycle for Hydrogenation with Shvo Catalyst

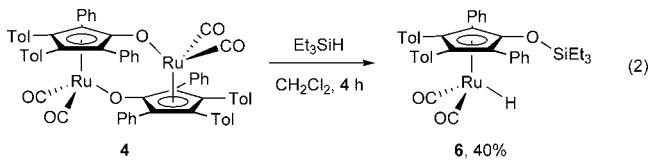


resistant to hydrolysis[18] and was expected to have significant reactivity as a Lewis acid. Several other common boron substituents (9-BBN, catecholborane, and dimesitylborane) were rejected due to the known uncatalyzed reactivity of H-BR_2 toward carbonyl compounds.[19,20]

Results and Discussion

[2,5-Ph_2-3,4-Tol_2(η^5-C_4COBpin)Ru(CO)$_2$H] (**5**) was synthesized by oxidative addition of pinacolborane (H-Bpin) to ruthenium dimer **4** (eq 1). A 74% isolated yield of **5** was achieved by heating H-Bpin with ruthenium dimer **4** at 50 °C for 2 h in toluene. Complex **5** was the sole regioisomer observed in the addition of H-Bpin to complex **4**. This regioisomer was anticipated by analogy to the reported addition of triethylsilane (Et_3Si-H) to complex **4**, providing ruthenium hydride **6** (eq 2).[6]





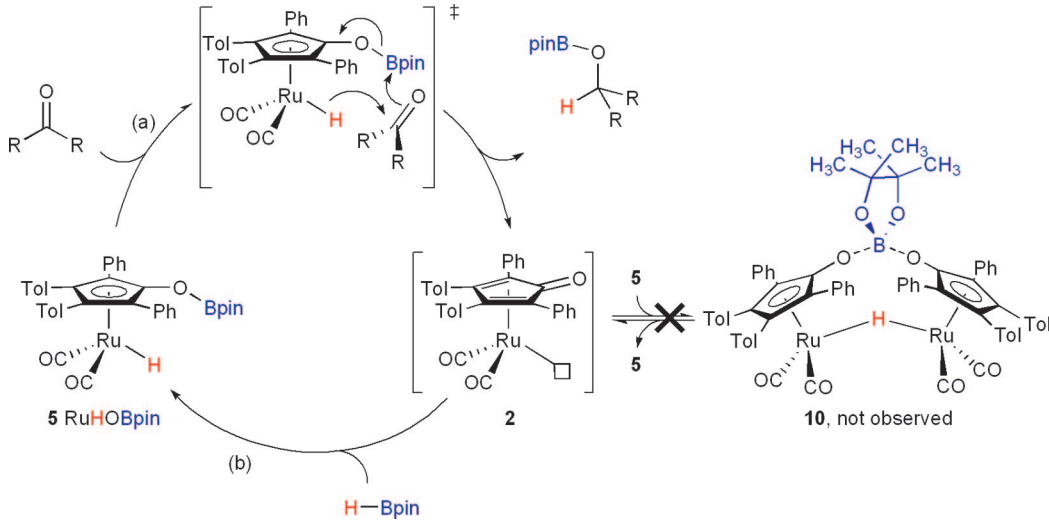
The characteristic spectroscopic data of RuHOBpin **5** includes the Ru-***H*** resonance in the ^{1}H NMR spectrum at −9.33 ppm (s, 1H),[6,21] a broad peak in the ^{11}B NMR spectra at 21.8 ppm (characteristic ^{11}B NMR chemical shift for B(OR)$_3$),[22] and the C═O stretching frequency in the IR spectrum at 2020 and 1959 cm^{-1}. Analogous ruthenium hydride complexes display characteristic chemical shifts in the ^{1}H NMR that depend on the molecularity of the complex. Monomeric ruthenium hydride complexes have chemical shifts in the range of −9 to −11 ppm {[2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)Ru(CO)$_2$H] **1′** (analogous to **1**, Scheme 1):[6] $\delta = -9.8$ ppm; [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)Ru(CO)(PPh$_3$)H][21] (**7**, Ru(PPh$_3$)HOH): $\delta = -10.4$ ppm}; dimeric ruthenium hydride complexes have chemical shifts in the range of −17 to −19 ppm {complex **3** (bridging hydride, Scheme 1):[6] $\delta = -17.7$ ppm}. The characteristic chemical shift in the ^{1}H NMR for complex **5** confirms the identity of the regioisomer formed and demonstrates that the complex is a monomer in solution.

