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Published on Web 05/07/2005

Ruthenium-Catalyzed Ionic Hydrogenation of Iminium Cations. Scope and Mechanism

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Abstract: Catalysis by CpRu(P−P)H (where P−P is a chelating diphosphine) of the ionic hydrogenation of an iminium cation inolves (1) the transfer of H^- to form an amine, (2) the coordination of H_2 to the resulting Ru cation, and (3) the transfer of H^+ from the coordinated dihydrogen to the amine formed in (1). With CpRu(dppe)H the principal Ru species during catalysis remains the hydride complex, and H_2 pressure has no effect on either the ee or the turnover frequency. Step (1), H^- transfer, can be carried out stoichiometrically if the H_2 is replaced by a coordinating solvent. A methyl substituent on the Cp ring decreases the H^- transfer rate and the turnover frequency slightly. Electron-donating substituents on the phosphine increase the H^- transfer rate and increase the turnover frequency up to a point: eventually the hydride ligand (i.e., the one in Cp*Ru(dmpe)H) becomes sufficiently basic to deprotonate the iminium cation to the corresponding enamine, and this pre-equilibrium competes with H^- transfer. Ionic hydrogenation of enamines is possible when a Ru(H_2) cation (i.e., [CpRu(dppm)(η^2-H_2)]$^+$) is used as the catalyst and the enamine is more basic than the product amine. Ionic hydrogenation of an α,β-unsaturated iminium cation saturates both the C=C and the C=N bonds. A C=N bond is more reactive toward ionic hydrogenation than a C=C one, but in some cases (i.e., CH=CH_2) the latter may compete with H_2 for a coordination site and decrease the turnover frequency.

Introduction

The homogeneous hydrogenation of C=N double bonds remains a challenge to catalysis, particularly when enantioface selectivity is needed.[1−4] Slight modifications in the substrate imine can have a substantial effect on the activity of various catalysts,[2c,4] or even destroy them.[2c] In a preliminary communication, we have reported[5] that CpRu(P−P)H can catalyze the hydrogenation of iminium cations by an ionic mechanism; we have reported ee's up to 60% with chiral diphosphines.

Such an ionic hydrogenation mimics biological reductions: it cleaves H_2 heterolytically and adds H^- and H^+ separately to the substrates. Coordination of the substrate *is not required* prior to hydride transfer; the hydride ligand is transferred *intermolecularly* to the substrate from the ruthenium. Hydrogenation by an ionic mechanism potentially offers advantages, such as (1) *compatibility with ionizing solvents such as water*[6] *and alcohols* and (2) *selectivity for polar C=X double bonds over C=C double bonds*. Noyori has emphasized the need for "preferential hydrogenation of a carbonyl function over olefinic and acetylenic bonds" and has noted that "currently available hydrogenation catalysts, either homogeneous or heterogeneous, are mostly selective for C=C functions over C=O bonds",[7] although he has reported a catalyst system ($RuCl_2L_3$/en/KOH) that reverses that selectivity.[8]

Ionic hydrogenation has been known for some time as a *stoichiometric* process with a silane, or a transition-metal hydride, serving as a source of the H^-.[9] We have reported the

(1) Reviews on the asymmetric hydrogenation of C=N: (a) Blaser, H.-U.; Spindler, F. Hydrogenation of Imine Groups. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: New York, 1999; Vol. 1, pp 247−265. (b) Ohkuma, T.; Noyori, R. Hydrogenation of Imino Groups. In *Comprehensive Asymmetric Catalysis, Supplement*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Berlin, 2004; Vol. 1, pp 43−53. (c) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069−1094. (d) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029−3069.

(2) A chiral titanocene catalyst that gives high ee's only for the hydrogenation of cyclic imines: (a) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1992**, *114*, 7562−7564. (b) Willoughby, C. A.; Buchwald, S. L. *J. Org. Chem.* **1993**, *58*, 7627−7629. (c) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952−8965. (d) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 11703−11714.

(3) An Ru catalyst for the transfer of hydrogen from formic acid that also gives high ee's only for the hydrogenation of cyclic imines: (a) Uematsu, N.; Fujii, A.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1996**, *118*, 4916−4917. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97−102.

(4) An Ir catalyst that gives high ee's with acyclic imines that have bulky substituents on N: (a) Zhu, G.; Zhang, X. *Tetrahedron: Asymmetry* **1998**, *9*, 2415−2418. (b) Xiao, D.; Zhang, X. *Angew. Chem., Int. Ed.* **2001**, *40*, 3425−3428.

(5) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778−1779.

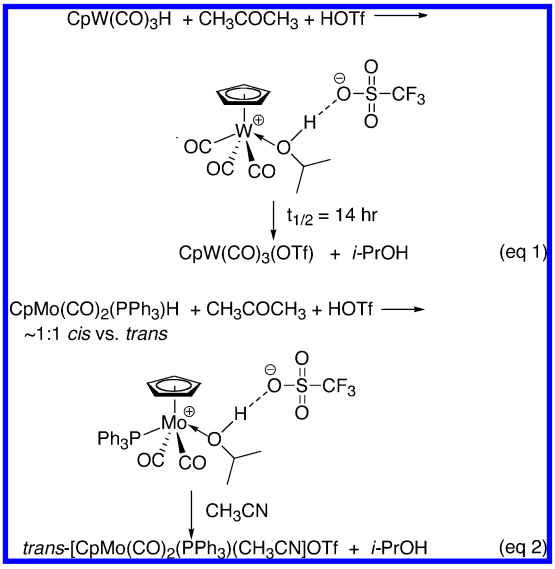
(6) A water-soluble ruthenium hydride, CpRu(PTA)$_2$H (PTA = 1,3,5-triaza-7-phosphaadamantane), has just been isolated and characterized: (a) Frost, B. J.; Mebi, C. A. *Organometallics* **2004**, *23*, 5317−5323. The same hydride has also been observed in solution: (b) Akbayeva, D. N.; Gonsalvi, L.; Oberhauser, W.; Peruzzini, M.; Vizza, F.; Brüggeller, P.; Romerosa, A.; Sava, G.; Bergamo, A. *Chem. Commun.* **2003**, 264−265. Such hydrides are potential catalysts for the ionic hydrogenation of polar double bonds in water.

(7) (a) Noyori, R. *Acta Chem. Scand.* **1996**, *50*, 380−390. (b) Noyori, R.; Ohkuma, T. *Pure Appl. Chem.* **1999**, *71*, 1493−1501.

(8) Ohkuma, T.; Ooka, H.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 10417−10418.

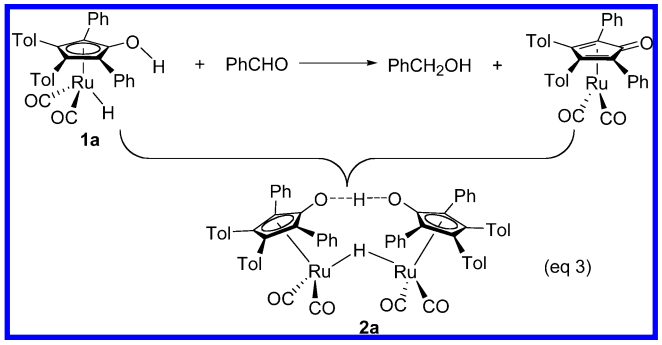
10.1021/ja0506861 CCC: $30.25 © 2005 American Chemical Society

example in eq 1 with the Bullock group,[10] and the example in eq 2 with the Tilset group.[11]

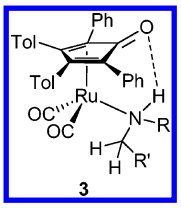


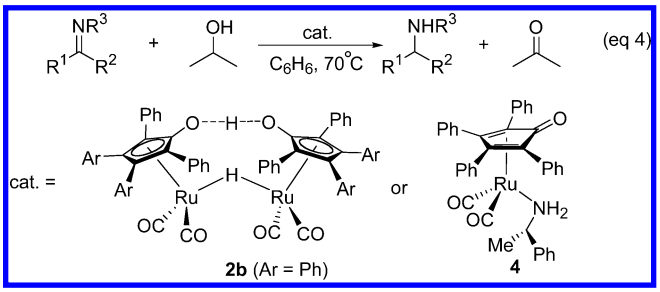
Bullock and co-workers have reported the catalytic (although not the asymmetric) ionic hydrogenation of ketones with $[CpM(CO)_2(PR_3)(ketone)]^+A^-$, where M = Mo or W, R = CH_3, Ph, or Cy, and A^- = PF_6^-, BF_4^-, or BAr'_4^- [Ar′ = 3,5-bis-(trifluoromethyl)phenyl].[12]

The Casey group has shown that the system in eq 3, derived from the one reported by Shvo,[13] can catalyze the ionic hydrogenation of PhCHO; **1a** can be regenerated from **2a** and H_2. They have reported isotope effects suggesting that the proton and the hydride are transferred simultaneously to the benzaldehyde in eq 3.[14a]

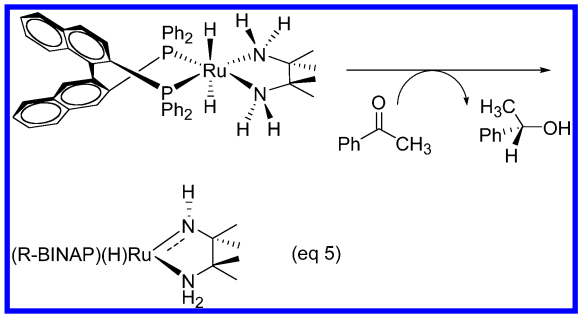


The Casey group has also reported transfer of hydrogen from **1a** to an imine to give **3**, but have not reported catalysis (the amine complex **3** is stable).[14] With the closely related **1b**/**2b** system in eq 4, Bäckvall and co-workers have catalyzed the *transfer* hydrogenation (with the H^+ and H^- coming from propan-2-ol) of an imine by an ionic mechanism; attempts to isolate a secondary amine complex were unsuccessful, although the primary amine complex **4** was isolated and shown to be an efficient catalyst for the transfer hydrogenation of imines.[15] Neither the Casey group nor the Bäckvall group has catalyzed an *asymmetric* hydrogenation with the **1**/**2** system, which does not lend itself to the incorporation of chiral ligands.