Reactivity of RuHOBpin 5 in the Hydroboration of Aldehydes. The stoichiometric reactivity of RuHOBpin (**5**) toward carbonyl compounds was examined to determine the effect of the boron substituent on the reactivity of this complex in reduction reactions.[23] Prior to this work, the Casey group showed that the acidic proton of [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)Ru(CO)$_2$H] **1′** is critical in the hydrogenation of carbonyls and imines.[6] The replacement of the acidic proton with a triethylsilyl substituent (RuHOSiEt_3, **6**) was shown to shut down the reactivity of these complexes toward aldehydes. We postulated that the empty p-orbital on boron might allow the resulting complex to react in a similar manner to the parent complex **1′**.

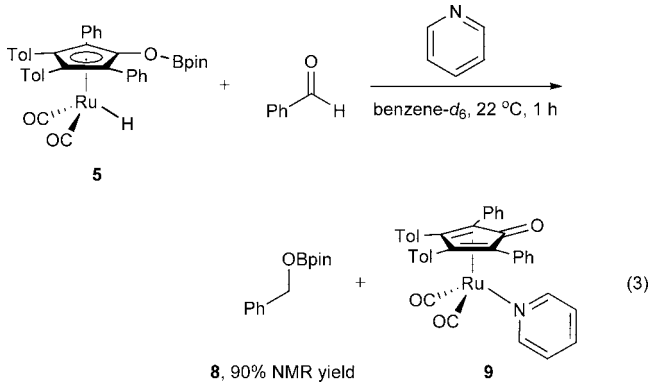
Stoichiometric hydroboration of benzaldehyde was examined with RuHOBpin **5**. Addition of **5** to benzaldehyde in the presence of pyridine (trapping agent for coordinatively unsaturated complex **2**, Scheme 1) provided the hydroboration product **8** in 90% NMR yield after 1 h at 22 °C (eq 3). A control experiment involving pinacolborane, pyridine, and benzaldehyde resulted in <5% conversion to hydroboration product **8**, ruling out the possibility that the hydroboration could be occurring

(18) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482–3485.
(19) Männig, D.; Nöth, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 878–879.
(20) Vogels, C. M.; Westcott, S. A. *Curr. Org. Chem.* **2005**, *9*, 687–699.
(21) Casey, C. P.; Strotman, N. A.; Beetner, S. E.; Johnson, J. B.; Priebe, D. C.; Vos, T. E.; Khodavandi, B.; Guzei, I. A. *Organometallics* **2006**, *25*, 1230–1235.
(22) Nöth, H.; Wrackmeyer, B. In *Nuclear Magnetic Resonance Spectroscopy of Boron Compounds*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; NMR Basic Principles and Progress 14, Springer-Verlag: Berlin, 1978; pp 136−138.

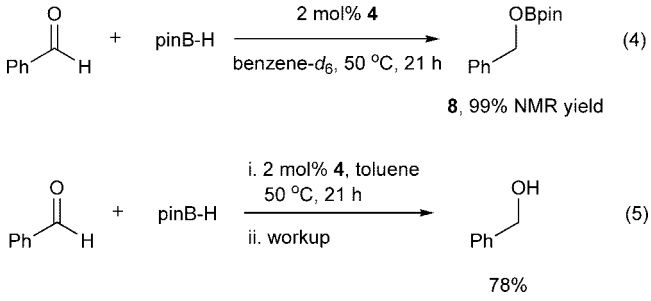
Scheme 2. Proposed Catalytic Cycle of Ruthenium-Catalyzed Hydroboration



by an uncatalyzed process. The observed hydroboration of benzaldehyde demonstrates that the boron substituent is Lewis acidic enough to promote hydroboration through a ligand−metal bifunctional catalyst system.



Upon successful stoichiometric hydroboration of benzaldehyde, the complex was tested for catalytic competence. Using 2 mol % of **4** as a precatalyst and 1.5 equiv of pinacolborane, the catalytic reduction of benzaldehyde provided quantitative NMR yield of **8** in 21 h at 50 °C (eq 4). A control experiment was conducted involving benzaldehyde, pinacolborane, and benzene-d_6 (in the absence of complex **4**), resulting in less than 25% conversion to product **8** after 21 h at 50 °C. Column chromatography of hydroboration product **8** resulted in a 78% yield of benzyl alcohol, resulting from hydrolysis of **8** (eq 5).



The stoichiometric and catalytic hydroboration reactions depicted in eqs 3−5 demonstrate the ability of the boronate ester to activate aldehydes toward hydride addition. Unlike RuHOSiEt$_3$ **6** (eq 2),[6] RuHOBpin **5** is a competent replacement for the Shvo hydrogenation catalyst **1** (Scheme 1). Complex **5** reduces benzaldehyde in stoichiometric reactions at higher temperatures (22 °C) than the parent RuHOH **1** (−40 °C). The decreased reactivity of RuHOBpin **5** in stoichiometric reductions is consistent with a decreased Lewis acidity of the boronate ester of **5** as compared to the acidic proton of **1**.

Catalytically, complex **5** mediates reduction of aldehydes at lower temperature (50 °C) and pressure (ambient, no H_2 gas required) than the Shvo catalyst (**3**). The Shvo catalyst typically requires either elevated temperatures (>90 °C) or high pressure of H_2 (35 atm, 60 °C) for aldehyde reduction. The increased catalytic reactivity of RuHOBpin **5** over complex **3** is consistent with a mechanism for **5** that does not require the rate-limiting dissociation of a bridging hydride (analogous to complex **3**, Scheme 1). RuHOBpin **5** exists in solution as a monomer due to the steric bulk of the boron substituent (indicated by the characteristic hydride chemical shift in the ^{1}H NMR spectra, $\delta = -9.33$ ppm). The large pinacol substituent on boron prohibits the formation of bridging hydride **10** (Scheme 2).[21,24,25]

The variety of aldehydes that were compatible with these catalytic reaction conditions was explored. Both electron-rich and electron-deficient aldehydes were tolerated (Table 1, entries 1−4), with qualitatively faster reactions for electron-deficient aldehydes such as 4-nitrobenzaldehyde (entry 1) as shown by shorter reaction times for comparable conversions. 4-Dimethylaminobenzaldehyde (entry 5) reacted more rapidly than 4-methoxybenzaldehyde (entry 4), which required higher temperature to achieve significant conversion. This atypical reactivity trend is attributed to coordination of the Lewis acidic boron substituent of pinacolborane to the amine, attenuating the electron-donating ability of the amine. Ortho-substituted benzaldehyde derivatives were also tolerated (entries 6 and 7), providing high yields of the desired alcohols. Hydrocinnamaldehyde was reactive under these conditions (entry 8), providing 3-phenylpropanol in moderate yield, demonstrating that an aromatic aldehyde is not required to afford the hydroboration product.

Hammett Plot of Para-Substituted Benzaldehyde Derivatives. The electronics of the transition state were further investigated using a Hammett correlation plot. Competition experiments between para-substituted benzaldehyde derivatives and benzaldehyde were examined using 5 equiv of each aldehyde, 1 equiv of pinB-H, and 4 mol % of precatalyst **4** at 50 °C for 2 h. The product ratios were determined using ^{1}H NMR spectroscopy with phenyltrimethylsilane as an internal

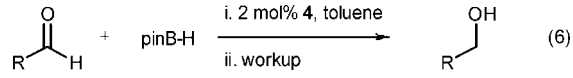
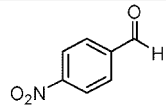
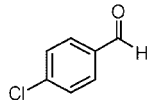
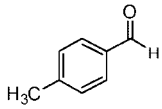
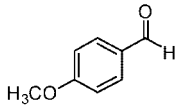
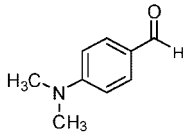
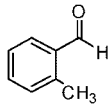
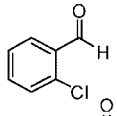
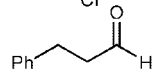
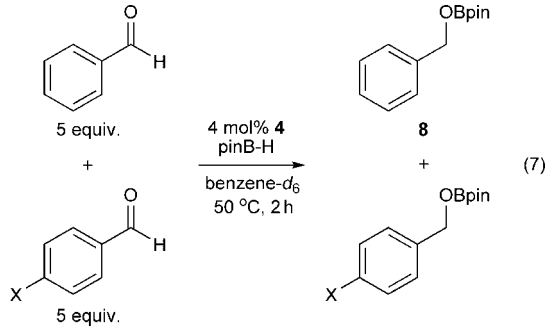