Morris has observed H^+/H^- transfer from RuH_2(chiral diphosphine)(diamine) to a substrate ketone (eq 5), regeneration of the starting material with H_2, and thus a catalytic cycle for the *asymmetric* hydrogenation of ketones by an ionic mechanism.[16] Because the catalyst in eq 5 is closely related to those of Noyori,[3b,17] it is possible that the latter catalysts also operate by ionic mechanisms, with the necessary H^+ and H^- coming either from H_2 or from an alcohol (transfer hydrogenation).[18]



We now report the scope of the ionic hydrogenation of iminium cations by CpRu(P−P)H and related catalysts. We have

(9) With silanes as the H^- donors: (a) Kursanov, D. N.; Parnes, Z. N.; Loim, N. M. *Synthesis* **1974**, 633−651. With transition-metal hydrides as the H^- donors: (b) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428−2434. (c) Gibson, D. H.; El-Omrani, Y. S. *Organometallics* **1985**, *4*, 1473−1475. (d) Geraty, S. M.; Harkin, P.; Vos, J. G. *Inorg. Chim. Acta* **1987**, *131*, 217−220. (e) Kelly, J. M.; Vos, J. G. *J. Chem. Soc., Dalton Trans.* **1986**, 1045−1048. (f) Bullock, R. M.; Rappoli, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1447−1448. (g) Bullock, R. M.; Song, J.-S. *J. Am. Chem. Soc.* **1994**, *116*, 8602−8612. (h) Bakhmutov, V. I.; Vorontsov, E. V.; Antonov, D. Y. *Inorg. Chim. Acta* **1998**, *278*, 122−126. (i) Minato, M.; Fujiwara, Y.; Ito, T. *Chem. Lett.* **1995**, 647−648. (j) Minato, M.; Fujiwara, Y.; Koga, M.; Matsumoto, N.; Kurishima, S.; Natori, M.; Sekizuka, N.; Yoshioka, K.-i.; Ito, T. *J. Organomet. Chem.* **1998**, *569*, 139−145.

(10) Song, J.-S.; Szalda, D. J.; Bullock, R. M.; Lawrie, C. J. C.; Rodkin, M. A.; Norton, J. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1233−1235.

(11) Smith, K.-T.; Norton, J. R.; Tilset, M. *Organometallics* **1996**, *15*, 4515−4520.

(12) (a) Bullock, R. M.; Voges, M. H. *J. Am. Chem. Soc.* **2000**, *122*, 12594−12595. (b) Voges, M. H.; Bullock, R. M. *J. Chem. Soc., Dalton Trans.* **2002**, 759−770. (c) Bullock, R. M. *Chem.−Eur. J.* **2004**, *10*, 2366−2374.

(13) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 7400−7402.

(14) (a) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090−1100. (b) Casey, C. P.; Johnson, J. B *J. Am. Chem. Soc.* **2005**, *127*, 1883−1894.

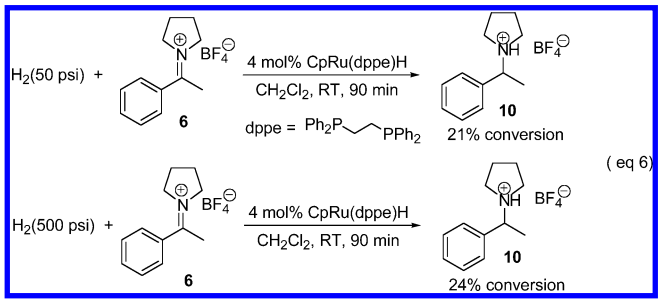
(15) (a) Samec, J. S. M.; Bäckvall, J.-E. *Chem.−Eur. J.* **2002**, *8*, 2955−2961. (b) Samec, J. S. M.; Éll, A. H.; Bäckvall, J.-E. *Chem. Commun.* **2004**, 2748−2749.

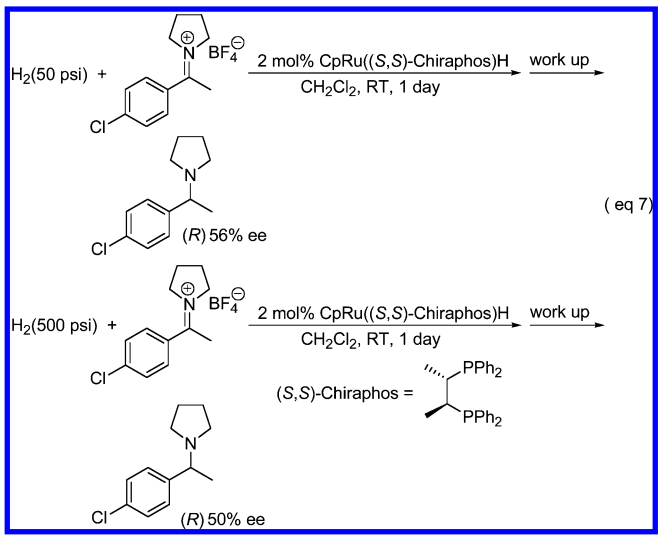
(16) (a) Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2000**, *19*, 2655−2657. (b) Abdur-Rashid, K.; Faatz, M.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 7473−7474. (c) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104−15118. (d) Rautenstrauch, V.; Hoang-Cong, X.; Churlaud, R.; Abdur-Rashid, K.; Morris, R. H. *Chem.−Eur. J.* **2003**, *9*, 4954−4967.

compared the effectiveness of various ruthenium hydrides in catalyzing this reaction, and we have explored its ability to hydrogenate various types of iminium cations as well as its selectivity for C=N hydrogenation over other reactions. Details of the enantioface selectivity that can be achieved in such hydrogenations will be reported separately.

Results and Discussion

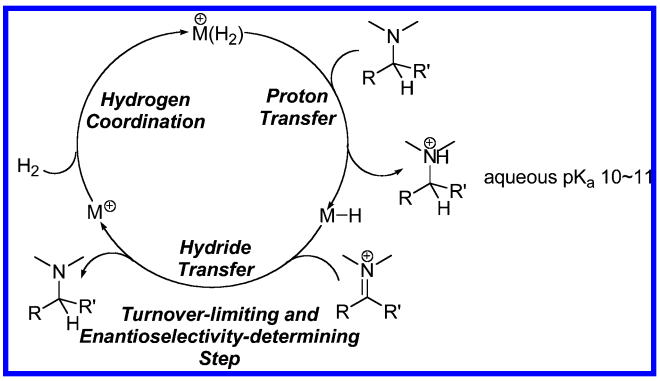
"Stoichiometric" Hydride Transfer from LRu(dppe)H (L = Cp (or C_5H_5), Cp′ (or C_5H_4Me), and Cp* (or C_5Me_5)) to an Iminium Cation. Both the turnover and the enantioselectivity of the catalytic hydrogenations in eqs 6 and 7 are unaffected by the hydrogen pressure, implying that H_2 uptake is a relatively fast step in the catalytic cycle (see Scheme 1) at any pressure. The transfer of an H^+ to the product amine must also be relatively fast,[19,20] as ^{1}H NMR observation of a catalytic reaction shows most (>80 mol %) of the ruthenium to be CpRu(dppe)H. Thus, the hydride transfer step determines the enantioselectivity and turnover frequency (TOF) of a catalytic hydrogenation by an ionic mechanism.[5]



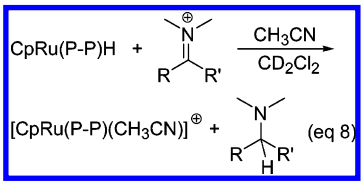


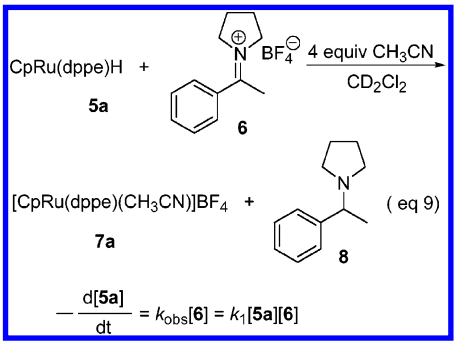
We can thus screen catalysts by examining the rate of the hydride transfer step when H_2 is not present. To go to completion, such a "stoichiometric" hydride transfer (eq 8) requires that a coordinating ligand, such as CH_3CN, fill the vacant coordination site that remains after H^- transfer. We have already reported that the rate of H^- transfer from CpRu(dppe)H

Scheme 1



(**5a**) to the iminium cation **6** is independent of [CH_3CN], but is first-order in both the ruthenium hydride and the iminium cation (eq 9).[21]





We have also reported that the ring size formed by the chelating diphosphine affects the rate of hydride transfer: the smaller the chelate ring size, the faster the transfer (CpRu(dppm)H > CpRu(dppe)H ≈ CpRu(dpbz)H > CpRu(dppp)H ≫ CpRu(dppb)H).[21] The energy of the LUMO of the coordinatively unsaturated, 16-electron, cation CpRu(P−P)$^+$ (which remains after H^- transfer) decreases as its chelate ring becomes larger, making it a better H^- acceptor and decreasing the rate of H^- transfer away from CpRu(P−P)H.

Stoichiometric H^- transfer reactions such as the ones in eqs 8 and 9 are convenient for comparing different Ru hydride complexes (e.g., those with different substituents on the cyclopentadienyl ring). When we treated the cation **6** with Cp′Ru-

(17) (a) Haack, K.-J.; Hashiguchi, S.; Fujii, A.; Ikariya, T.; Noyori, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 285−288. (b) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 40−73.

(18) (a) Aranyos, A.; Csjernyik, G.; Szabó, K. J.; Bäckvall, J.-E. *Chem. Commun.* **1999**, 351−352. (b) Laxmi, Y. R. S.; Bäckvall, J.-E. *Chem. Commun.* **2000**, 611−612.

(19) Rate constants for the isomerization of dihydrogen complexes to the corresponding dihydrides have been reported by Chinn and Heinekey for related [CpRu(P−P)(η^2-H_2)]BF_4.[20] From their data at room temperature with other P−P, the first-order rate constant for [CpRu(dppe)(η^2-H_2)]BF_4 → [CpRu(dppe)$(H)_2$]BF_4 can be estimated as 10^{-2} s^{-1}. At the same temperature, the first-order rate constant for the disappearance of CpRu(dppe)H by H^- transfer is 10^{-3} s^{-1} under catalytic conditions, suggesting (because the η^2-H_2 cation never reaches an observable concentration) that the rate constant for deprotonation of the η^2-H_2 cation is at least 10^{-1} s^{-1} and that deprotonation of that cation is probably faster than its isomerization to the Ru$(H)_2$ cation.

(20) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166−5175.

(21) Guan, H.; Iimura, M.; Magee, M. P.; Norton, J. R.; Janak, K. E. *Organometallics* **2003**, *22*, 4084−4089. Abbreviations: dppm = bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, dpbz = 1,2-bis(diphenylphosphino)benzene, dppp = 1,3-bis(diphenylphosphino)propane, dppb = 1,4-bis(diphenylphosphino)butane.

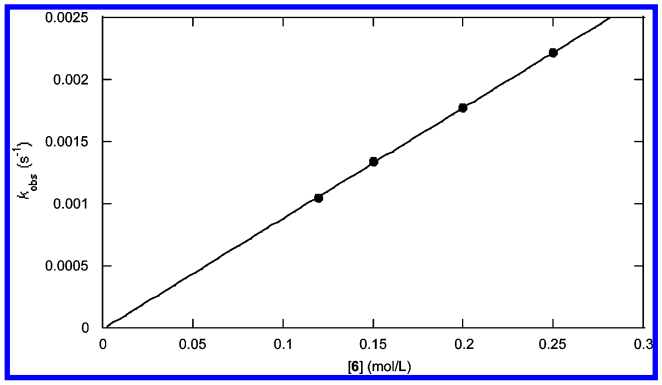
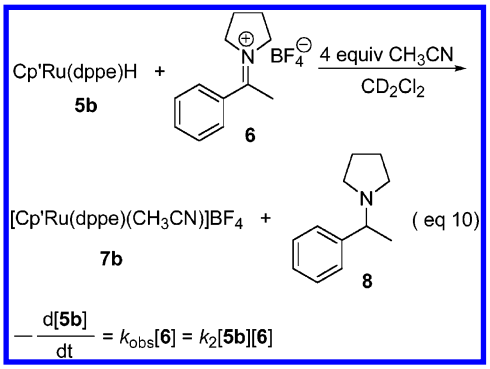


Figure 1. Plot of k_{obs} versus [**6**] for hydride transfer from **5b** to the iminium cation **6** at 300 K with CH_3CN present.

(dppe)H (**5b**) in the presence of CH_3CN, the free amine **8** and [Cp′Ru(dppe)(CH_3CN)]BF_4 (**7b**) were formed (eq 10). Monitoring the disappearance of **5b** by ^1H NMR in the presence of excess **6** (10 equiv) gave a pseudo-first-order rate constant k_{obs}. Variation of [**6**] from 0.12 to 0.25 M (Figure 1) showed a linear relationship between k_{obs} and [**6**], confirming that this H^- transfer is also a second-order reaction.

The slope of Figure 1 implies a value of $8.9(1) \times 10^{-3}$ M^{-1} s^{-1} for the rate constant k_2. Comparison with the analogous rate constant k_1 for **5a** ($2.0(1) \times 10^{-2}$ M^{-1} s^{-1})[21] shows that the addition of one methyl group to the cyclopentadienyl ring *decreases* the rate of H^- transfer by a factor of 2; apparently the steric effect of the methyl group outweighs its electronic effect.



Structural Effects of Methyl Substituents on the Cyclopentadienyl Ring. Structures of Cp′Ru(dppe)H (5b) and Cp*Ru(dppe)H (5c). The solid-state structures of **5b** and **5c** have been determined by X-ray crystallography; thermal ellipsoid plots are shown in Figures 2 and 3, respectively. The structure of **5a** has been reported previously.[21]

The methyl substituents have little effect on the P−Ru−P bite angle, which is 84.50° in **5a**, 85.40° in **5b**, and 83.73° in **5c**, or on the angle between the Cp ring and the Ru−P−P plane,[6,22,23] which is 69.7° in **5a**, 71.0° in **5b**, and 71.3° in **5c**. The methyl substituent of **5b**, which in the crystal (Figure 2) lies over a phenyl ring of the diphosphine, must be

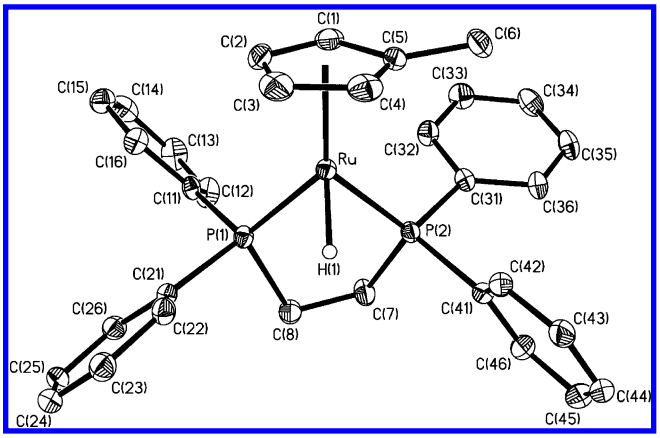


Figure 2. Molecular structure of Cp′Ru(dppe)H (**5b**) (20% probability level). Selected bond lengths (Å) and angle (deg): Ru−P1, 2.2248(6); Ru−P2, 2.2277(7); Ru−H1, 1.60(3); P1−Ru−P2, 85.40(2).

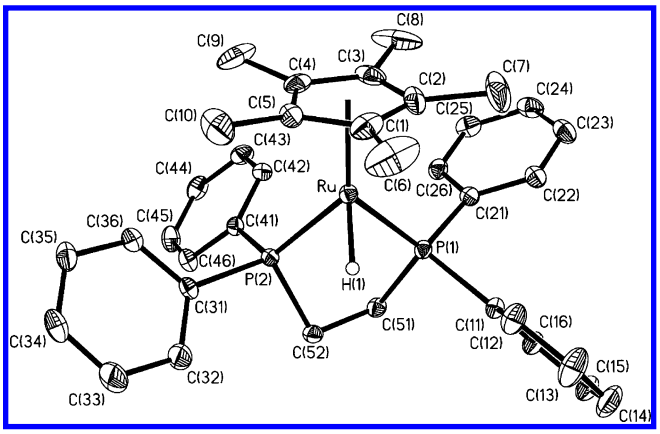


Figure 3. Molecular structure of Cp*Ru(dppe)H (**5c**) (20% probability level). Selected bond lengths (Å) and angle (deg): Ru−P1, 2.2363(6); Ru−P2, 2.2291(6); Ru−H1, 1.59(2); P1−Ru−P2, 83.73(2).

able in solution to interfere slightly with the approach of substrate.

Effect of Additional Methyl Substituents on the Rate of Hydride Transfer. The work of Bullock and co-workers has shown that, with $[Ph_3C]BF_4$ as the hydride acceptor, H^- transfer is about 20 times faster for Cp*$W(CO)_3H$ than for $CpW(CO)_3H$, and about 20 times faster for Cp*$Mo(CO)_3H$ than for $CpMo(CO)_3H$.[24] Apparently the electronic effect of the methyl substituents on the Cp ring is dominant.

However, with the iminum cation **6** as the hydride acceptor, we have found that complete methyl substitution can suppress hydride transfer in favor of side reactions. A solution of **6**, **5c**, and CH_3CN in CD_2Cl_2 showed negligible H^- transfer to **6** (<2 mol % by ^1H NMR) after 24 h. However, a new triplet with $J_{P-H} = 28.8$ Hz appeared in the hydride region alongside the signal of **5c**. The chemical shift of this new triplet was consistent with [Cp*Ru(dppe)$(H)_2$]BF_4,[25] suggesting the proton-transfer equilibrium in eq 11.[26] However, overlap with the resonances of **6** precluded identification of the enamine peaks, and further complications arose from the reaction of **5c** with the solvent

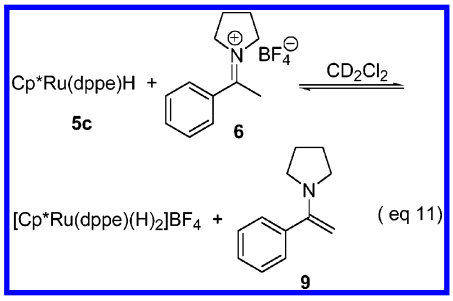
(22) The utility of this interplanar angle as a way of assessing the geometry of such hydride complexes has been pointed out by Lemke and Brammer,[23] and Frost and Mebi have noted[6] that it (the angle between the Cp ring and the Ru−P−P plane) decreases with increasing P−Ru−P bite angle within the CpRu(P−P)H series in ref 21.
(23) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980−3987.
(24) (a) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **1995**, *14*, 4031−4033. (b) Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121−13137.
(25) Jia, G.; Ng, W. S.; Chu, H. S.; Wong, W.-T.; Yu, N.-T.; Williams, I. D. *Organometallics* **1999**, *18*, 3597−3602.
(26) We were not able to determine the equilibrium constant accurately because of the side reaction, but a 1:1 mixture of **5c** and **6** showed about 20 mol % [Cp*Ru(dppe)$(H)_2$]BF_4 after 24 h.