Table 1. Catalytic Hydroboration of Aldehydes (Eq 6)[a]

Entry	Aldehyde	Temp	Time (h)	Yield [b]
1		50 °C	1	91%
2		50 °C	40	62%
3		70 °C	17	73%
4		70 °C	23	88%
5		50 °C	20	60%
6		50 °C	23	80%
7		50 °C	23	71%
8		50 °C	6	58%

[a] Reactions conducted using Ru dimer **4** (2 mol %) and H-Bpin (1.5 equiv) and heated in a sealed reaction vessel. Workup involves passing crude reaction mixture through a plug of silica gel. [b] Isolated yield of alcohol.

standard, providing >70% combined NMR yields in each case.[26,27] As was qualitatively observed by the reaction times, electron-withdrawing substituents accelerate the hydroboration reaction and electron-donating substituents decelerate the reaction rate. Using the relative rates determined by each competition experiment, a Hammett plot was constructed using $\log(k_X/k_H)$ vs σ,[28] where X is the para substituent of the benzaldehyde analogue (Table 2, Figure 2). This plot gave a ρ value of $+0.91$ ($R^2 = 0.98$).



The reversibility of the catalytic hydroboration reaction was examined to determine the validity of the results obtained in the Hammett correlation plot. To determine if the hydroboration reaction is reversible, 4-methoxybenzaldehyde or 4-methylbenzaldehyde was subjected to the optimized reaction conditions (1.2 equiv of pinacolborane used, 1.0 equiv could not be used due to low conversions) (Scheme 3). The reactions were run in benzene-d_6 and monitored by ^{1}H NMR spectroscopy. Upon consumption of the aldehyde, 1 equiv of 4-nitrobenzaldehyde was added to the reaction mixture. The reaction mixture was heated to 50 °C for ~2 h (conditions for competition experiments) and examined by ^{1}H NMR spectroscopy. In both cases, there was no loss of the original hydroboration product, but some hydroboration of the added 4-nitrobenzaldehyde was observed. The small amounts of hydroboration of 4-nitrobenzaldehyde that were observed is attributed to the reaction of 4-nitrobenzaldehdye with the slight excess of pinacolborane required to consume the initial aldehyde (vide supra). When these reactions were continued for extended times (~24 h), significant hydroboration of 4-nitrobenzaldehyde and regenera-

Table 2. Relative Rates of Hydroboration Reactions for Para-Substituted Benzaldehydes (Eq 7)

substituent (X)	σ	k_X/k_H[a]	$\log(k_X/k_H)$
$-OCH_3$	−0.28	0.40	−0.40
$-CH_3$	−0.14	0.71	−0.15
−H	0	1.00	0
−Cl	0.24	1.47	0.17
$-NO_2$[b]	0.81	4.52	0.66

[a] Product ratios determined by ^{1}H NMR with phenyltrimethylsilane as the internal standard and a 10 s relaxation delay. [b] Reaction run at 22 °C for 2 h.

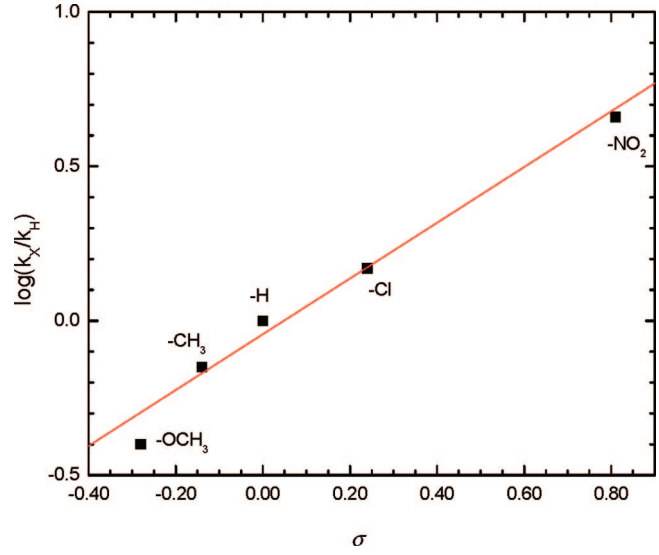


Figure 2. Hammett plot of $\log(k_X/k_H)$ vs σ for catalytic hydroboration of para-substituted benzaldehydes.

(23) For examples of ruthenium-catalyzed hydroboration reactions, see: (a) Caballero, A.; Sabo-Etienne, S. *Organometallics* **2007**, *26*, 1191–1195. (b) Montiel-Palma, V.; Lumbierres, M.; Donnadieu, B.; Sabo-Etienne, S.; Chaudret, B. *J. Am. Chem. Soc.* **2002**, *124*, 5624–5625. (c) Burgess, K.; Jaspars, M. *Organometallics* **1993**, *12*, 4197–4200.

(24) Casey, C. P.; Strotman, N. A.; Beetner, S. E.; Johnson, J. B.; Priebe, D. C.; Guzei, I. A. *Organometallics* **2006**, *25*, 1236–1244.

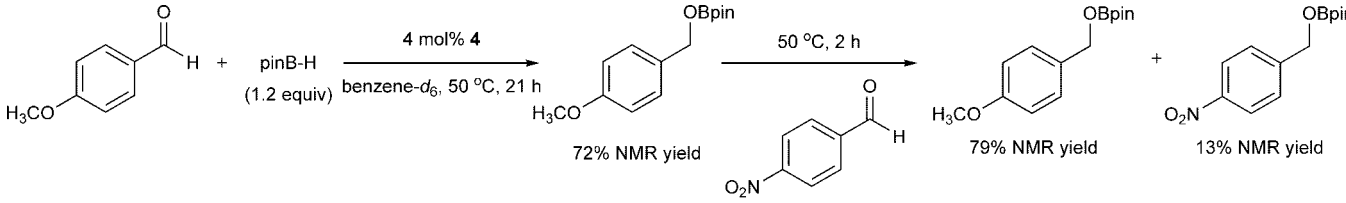
(25) Casey, C. P.; Vos, T. E.; Singer, S. W.; Guzei, I. A. *Organometallics* **2002**, *21*, 5038–5046.

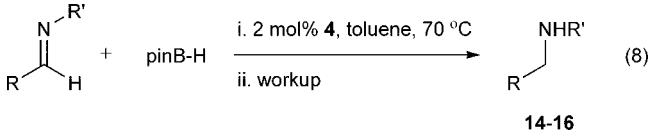
(26) The relative rates (k_X/k_H) were determined by using an excess of each aldehyde (5 equivalents) and assuming that the concentration of each aldehyde is approximately unchanged under the reaction conditions.

(27) See the Supporting Information for details.

(28) σ values were obtained from: Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 5th ed; Wiley: New York, 2001; p 370.

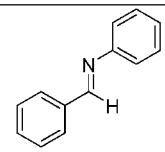
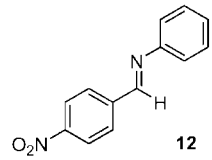
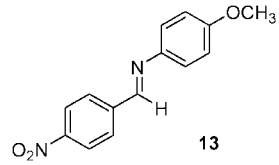
Scheme 3. Irreversibility of Hydroboration Reaction under Competition Experiment Conditions





14-16

Table 3. Catalytic Hydroboration of Imines (Eq 8)

Entry	Imine	Time (h)	Yield [a]
1 [b]		120	82%
2	 **12**	22	86%
3	 **13**	17	74%

[a] Isolated yield of amines. [b] 4 mol % complex **4** used.

tion of tolualdehyde and anisaldehyde was observed, demonstrating that the hydroboration of aldehydes is reversible over extended reaction times. The reversibility of the hydroboration reaction at extended reaction times is analogous to hydrogenation reactions using the Shvo catalyst,[29] which is reversible at elevated temperatures. The competition experiments used in the Hammett correlation plot were heated for 2 h at 50 °C, conditions under which the reaction was shown to be irreversible. These control experiments verify that the competition experiments were performed under kinetic control rather than thermodynamic control.