Table 1. pK_a Determination of Ruthenium Dihydrogen and Dihydride Complexes at Room Temperature

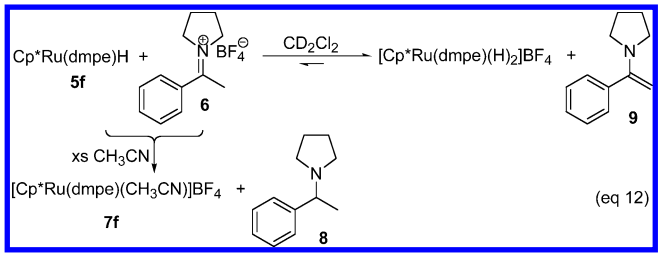
RuH	BH^+	K_1	pK_a (Ru(η^2-H_2)$^+$)[a]	K_2	pK_a (Ru$(H)_2^+$)[a]
Cp′Ru(dppe)H (**5b**)	[CpRu(dppm)(η^2-H_2)]BF_4	2.49	7.5	10.8	8.1
Cp*Ru(dppe)H (**5c**)	[Cp*Ru$(PPh_3)_2(H)_2$] BF_4			0.75[b]	11.0
CpRu(dpbz)H (**5e**)	[CpRu(dppm)(η^2-H_2)]BF_4	0.15	6.3	0.080	6.0
Cp*Ru(dmpe)H (**5f**)	[Cp*Ru$(PPhMe_2)_2(H)_2$]BPh_4			4.30[b,c]	14.9
(Ind)Ru(dppm)H (**5g**)	[CpRu(dppm)(η^2-H_2)]BF_4	>0.14	>6.2		
(Ind)Ru(dppe)H (**5h**)	[CpRu(dppm)(η^2-H_2)]BF_4	>0.060	>5.9	>0.036	>5.7

[a] Aqueous pK_a. [b] Equilibrium was established in THF-d_8. [c] For the reverse reaction, [Cp*Ru(dmpe)$(H)_2$]BF_4 was used, instead of [Cp*Ru(dmpe)$(H)_2$]BPh_4.

CD_2Cl_2, forming Cp*Ru(dppe)Cl.[27]

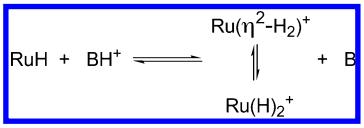


In an effort to find a less ambiguous example of eq 11, we treated Cp*Ru(dmpe)H(**5f**) (dmpe = 1,2-bis(dimethylphosphino)ethane) (which only reacts very slowly with CD_2Cl_2) with the iminium cation **6** in the presence of CH_3CN, and indeed we did observe complete deprotonation of the iminum cation to the enamine (eq 12). We also found, however, that complete H^- transfer eventually occurred despite the presence of the unfavorable pre-equilibrium.



Equilibrium Constants for Deprotonation of Iminium Cations by Electron-Rich Ru Hydride Complexes. Jia and Morris[28] have estimated the aqueous pK_a values of many ruthenium dihydrogen and/or dihydride cations containing Cp*Ru(P−P) or CpRu(P−P) by comparing their relative acidities in THF or CH_2Cl_2 with those of "secondary standard" acids with established aqueous pK_a values; as secondary standards they used protonated tertiary phosphines R_3PH^+ and other dihydrogen/dihydride cations. Aqueous pK_a values for most of the ruthenium dihydrogen/dihydride complexes in the present study are available from their compilation.[28]

When we treated **5b** with [CpRu(dppm)(η^2-H_2)]BF_4 in CD_2Cl_2 at room temperature, a mixture of Cp′Ru(dppe)(η^2-H_2)]BF_4 and Cp′Ru(dppe)$(H)_2$]BF_4 (ratio 1:3.9, distinguished by a broad singlet versus a triplet for the hydride signals) was formed, as well as CpRu(dppm)H (**5d**); equilibrium was achieved within 1 h (as monitored by ^{1}H NMR). The same equilibrium was approached from the reverse direction by treating **5d** with a mixture of Cp′Ru(dppe)(η^2-H_2)]BF_4 and Cp′Ru(dppe)$(H)_2$]BF_4 (prepared by the direct protonation of **5b** with HBF_4·Me_2O). The equilibrium constants and pK_a values (given in Table 1) were then calculated from eqs 13−16 (in this case BH^+ = [CpRu(dppm)(η^2-H_2)]BF_4, and pK_a (BH^+) = 7.1[28]). The difference between the pK_a values for Cp′Ru(dppe)(η^2-H_2)]$^+$ and Cp′Ru(dppe)$(H)_2$]$^+$ in Table 1 (a ΔpK_a of 0.6, implying a K_2/K_1 of 4.3) is consistent with the observed equilibrium ratio (3.9) of the dihydride to the dihydrogen complex.



$$K_1 = \frac{[\mathrm{Ru}(\eta^2\text{-}\mathrm{H_2})^+][\mathrm{B}]}{[\mathrm{RuH}][\mathrm{BH}^+]} \quad (13)$$

$$K_2 = \frac{[\mathrm{Ru(H)_2}^+][\mathrm{B}]}{[\mathrm{RuH}][\mathrm{BH}^+]} \quad (14)$$

$$\mathrm{p}K_a[\mathrm{Ru}(\eta^2\text{-}\mathrm{H_2})^+] = \mathrm{p}K_a(\mathrm{BH}^+) + \log K_1 \quad (15)$$

$$\mathrm{p}K_a[\mathrm{Ru(H)_2}^+] = \mathrm{p}K_a(\mathrm{BH}^+) + \log K_2 \quad (16)$$

Similar results (the pK_a values of the resulting dihydrogen/dihydride cations are also given in Table 1) were obtained when we treated CpRu(dpbz)H (**5e**) with [CpRu(dppm)(η^2-H_2)]BF_4. However, [CpRu(dppm)(η^2-H_2)]BF_4 completely protonated **5c** and **5f**, and therefore less acidic RuH_2 cations (the established[28] pK_a of [Cp*Ru$(PPh_3)_2(H)_2$]BF_4 is 11.1, and that of [Cp*Ru-$(PPhMe_2)_2(H)_2$]BPh_4 is 14.3) were used to determine the pK_a values (Table 1) of [Cp*Ru(dppe)$(H)_2$]$^+$ and [Cp*Ru(dmpe)-$(H)_2$]$^+$.

We attempted to determine the pK_a values of the related indenyl complexes (Ind)Ru(dppe)H(**5h**) (Ind = indenyl) and (Ind)Ru(dppm)H (**5g**). Protonation of **5h** by CF_3SO_3H or HBF_4·Et_2O at −60 °C in THF-d_8 has been reported by Lau, Jia, and co-workers to give a mixture of [(Ind)Ru(dppe)(η^2-H_2)]$^+$ and [(Ind)Ru(dppe)$(H)_2$]$^+$,[29] and by ^{1}H NMR we obtained a mixture of the same cations (along with **5d**) when **5h** was treated with [CpRu(dppm)(η^2-H_2)]BF_4 in CD_2Cl_2 at room temperature. However, we were unable to isolate [(Ind)Ru(dppe)(η^2-H_2)]BF_4 and [(Ind)Ru(dppe)$(H)_2$]BF_4 and were thus unable to approach the equilibrium in eq 17 from the right. Furthermore, even when

(27) The reaction of **5c** with CD_2Cl_2 was much slower than that previously reported[21] for CpRu(dppp)H (which reacts with CD_2Cl_2 in minutes). In one case, 46 mol % of **5c** ($[\mathbf{5c}]_0 = 6 \times 10^{-3}$ M in CD_2Cl_2) was converted to Cp*Ru(dppe)Cl after 24 h. As before,[21] treatment with 1% (by weight) TEMPO (TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy) stopped the reaction.

(28) (a) Jia, G.; Morris, R. H. *Inorg. Chem.* **1990**, *29*, 581−582. (b) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883.

(29) Hung, M. Y.; Ng, S. M.; Zhou, Z.; Lau, C. P.; Jia, G. *Organometallics* **2000**, *19*, 3692−3699.

Table 2. Relative Catalytic Activity of Various Ruthenium Hydrides for Hydrogenation[h]

catalyst	initial TOF (h^{-1}) exptl	initial TOF (h^{-1}) calcd[a]	time (h)	conversion (%)	yield[b] (%)	pK_a of $Ru(H)_2^+$ [c]
CpRu(dppe)H (**5a**)	8.9	(13.7)	40	95	81	7.3 (7.0)[d]
	7.9[e]		50	95	83	
	2.4[f]		70	74	51	
Cp′Ru(dppe)H (**5b**)	4.0	(6.1)	70	84	70	8.1 (7.5)
Cp*Ru(dppe)H (**5c**)[e]	<0.025[g]		40	<1	−	11.0
CpRu(dppm)H (**5d**)	297	(437)	2	98	84	(7.1)[d]
CpRu(dpbz)H (**5e**)	9.1	(14.4)	40	99	83	6.0 (6.3)
Cp*Ru(dmpe)H (**5f**)[e]	<0.05[g]		95	<5	−	14.9
(Ind)Ru(dppm)H (**5g**)	153		3	97	84	(>6.2)
(Ind)Ru(dppe)H (**5h**)	0.75		95	63	40	>5.7 (>5.9)
CpRu(dmpe)H (**5i**)	579		2	99	86	(9.8)[d]
$CpRu(PPh_3)_2H$ (**5j**)	0.04		50	2	−	8.3[d]

[a] The predicted initial TOF was calculated from the rate constants of the H^- transfer at 300 K (k_2 for **5b**, ref 21 for others). [b] Isolated yield. [c] Estimated aqueous pK_a of $Ru(\eta^2\text{-}H_2)^+$ is listed in the parenthesis. [d] From ref 28. [e] CH_3OH was used as the solvent. [f] Acetone was used as the solvent. [g] Other unidentified products were present. [h] Reaction conditions: [**6**] = 0.2 mol/L, [catalyst] = 0.002 mol/L, H_2 pressure 50 psi, in CH_2Cl_2, T = 298 K.