While there is a clear dependence of the reaction rate on the electron density of the aldehyde, the magnitude of the dependence is much lower than other hydride addition reactions. The ρ value for the hydroboration reaction is much smaller than that for the reduction of substituted benzaldehydes by $NaBH_4$ ($\rho = +3.8$),[30] substituted acetophenones by $NaBH_4$ ($\rho = +3.06, +2.02$),[31,32] and the reduction of substituted benzophenones by $LiAlH_4$ ($\rho = +1.95$).[33] More significantly, the ρ value of the hydroboration reaction using RuHOBpin **5** was considerably lower than the ρ value for the stoichiometric hydrogenation of substituted benzaldehydes with an analogue of the Shvo catalyst [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)Ru(CO)(PPh_3)H] **7** ($\rho = +1.77$),[24] which was shown to react through a concerted, outer-sphere reduction mechanism. The decreased ρ value indicates a decreased charge build-up in the transition state involving complex **5** as compared to that of complex **7**.

Catalytic Hydroboration of Imines. The scope of substrates that are compatible with this catalyst was further investigated by determining its reactivity with imines. *N*-Benzylideneaniline was examined under the reaction conditions optimized for aldehydes (50 °C, 2 mol % **4**, toluene). Under these conditions, the reaction was slow; complete consumption of the imine required heating at 70 °C for over 5 days. By using 4 mol % of precatalyst **4**, the reaction rate was accelerated, providing amine **14** (after hydrolysis by silica gel chromatography) in 82% yield after 5 days at 70 °C (entry 1). Electron-withdrawing groups were also found to accelerate the reaction of imines. In the case of imine **12** (entry 2), only 22 h at 70 °C was required to provide amine **15** (after hydrolysis). Imine **13** was subjected to the reaction conditions to determine if a significant rate effect would be observed based on the nitrogen substituent (entry 3). No qualitative difference in rates was observed with imine **13** over imine **12**.[34]

Catalytic Hydroboration of Ketones. The hydroboration of ketones was desired due to the potential for a catalytic asymmetric reduction reaction.[1] Acetophenone was treated with pinB-H and 4 mol % of precatalyst **4** at 70 °C, but low conversion to product **17** was observed (eq 9). Because electron-deficient aldehydes and imines displayed accelerated reaction rates, hydroboration of 4′-nitroacetophenone was explored (eq 10). After 4.5 days at 70 °C, >95% conversion was observed and alcohol **18** was isolated in 79% yield. Because the conditions

(29) For examples of dynamic kinetic asymmetric resolutions by transfer hydrogenation with the Shvo catalyst, see:(a) Martín-Matute, B.; Edin, M.; Bogár, K.; Kaynak, F. B.; Bäckvall, J.-E. *J. Am. Chem. Soc.* **2005**, *127*, 8817–8825. (b) Fransson, A.-B. L.; Borén, L.; Pàmies, O.; Bäckvall, J.-E. *J. Org. Chem.* **2005**, *70*, 2582–2587. (c) Martín-Matute, B.; Bäckvall, J.-E. *J. Org. Chem.* **2004**, *69*, 9191–9195. (d) Pàmies, O.; Bäckvall, J.-E. *J. Org. Chem.* **2002**, *67*, 1261–1265.

(30) Jacobs, J. W.; McFarland, J. T.; Wainer, I.; Jeanmaier, D.; Ham, C.; Hamm, K.; Wnuk, M.; Lam, M. *Biochemistry* **1974**, *13*, 60–64.

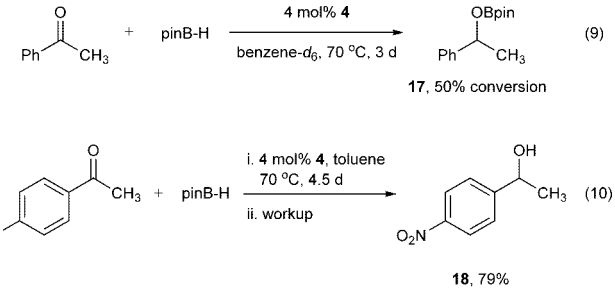
(31) Bowden, K.; Hardy, M. *Tetrahedron* **1966**, *22*, 1169–1174.

(32) Mullins, R. J.; Vedernikov, A.; Viswanathan, R. *J. Chem. Educ.* **2004**, *81*, 1357–1361.

(33) Wiegers, K. E.; Smith, S. G. *J. Am. Chem. Soc.* **1977**, *99*, 1480–1487.