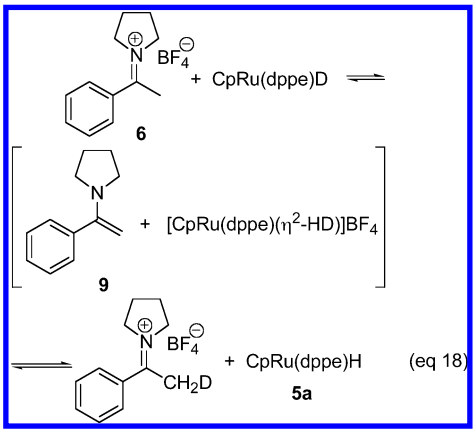
we approached the equilibrium from the left, decomposition began (after 30 min) before it was established; the extent of product formation we observed thus gave a lower limit to the equilibrium constant for eq 17 and implied a pK_a > 5.9 for $[(Ind)Ru(dppe)(\eta^2\text{-}H_2)]BF_4$ and a pK_a > 5.7 for $(Ind)Ru(dppe)(H)_2BF_4$. Similar experiments gave a pK_a > 6.2 for $[(Ind)Ru(dppm)(\eta^2\text{-}H_2)]BF_4$. All three p$K_a$ values are shown in Table 1.

$$\underset{\mathbf{5h}}{(Ind)Ru(dppe)H} + [CpRu(dppm)(\eta^2\text{-}H_2)]BF_4 \overset{CD_2Cl_2}{\rightleftharpoons} [(Ind)Ru(dppe)(\eta^2\text{-}H_2)]BF_4 + [(Ind)Ru(dppe)(H)_2]BF_4 + \underset{\mathbf{5d}}{CpRu(dppm)H} \quad (17)$$

When we generated $[(Ind)Ru(dppe)(\eta^2\text{-}H_2)]BF_4$ and $[(Ind)Ru(dppe)(H)_2]BF_4$ by eq 17, we did not reproduce one observation of Lau, Jia, and co-workers.[29] Upon warming to room temperature, their dihydrogen and dihydride cations (generated from CF_3SO_3H or $HBF_4{\cdot}Et_2O$ at −60 °C) isomerized to an η^6-indene complex, $[(\eta^6\text{-}C_9H_8)Ru(dppe)H]^+$. We did not observe the formation of the η^6-indene complex when we carried out eq 17 at room temperature, suggesting that the isomerization of $[(Ind)Ru(dppe)(\eta^2\text{-}H_2)]BF_4$ and/or $[(Ind)Ru(dppe)(H)_2]BF_4$ to the η^6-indene complex is probably not intramolecular as proposed.[29]

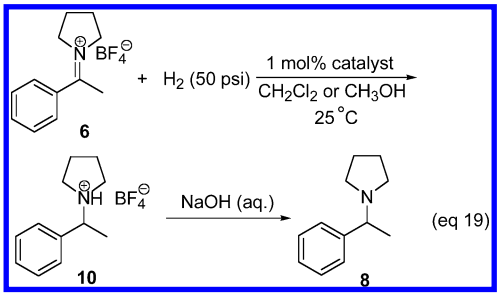
H/D Exchange between the Iminium Cation 6 and CpRu(dppe)D. When equimolar amounts of iminium cation **6** and CpRu(dppe)D were mixed in CH_2Cl_2 at room temperature, ^2H NMR showed a rapid H/D exchange between two reagents, with the formation of deuterated **6** and a decrease in the amount of CpRu(dppe)D (Figure S-2 in Supporting Information); ^1H NMR in CD_2Cl_2 confirmed the formation of CpRu(dppe)H(**5a**). Over time, the amine product **8** was formed smoothly by H^- transfer. Presumably **6** transfers H^+ to the CpRu(dppe)D,[30] giving the enamine and $[CpRu(dppe)(\eta^2\text{-}HD)]BF_4$ (which may not be in equilibrium with $[CpRu(dppe)(H)(D)]BF_4$[19]); transfer of D^+ back to the enamine carbon finishes the exchange shown in eq 18.

The slow H^- transfer made it difficult to measure the equilibrium isotope effect (EIE) for the H/D exchange in eq 18 with high precision, but it appears to be about 6.1 (see Supporting Information) at room temperature. This EIE reflects the operation of a statistical factor of 3 and a zero-point energy



factor of about two, similar to the EIEs observed for $Cp_2W(D)CH_3/Cp_2W(H)CH_2D$[31] and related exchanges.[32]

Activity of Various Catalysts for Hydrogenation of the Iminium Cation 6. To compare activities, reaction 19 was performed under 50 psi H_2 pressure with 1 mol % of various ruthenium catalysts; the solvent used was CH_2Cl_2 (or CH_3OH if the ruthenium hydride proved unstable in CH_2Cl_2). The initial TOF was determined when less than 10% of the **6** had been hydrogenated. The results are given in Table 2.



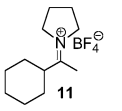
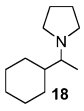
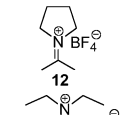
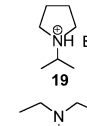
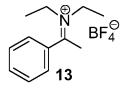
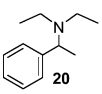
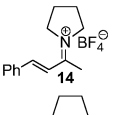
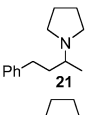
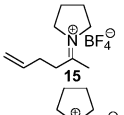
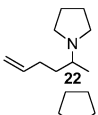
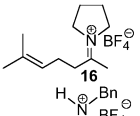
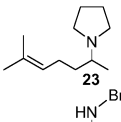
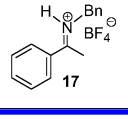
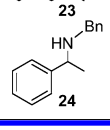
The TOF observed for **6** at the beginning of its catalytic hydrogenation (the second column in Table 2) agrees well with

(30) The aqueous pK_a values of related iminium cations have been compiled: Acidity and Basicity of Enamines. In *The Chemistry of Enamines*; Rappoport, Z., Ed.; Wiley & Sons: New York, 1994; p 709. The comparable acidities of Cp*Ru(dppe)H (pK_a = 11.0, see Table 2) and iminium **6** in eq 11 suggest that the pK_a of **6** is about 11.

(31) Bullock, R. M.; Headford, C. E. L.; Hennessy, K. M.; Kegley, S. E.; Norton, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 3897−3908.

(32) (a) Churchill, D. G.; Janak, K. E.; Wittenberg, J. S.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 1403−1420. (b) Janak, K. E.; Churchill, D. G.; Parkin, G. *Chem. Commun.* **2003**, 22−23. (c) Janak, K. E.; Parkin, G. *J. Am. Chem. Soc.* **2003**, *125*, 6889−6891.

Table 3. Scope of Ionic Hydrogenation of Various Iminium Cations[d]

Entry	Iminum Cation	Catalyst	Amine Product	Time (h) [a]	Yield (%)
1	 **11**	1mol% **5d**	 **18**	90	54
2	 **12**	1mol% **5a**	 **19**	40	84 [b]
3	 **13**	1mol% **5d** 10mol% **5d**	 **20**	48 12	– 73
4	 **14**	2mol% **5a**	 **21**	50	83
5	 **15**	2mol% **5d**	 **22**	24	– [c]
6	 **16**	2mol% **5d**	 **23**	36	71
7	 **17**	2mol% **5a**	 **24**	50	80

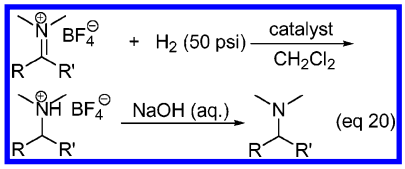
[a] All entries other than 3 (1 mol %) and 5 have >95% conversion for the given reaction time. [b] Isolated as the ammonium salt instead of the amine product. [c] 6% conversion by ^{1}H NMR suggested three turnovers. [d] Reaction conditions: [iminium cation] = 0.1 mol/L, H_2 pressure 50 psi, room temperature.

that calculated (in parentheses in the same column) from the rate of the stoichiometric H^- transfer, confirming that (as shown in Scheme 1) the turnover-limiting step in the catalytic cycle is the H^- transfer step.[33]

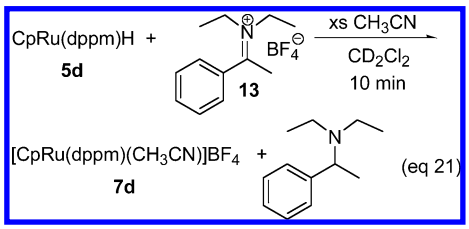
With a Cp ligand, alkyl-substituted phosphines make hydrogenation more facile; hydride transfer, and thus turnover, decreases in the order CpRu(dmpe)H (**5i**) > **5a** > CpRu-$(PPh_3)_2$H (**5j**). However, such hydride complexes remain sufficiently weak bases that their Ru(η^2-H_2)/Ru$(H)_2$ cations, which have aqueous pK_a values (Table 1 and ref 28) in the range of 5−10, are acidic enough to protonate the product amine[34] (the "Proton Transfer" step in Scheme 1). Substitution of a Cp* ligand makes the hydride ligand sufficiently basic that a proton transfer like the one in eq 12 will decrease [RuH] and retard hydride transfer and catalytic hydrogenation. The pK_a of [Cp*Ru(dmpe)$(H)_2$]BF_4 is 14.9, whereas that of **6** is about 11.[30] Cp*Ru(dmpe)H is thus a very poor catalyst (TOF < 0.05 h^{-1}), even though the stoichiometric hydride transfer in eq 12 is reasonably fast (complete in 10 h).

Ionic Hydrogenation of Other Iminium Cations. We have examined the scope of ionic hydrogenation catalyzed by **5a** and **5d** (eq 20). The results are summarized in Table 3.

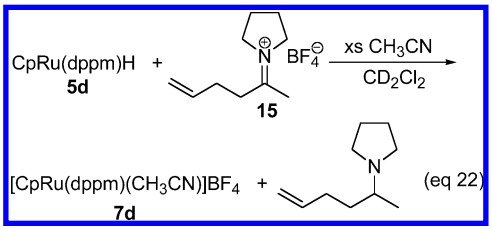
The hydrogenation of alkyl−alkyl disubstituted iminium cations **11** and **12** was straightforward (entries 1 and 2 in Table 3), as was that of aryl−alkyl substituted ones such as **6** (for



which TOF data were given in Table 2). We observed no hydrogenation under standard conditions when the pyrrolidinium ring in **6** was replaced with two ethyl substituents on the iminium nitrogen (entry 3); however, stoichiometric H^- transfer from **5d** to **13** was facile (eq 21), and catalytic hydrogenation did occur when we increased the catalyst loading to 10 mol %. At low catalyst loading the hydride **5d** is probably protonated, to [CpRu(dppm)(η^2-H_2)]BF_4, by traces of acid remaining from the preparation of the iminium cation **13**; we observed the formation of [CpRu(dppm)(η^2-H_2)]BF_4 when we used an excess (10 equiv) of the iminium cation **13** in eq 21. The iminium cation **13** itself (aqueous pK_a ≈ 11[30]) is not a strong enough acid to protonate **5d**.



We would expect an ionic mechanism to hydrogenate C═N double bonds selectively in preference to C═C double bonds, and this result was observed stoichiometrically with the substrate **15** (eq 22 and entry 5, Table 3) and catalytically with substrates **15** and **16** (entry 6, Table 3), although the turnover with **16** far exceeded that with **15**. Apparently the terminal C═C double bond in **15** competes effectively with H_2 for the coordination site remaining after an H^- transfer,[35,36] whereas the substituents on the olefin in **16** prevent its coordination and promote catalytic hydrogenation.