(34) A competition experiment between the two imines showed a 1.2:1 ratio of hydroboration of imine **13** over imine **12**.

for hydroboration of ketones proved to be too harsh, attempts to determine the generality of the reaction and develop an asymmetric method were not pursued.



Conclusions

RuHOBpin **5** was synthesized and shown to possess reactivity in the hydroboration of carbonyls and imines. Catalytic conditions for the hydroboration of aldehydes and imines were developed requiring 50−70 °C and 2−4 mol % of ruthenium dimer **4**. The corresponding alcohols and imines were typically isolated in high yields. A Hammett correlation plot quantified the rate acceleration of electron-deficient aldehydes, providing a ρ value of +0.91. Thus, boron is a suitable surrogate for the acidic hydrogen of the Shvo catalyst.

Experimental Section

[2,5-Ph_2-3,4-Tol_2(η^4-C_4OBpin)]Ru$(CO)_2$H (5). A slurry of {[2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)Ru$(CO)_2$}$_2$ (**4**) (0.500 g, 0.439 mmol) and pinacolborane (0.130 mL, 0.895 mmol) in 25 mL of toluene was stirred for 2 h at 50 °C. The reaction mixture was removed from heat and the solvent evaporated under high vacuum. The resulting solid was suspended in 15 mL of pentane and filtered, and the filtrate was rinsed with pentane (3 × 5 mL). The solid was dried under high vacuum to give **5** as a brown/yellow solid (0.455 g, 74%): ^{1}H NMR (C_6D_6, 500 MHz) δ 7.72 (d, J = 7.5 Hz, 4H), 7.20 (d, J = 8.0 Hz, 4H), 7.04 (t, J = 7.5 Hz, 4H), 6.96 (m, 2H), 6.61 (d, J = 10 Hz, 4H), 1.85 (s, 6H), 0.81 (s, 12H), −9.33 (s, 1H); ^{13}C NMR (C_6D_6, 125 MHz) δ 202.5, 137.6, 133.6, 133.1, 131.9, 129.3, 129.1, 128.72, 128.70, 128.2, 104.2, 97.9, 84.3, 24.5, 21.3; ^{11}B NMR (C_6D_6, 160 MHz) δ 21.7; IR (thin film) 3053, 2981, 2926, 2020, 1959, 1444, 1399 cm^{-1}. Anal. Calcd for $C_{39}H_{37}O_5BRu$: C, 66.95; H, 5.62. Found: C, 66.57; H, 5.42.

General Procedure for the Catalytic Hydroboration of Aldehydes, Imines, and 4′-Nitroacetophenone. Benzyl Alcohol.[35] To a resealable glass tube containing {[2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)Ru$(CO)_2$}$_2$ (**4**) (0.068 g, 0.060 mmol), 15 mL of toluene, and pinacolborane (0.700 mL, 4.50 mmol) was added benzaldehyde (0.305 mL, 3.00 mmol). After 26 h at 50 °C, the reaction mixture was stirred over silica gel for 3 h, filtered through a silica plug with ethyl acetate (∼500 mL), and concentrated in vacuo to an orange/brown oil. Purification by bulb-to-bulb distillation (70−110 °C, 5 mmHg) and column chromatography (2:98 to 3:97 ethyl acetate/CH_2Cl_2) provided benzyl alcohol as a colorless oil (0.254 g, 78%): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.37 (m, 4H), 7.32 (m, 1H), 4.69 (s, 2H), 1.98 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.1, 128.7, 127.8, 127.2, 65.3; IR (thin film) 3335, 3064, 3031, 2931, 2873, 1496, 1454, 1020, 734, 698 cm^{-1}.

Acknowledgment. Financial support to C.P.C was provided by the Department of Energy, Office of Basic Energy Sciences and the National Science Foundation (CHE-0209476). Financial support to T.B.C. was provided by the National Institutes of Health in the form of a NRSA fellowship (GM077962-01), the Petroleum Research Fund, administered by the American Chemical Society (47598-GB3), the M.J. Murdock Charitable Trust and Research Corporation in the form of a department development grant, and Western Washington University.

Supporting Information Available: General experimental information, characterization data, details of the competition experiments, and selected spectra of products. This material is available free of charge via the Internet at http://pubs.acs.org.

OM801228M

(35) Shaikh, N. S.; Junge, K.; Beller, M. *Org. Lett.* **2007**, *9*, 5429–5432.