When a C═C double bond was conjugated with a C═N double bond, both were hydrogenated (entry 4 in Table 3). Presumably a 1,4-hydride transfer (and protonation) is followed by a 1,2-hydride transfer (and protonation) (Scheme 2).

The protonated imine **17** (entry 7) also underwent ionic hydrogenation. Unprotonated imines were, as expected, unreactive.

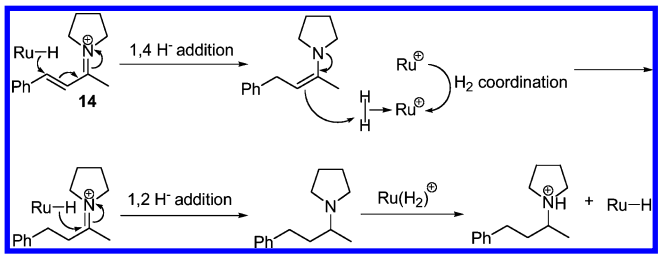
(33) The catalytic TOF values were measured at a temperature (298 K) two degrees below that (300 K) at which the rate constants for hydride transfer were determined, and thus the agreement between the rates of the catalytic and stoichiometric reactions is even closer than the numbers in Table 2 suggest.

(34) The pK_a of trialkylamines lies between 10 and 11: Smith, M. B., March, J. Acids and Bases. In *March's Advanced Organic Chemistry*; 5th ed.; Wiley & Sons: New York, 2001; p 330.

(35) Performing the same catalytic reaction with 20 mol % catalyst loading gave upfield vinyl protons at δ 3.47, 3.02, and 1.42, which were similar to those reported for other olefin complexes of CpRu cations.[36]

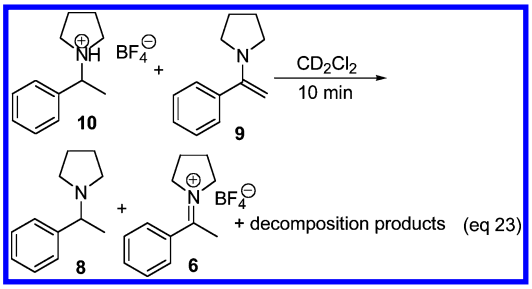
(36) (a) Davies, S. G.; Scott, F. *J. Organomet. Chem.* **1980**, *188*, C41−C42. (b) Consiglio, G.; Fregosin, P.; Morandini, F. *J. Organomet. Chem.* **1986**, *308*, 345−351. (c) Consiglio, G.; Morandini, F. *J. Organomet. Chem.* **1986**, *310*, C66−C68. (d) Ohkita, K.; Kurosama, H.; Hirao, T.; Ikeda, I. *J. Organomet. Chem.* **1994**, *470*, 189−190. (e) Ohkita, K.; Asano, H.; Kurosama, H.; Hirao, T.; Miyaji, Y.; Ikeda, I. *Can. J. Chem.* **1996**, *74*, 1936−1944.

Scheme 2

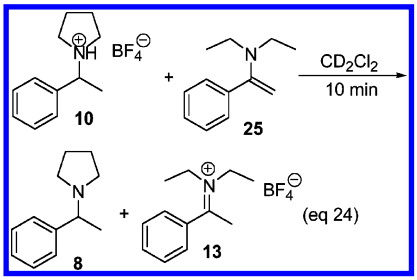


Catalytic Hydrogenation of an Enamine. The results in eqs 12 and 18, and the interpretation in Scheme 2 of the result in entry 4 of Table 3, suggested that ionic hydrogenation of an enamine to a neutral amine might be feasible with a dihydrogen complex as the catalyst. The potential catalytic cycle is shown in Scheme 3.

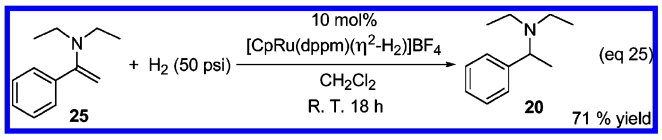
To carry out Scheme 3, the enamine must compete with the product amine for a proton from the dihydrogen complex. Known equilibrium basicities are consistent with this requirement: most enamines are more basic than their saturated counterparts,[37] although there are exceptions.[38] Indeed, the enamine **9** proved to deprotonate the ammonium cation **10**, although side reactions occurred as well (which prevented the successful catalytic hydrogenation of **9**).



Enamine **25**, on the other hand, cleanly deprotonated **10** in eq 24.



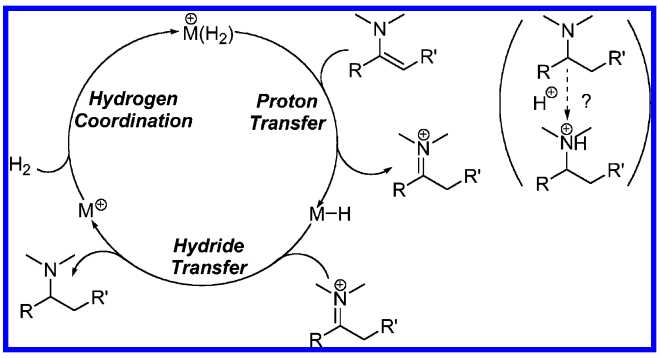
As we expected from this result, it proved possible to carry out the ionic hydrogenation of **25**, in 71% yield (eq 25), with 10 mol % [CpRu(dppm)(η^2-H_2)]BF_4 as catalyst.



Summary and Conclusions

The ionic hydrogenation of an iminium cation (Scheme 1) involves (1) the coordination of H_2, followed by (2) the transfer of H^+ to the amine product. Both processes are sufficiently fast that their rate has little impact on the turnover frequency. The rate of the slow step in the catalytic cycle, H^- transfer, can be measured directly by observing the rate at which the hydride complex reacts with the iminium cation in the presence of a coordinating solvent instead of H_2—a "stoichiometric" reaction.

Scheme 3



These stoichiometric H^- transfers become faster as the chelate ring in CpRu(P−P)H becomes smaller or as more electron-donating substituents are introduced onto the phosphine. However, with sufficient electron density the hydride ligand becomes more basic as well as more hydridic and is able to deprotonate the substrate. As the deprotonation of an iminium cation to an enamine occurs at a pK_a of around 11, an Ru(H_2) cation with a pK_a between 10 and 11 would be ideal. (CpRu(dmpe)H, with a pK_a of 9.8, is the best we have found to date.) The ionic hydrogenation of enamines is possible, but complicated by the competition between the enamine and the amine product for the deprotonation of the Ru(H_2) cation.

Ionic hydrogenation shows the expected preference for the hydrogenation of C=N over the hydrogenation of C=C, although a terminal C=C can block the coordination of another H_2 after H^- transfer. With an α,β-unsaturated iminium cation the initial H^- transfer is 1,4, giving an enamine that is then protonated and hydrogenated to an ammonium cation.

Experimental Section

General Procedures. All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Et_2O and CH_2Cl_2 were deoxygenated and dried over two successive activated alumina columns under argon. Benzene and THF-d_8 were distilled from Na and benzophenone under a nitrogen atmosphere. CD_2Cl_2 was dried over CaH_2, degassed by three freeze−pump−thaw cycles, and then purified by vacuum transfer at room temperature. CpRu(dppe)H (**5a**),[39] CpRu(dppe)D,[36a] Cp*Ru(dppe)H (**5c**),[40] CpRu(dppm)H (**5d**),[39] CpRu(dpbz)H (**5e**),[21] (Ind)Ru(dppm)H (**5g**),[41] (Ind)Ru(dppe)H (**5h**),[41] CpRu(dmpe)H (**5i**),[20] CpRu(PPh_3)$_2$H (**5j**),[42] [Cp*Ru(dppe)(H_2)]BF_4,[25] Cp′Ru(dppe)Cl,[43] Cp*Ru(dmpe)Cl,[44] 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate (**6**),[45] 1-isopropylidenepyrrolidinium tetrafluoroborate (**12**),[45] 1-(α-

(37) (a) Adams, R.; Mahan, J. E. *J. Am. Chem. Soc.* **1942**, *64*, 2588−2593. (b) Hinman, R. L. *Tetrahedron* **1968**, *24*, 185−190.
(38) Stamhuis, E. J.; Maas, W.; Wynberg, H. *J. Org. Chem.* **1965**, *30*, 2160−2163.
(39) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747−1755.
(40) Lee, D.-H. *J. Korean Chem. Soc.* **1992**, *36*, 248−254.
(41) Bassetti, M.; Casellato, P.; Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Martín-Vaca, B. *Organometallics* **1997**, *16*, 5470−5477.
(42) Baird, G. J.; Davies, S. G.; Moon, S. D.; Simpson, S. J.; Jones, R. H. *J. Chem. Soc., Dalton Trans.* **1985**, 1479−1486.
(43) Alonso, A. G.; Reventós, L. B. *J. Organomet. Chem.* **1988**, *338*, 249−254.
(44) Luo, L.; Zhu, N.; Zhu, N.-J.; Stevens, E. D.; Nolan, S. P.; Fagan, P. J. *Organometallics* **1994**, *13*, 669−675.
(45) Leonard, N. J.; Paukstelis, J. V. *J. Org. Chem.* **1963**, *28*, 3021−3024.

Table 4. Summary of Crystallographic Data

	5b	5c
empirical formula	$C_{32}H_{32}P_2Ru$	$C_{36}H_{40}P_2Ru$
fw	579.59	635.69
temp, K	243(2)	243(2)
cryst syst	orthorhombic	monoclinic
space group	$Pna2_1$	$P2_1/c$
a, Å	17.6272(10)	15.7131(12)
b, Å	11.2434(6)	15.8159(12)
c, Å	13.4570(7)	12.8624(9)
α, deg	90	90
β, deg	90	101.421(2)
γ, deg	90	90
V, Å^3	2667.0(2)	3133.2(4)
Z	4	4
d_{calcd}, g/cm^3	1.443	1.348
λ (Mo Kα), Å	0.71073	0.71073
μ, mm^{-1}	0.727	0.625
No. of data collected	16 969	21 053
No. of unique data	5174	7139
No. of data/restraints/params	5174/1/322	7139/0/357
goodness-of-fit on F^2	1.053	1.036
R1, wR2 ($I > 2\sigma(I)$)	0.0217, 0.0555	0.0300, 0.0709
R1, wR2 (all data)	0.0232, 0.0563	0.0499, 0.0759

methylcinnamylidene)pyrrolidinium tetrafluoroborate (**14**),[46] 1-(1-pyrrolidinyl)-1-phenylethene (**9**),[47] α-(diethylamino)styrene (**25**),[47] and *N*-(1-phenylethyl)pyrrolidine (**8**)[48] were prepared as described in the literature. Experimental details on eqs 6 and 7 were reported in the Supporting Information of ref 5.

Cp′Ru(dppe)H (5b). Under a nitrogen atmosphere, sodium (142 mg, 6.17 mmol) was added to an orange suspension of Cp′Ru(dppe)Cl (1.12 g, 1.82 mmol) in 40 mL of CH_3OH. Boiling the resulting mixture for 3 h gave a yellow suspension, from which (after cooling to room temperature) the supernatant liquid was removed by cannula. The solid was washed with CH_3OH (3 × 20 mL) and then dried under vacuum, leaving 580 mg (55% yield) of a yellow powder. ^{1}H NMR (400 MHz, C_6D_6): δ −13.25 (t, Ru*H*, J_{P-H} = 34.4 Hz, 1H), 1.72 (s, Cp*Me*, 3H), 1.86−1.92 (m, PCH_2CH_2P, 2H), 2.07−2.12 (m, PCH_2CH_2P, 2H), 4.65−4.66 (m, *Cp*Me, 2H), 4.73−4.74 (m, *Cp*Me, 2H), 6.99−7.18 (m, *Ar*, 12H), 7.48−7.53 (m, *Ar*, 4H), 7.89−7.93 (m, *Ar*, 4H). ^{31}P {^{1}H} NMR (162 MHz, C_6D_6): δ 94.10 (s). Anal. Calcd for $C_{32}H_{32}P_2Ru$: C, 66.31; H, 5.56. Found: C, 66.20; H, 5.64.

X-ray Structure Determinations of 5b and 5c. Crystals were grown by letting a layer of CH_3OH slowly diffuse into a saturated benzene solution of the hydrides. Data collection and refinement parameters are summarized in Table 4. Data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques and refined by full-matrix least-squares procedures using SHELXTL. Hydrogen atoms on carbon were included in calculated positions.

Cp*Ru(dmpe)H (5f). Under a nitrogen atmosphere, sodium (110 mg, 4.78 mmol) was added to an orange suspension of Cp*Ru(dmpe)Cl (600 mg, 1.42 mmol) in 40 mL of CH_3OH. The mixture was refluxed for 3 h to give a bright yellow solution. The solvent was removed under vacuum, and the residue was extracted with benzene (2 × 15 mL) to give a yellow solution. The solvent was removed again under vacuum to afford a yellow solid, which gave the pure product (365 mg, 66% yield) after sublimation (100 °C at 0.01 mmHg). ^{1}H NMR (300 MHz, C_6D_6): δ −14.37 (t, Ru*H*, J_{P-H} = 37.3 Hz, 1H), 1.08−1.15 (m, P*Me*, 6H), 1.12−1.24 (m, PCH_2CH_2P, 4H), 1.28−1.32 (m, P*Me*, 6H), 2.03 (s, C_5*Me*$_5$, 15H). ^{31}P {^{1}H} NMR (121 MHz, C_6D_6): δ 52.17 (s). Anal. Calcd for $C_{16}H_{32}P_2Ru$: C, 49.60; H, 8.32. Found: C, 49.77; H, 8.33.

[Cp*Ru(dmpe)(H)$_2$]BF$_4$. To a solution of Cp*Ru(dmpe)H (77.4 mg, 0.20 mmol) in 20 mL of Et_2O was added the solution of HBF_4·OMe_2 (100 μL, 0.72 mmol) in 20 mL of Et_2O. A white precipitate was formed immediately, and the resulting suspension was stirred for 30 min. The solid was collected by filtration, washed with Et_2O, and dried under vacuum to give a white powder (75 mg, 79% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −9.97 (t, Ru(*H*)$_2$, J_{P-H} = 32.1 Hz, 2H), 1.57−1.60 (m, P*Me*, 12H), 1.71−1.74 (m, PCH_2CH_2P, 4H), 2.04 (s, C_5*Me*$_5$, 15H). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): δ 41.84 (s). [Cp*Ru(dmpe)(H)$_2$]BF$_4$/[Cp*Ru(dmpe)(η^2-H$_2$)]BF$_4$ > 50:1. Anal. Calcd for $C_{16}H_{33}P_2RuBF_4$: C, 40.44; H, 7.00. Found: C, 40.75; H, 7.09.

[CpRu(dpbz)H$_2$]BF$_4$ was prepared in 73% yield by a procedure similar to that used for [Cp*Ru(dmpe)(H)$_2$]BF$_4$. [CpRu(dpbz)(H)$_2$]BF$_4$: ^{1}H NMR (400 MHz, CD_2Cl_2): δ −7.96 (t, Ru(*H*)$_2$, J_{P-H} = 28.4 Hz, 2H), 5.44 (s, *Cp*, 5H), 7.16−7.71 (m, *Ar*). ^{31}P NMR (162 MHz, CD_2Cl_2): 67.2. [CpRu(dpbz)(η^2-H$_2$)]BF$_4$: ^{1}H NMR (400 MHz, CD_2Cl_2): δ −8.90 (bs, Ru(η^2-*H*$_2$), 2H), 4.95 (s, *Cp*, 5H), 7.16−7.71 (m, *Ar*). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): 78.7. [CpRu(dpbz)(H)$_2$]BF$_4$/[CpRu(dpbz)(η^2-H$_2$)]BF$_4$ = 1:1.8. Anal. Calcd for $C_{35}H_{31}P_2RuBF_4$: C, 59.93; H, 4.45. Found: C, 58.78; H, 4.33 (the carbon analysis remained low in repeated analyses).

[Cp′Ru(dppe)H$_2$]BF$_4$ was prepared in 74% yield by a procedure similar to that used for [Cp*Ru(dmpe)(H)$_2$]BF$_4$. [Cp′Ru(dppe)(H)$_2$]BF$_4$: ^{1}H NMR (400 MHz, CD_2Cl_2): δ −8.60 (t, Ru(*H*)$_2$, J_{P-H} = 28.1 Hz, 2H), 1.60 (s, C*H*$_3$, 3H), 2.45−2,50 (m, PCH_2CH_2P, 4H), 5.36 (bs, *Cp*, 2H), 5.40 (bs, *Cp*, 2H), 7.40−7.55 (m, *Ar*). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): 71.0. [Cp′Ru(dppe)(η^2-H$_2$)]BF$_4$: ^{1}H NMR (400 MHz, CD_2Cl_2): δ −8.84 (bs, Ru(η^2-*H*$_2$), 2H), 1.87 (s, C*H*$_3$, 3H), 2.34−2.84 (m, PCH_2CH_2P, 4H), 4.50 (bs, *Cp*, 2H), 4.95 (bs, *Cp*, 2H), 7.28−7.69 (m, *Ar*). ^{31}P {^{1}H} NMR (162 MHz, CD_2Cl_2): 81.0. [Cp′Ru(dppe)(H)$_2$]BF$_4$/[Cp′Ru(dppe)(η^2-H$_2$)]BF$_4$ = 3.9:1. Anal. Calcd for $C_{32}H_{33}P_2RuBF_4$: C, 57.59; H, 4.98. Found: C, 57.45; H, 4.92.

Determination of Equilibrium Constants for Exchange of H$^+$ between a Ruthenium Dihydrogen (and/or Dihydride) Cation and a Neutral Hydride Complex. The dihydrogen (and/or dihydride) cation and the neutral hydride complex were dissolved in CD_2Cl_2 or THF-d_8 under N_2. The resulting solution was transferred into a J-Young NMR tube, and the approach to equilibrium was monitored by ^{1}H NMR of the hydride signals. (A delay of 5 s was inserted between the end of each data acquisition and the next pulse; the observed ratios did not change appreciably with a 10-s delay time.) The equilibrium was established within 1 h for unhindered hydrides, in several hours for more crowded hydrides.

***N*-(1-Cyclohexylethylidene)pyrrolidinium Tetrafluoroborate (11).** Pyrrolidinium tetrafluoroborate (3.18 g, 20 mmol), acetylcyclohexane (5.04 g, 40 mmol), and two or three drops of morpholine were added to 50 mL of benzene, and the resulting mixture was refluxed under nitrogen as the water formed was collected in a Dean−Stark trap. When the volume of the water reached 0.5 mL, the reaction mixture was cooled to room temperature and the solvent was removed under vacuum. The addition of 20 mL of Et_2O caused the residue to solidify; the solid was collected by filtration, washed with Et_2O, and recystallized in CH_2Cl_2/Et_2O to give colorless needles (4.18 g, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21−1.43 (m, Cy, 5H), 1.74−1.94 (m, Cy, 5H), 2.17−2.20 (m, NCH$_2$CH_2, 4H), 2.35 (s, *CH*$_3$, 3H), 2.70−2.77 (m, N=CC*H*, 1H), 3.96−3.98 (m, NCH_2CH$_2$, 4H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 20.09, 24.04, 24.49, 25.18, 25.42, 28.11, 46.79, 53.55, 54.94, 190.31. IR (in fluorolube): 1665 cm^{-1} (C=N). Anal. Calcd for $C_{12}H_{22}BF_4N$: C, 53.96; H, 8.30; N, 5.24. Found: C, 53.87; H, 8.55; N, 5.27.

***N*-(1-Methylpent-4-enylidene)pyrrolidinium Tetrafluoroborate (15)** was prepared by a known procedure[46] in 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$): 2.10−2.14 (m, NCH$_2$CH_2, 4H), 2.37 (s, N=CC*H*$_3$, 3H), 2.34−2.43 (m, N=CCH$_2$CH_2, 2H), 2.70−2.74 (m, N=CCH_2CH$_2$, 2H), 3.87−3.92 (m, NCH_2CH$_2$, 4H), 5.02−5.10 (m, C=CH_2, 2H), 5.72−5.82 (m, CH$_2$=C*H*, 1H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 23.03, 24.19, 24.45, 28.60, 37.39, 53.87, 54.52, 116.93, 134.74, 186.87.

(46) Yamaguchi, M.; Shiraishi, T.; Hirama, M. *J. Org. Chem.* **1996**, *61*, 3520−3530.
(47) Lee, N. E.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 5985−5986.
(48) Shapiro, S. L.; Soloway, H.; Freedman, L. *J. Am. Chem. Soc.* **1958**, *80*, 6060−6064.

IR (in fluorolube): 1676 cm^{-1} (C═N), 1643 cm^{-1} (C═C). Anal. Calcd for $C_{10}H_{18}BF_4N$: C, 50.24; H, 7.59; N, 5.86. Found: C, 50.31; H, 7.52; N, 5.94.

***N*-(1,5-Dimethylhex-4-enylidene)pyrrolidinium Tetrafluoroborate (16)** was prepared in 60% yield by a procedure similar to that used for *N*-(1-cyclohexylethylidene)pyrrolidinium tetrafluoroborate. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.61 (s, C═CCH_3, 3H), 1.68 (s, C═CCH_3, 3H), 2.15−2.20 (m, NCH$_2$CH_2, 4H), 2.33−2.41 (m, N═CCH$_2$CH_2, 2H), 2.43 (s, N═CCH_3, 3H), 2.68−2.73 (m, N═CCH_2CH$_2$, 2H), 3.91−3.97 (m, NCH_2CH$_2$, 4H), 5.04−5.09 (m, C═CH, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ 17.69, 23.04, 23.49, 24.19, 24.46, 25.58, 38.33, 53.87, 54.56, 120.52, 135.19, 187.81. IR (in fluorolube): 1680 cm^{-1} (C═N). Anal. Calcd for $C_{12}H_{22}BF_4N$: C, 53.96; H, 8.30; N, 5.24. Found: C, 53.67; H, 8.27; N, 5.35.

We were unable to prepare ***N*-(1-phenylethylidene)diethylammonium tetrafluoroborate (13)** by the condensation of acetophenone and diethylammonium tetrafluoroborate, under azeotropic distillation conditions or with $TiCl_4$. We were, however, able to prepare it by protonation of the corresponding enamine. In a Schlenk flask, HBF_4·OMe_2 (2.68 mL, 22 mmol) was added dropwise to a cooled (−10 °C) solution of α-(diethylamino)styrene (3.82 g, 22 mmol) in 40 mL of Et_2O. As the mixture warmed to room temperature, an oily product settled to the bottom of the flask. The top (ether) layer was removed by cannula, while the product was washed several times with ether and dried under vacuum to give a pale yellow oil (4.79 g, 84% yield). At −30 °C, the oil solidified. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (t, CH$_2$CH_3, J_{H-H} = 7.3 Hz, 3 H), 1.51 (t, CH$_2$CH_3, J_{H-H} = 7.4 Hz, 3 H), 2.78 (s, N═CCH_3, 3H), 3.74 (q, CH_2CH$_3$, J_{H-H} = 7.3 Hz, 2H), 4.09 (q, CH_2CH$_3$, J_{H-H} = 7.4 Hz, 2H), 7.45−7.48 (m, *Ar*, 5H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ 12.27, 12.94, 26.11, 49.93, 52.04, 125.38, 129.45, 131.63, 134.34, 187.85. IR (in fluorolube): 1651 cm^{-1} (C═N). Anal. Calcd for $C_{12}H_{18}BF_4N$: C, 54.78; H, 6.90; N, 5.32. Found: C, 52.92; H, 6.93; N, 5.35. While a satisfactory carbon analysis was not obtained even after repeated purification, ^{1}H NMR showed >99% purity. HRMS-FAB (*m*/*z*): (aggregate $[2A + B]^+$ for an ionic compound A^+B^-) calcd for $C_{24}H_{36}N_2BF_4$ 439.2912 (for ^{11}B); found: 439.2903.

Catalysis of the Hydrogenation of Iminium Cations by Ruthenium Hydrides. Determination of the Initial Turnover Frequency. A solid iminium cation (2 mmol) and ruthenium hydride (0.02 mmol) were added to a Fisher−Porter bottle under a nitrogen atmosphere. The bottle was flushed several times with hydrogen gas and placed in a 25 °C water bath. Then 10 mL of CH_2Cl_2 (or CH_3OH) was added by syringe under a flow of hydrogen, and the resulting solution was stirred under 50 psi of hydrogen. At appropriate intervals an aliquot was removed by syringe. The solvent was removed from the aliquot, and the residue was dissolved in $CDCl_3$ and its ^{1}H NMR was recorded. The conversion was calculated from the relative integrals of the starting material and the hydrogenation product. The initial TOF was determined from data collected when less than 10% of the iminium cation had been hydrogenated.

Isolation of Amines from the Catalytic Hydrogenation of Iminium Cations (except 12). When the reaction was complete, the solvent was removed under vacuum. The residue was treated with 20 mL of water, then washed by ether (2 × 20 mL). A saturated aq KOH solution (10 mL) was added, and the amine was removed by ether extraction (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, then the ether was removed to afford a light yellow oil. The results are summarized in Table 3. The ^{1}H NMR spectra of the products **18**,[49] **20**,[50] and **24**[51] were consistent with those reported in the literature. Amines **21**[52] and **23**[53] were prepared previously; however, no NMR data was reported. NMR data of **21**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.18 (d, CH_3, J_{H-H} = 6.4 Hz, 3 H), 1.63−1.76 (m, NCHCH_2, 1H), 1.78−1.85 (m, NCH$_2$CH_2, 4 H), 1.90−1.99 (m, NCHCH_2, 1H), 2.38−2.45 (m, CHCH$_3$, 1H), 2.51−2.79 (m, PhCH_2, 2H), 2.55−2.72 (m, NCH_2CH$_2$, 4H), 7.14−7.30 (m, *Ar*, 5H). NMR data of **23**: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.08 (d, NCHCH_3, J_{H-H} = 6.4 Hz, 3 H), 1.31−1.39 (m, NCHCH_2, 1H), 1.53−1.62 (m, NCHCH_2, 1H), 1.61 (s, CH═CCH_3, 3H), 1.69 (s, CH═CCH_3, 3H), 1.74−1.79 (m, NCH$_2$CH_2, 4 H), 1.89−2.11 (m, C═CHCH_2, 2H), 2.31−2.38 (m, CHCH$_3$, 1H), 2.53−2.57 (m, NCH_2CH$_2$, 4H), 5.05−5.14 (m, C═CH, 1H).

1-Isopropylpyrrolidinium Tetrafluoroborate (19) from 12. When the hydrogenation of 1-isopropylidenepyrrolidinium tetrafluoroborate (**12**) was complete, the reaction mixture was transferred to a Schlenk flask and the solvent was removed under vacuum. The residue was washed with Et_2O several times and dried under vacuum to afford a white powder (84% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.41 (d, CH_3, J_{H-H} = 6.5 Hz, 6 H), 2.10−2.16 (m, NCH$_2$CH_2, 4 H), 3.03−3.09 (m, NCH_2CH$_2$, 2H), 3.37−3.48 (m, NCH, 1H), 3.67−3.72 (m, NCH_2-CH$_2$, 2H), 7.40 (bs, NH, 1H). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ 18.90, 23.03, 52.50, 58.13. Anal. Calcd for $C_7H_{16}BF_4N$: C, 41.83; H, 8.02; N, 6.97. Found: C, 41.94; H, 7.86; N, 6.85.

1-(1-Phenylethyl)pyrrolidinium Tetrafluoroborate (10). A solution of 1-(1-phenylethyl)pyrrolidine (**8**) (200 mg, 1.14 mmol) in 30 mL of Et_2O was added dropwise to the diluted HBF_4·OMe_2 (173 μL, 1.25 mmol) in 10 mL of Et_2O. A white precipitate formed immediately. The suspension was stirred for 15 min, removed by filtration, washed with Et_2O several times, and dried under vacuum to afford a white powder (278 mg, 93% yield). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.78 (d, CH_3, J_{H-H} = 6.84 Hz, 3H), 2.00−2.08 (m, NCH$_2$CH_2, 2H), 2.12−2.23 (m, NCH$_2$CH_2, 2H), 2.84−2.91 (m, NCH_2CH$_2$, 1H), 3.10−3.19 (m, NCH_2CH$_2$, 2H), 3.91−3.96 (m, CHCH$_3$, 1H), 4.16−4.21 (m, NCH_2-CH$_2$, 1H), 7.47−7.49 (m, *Ar*, 5H), 7.83 (bs, NH, 1H). ^{13}C {^{1}H} NMR (75 MHz, CD_2Cl_2): δ 19.47, 23.06, 23.40, 54.39, 67.29, 127.88, 129.96, 130.35, 136.10. Anal. Calcd for $C_{12}H_{18}BF_4N$: C, 54.78; H, 6.90; N, 5.32. Found: C, 54.56; H, 6.90; N, 5.32.

Catalytic Hydrogenation of Enamines. [CpRu(dppm)(η^2-H$_2$)]BF_4 (0.02 or 0.10 mmol) was added to a Fisher−Porter bottle under a nitrogen atmosphere. The bottle was flushed several times with hydrogen gas and placed in a 25 °C water bath. A deoxygenated solution of the enamine (1.0 mmol) in 10 mL of CH_2Cl_2 was added by syringe under a flow of hydrogen, and the resulting solution was stirred under 50 psi of hydrogen. When ^{1}H NMR showed that the reaction was complete (as in the formation of **20** from **25**), excess aq HCl (1 M) was added to acidify the mixture; the product was isolated as that of hydrogenation of iminium cations.

Acknowledgment. This research was supported by NSF Grants CHE-0211310 and CHE-0451385. We thank Prof. G. Parkin for assistance with the X-ray structure determinations.

Supporting Information Available: Details of the crystallographic study (PDF and CIF), kinetic data, plots of these data, ^{2}H NMR spectra for the reaction between iminium cation **6** and CpRu(dppe)D, a derivation of the equations used in determining the EIE, and a complete citation for ref 49. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0506861

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