Protonated Aminocyclopentadienyl Ruthenium Hydride Reduction of Benzaldehyde and the Conversion of the Resulting Ruthenium Triflate to a Ruthenium Hydride with H_2 and Base

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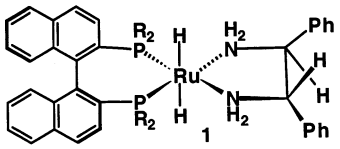
Reaction of *N*-phenyl-2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienimine (**6**) with Ru_3CO_{12} formed two isomers of {[2,5-Me_2-3,4-Ph_2(η^5-C_4CNHPh)]Ru(CO)(μ-CO)}$_2$ (**8-trans** and **8-cis**). Photolysis of **8** under a H_2 atmosphere led to the formation of the aminocyclopentadienyl ruthenium hydride [2,5-Me_2-3,4-Ph_2(η^5-C_4CNHPh)]Ru(CO)$_2$H (**9-H**). **9-H** reduced benzaldehyde slowly at 75 °C to give benzyl alcohol and **8**. Protonation of **9-H** with triflic acid produced {[2,5-Me_2-3,4-Ph_2(η^5-C_4CNH_2Ph)]Ru(CO)$_2$H}OTf (**11-H**), which reacted rapidly with benzaldehyde at −80 °C to give benzyl alcohol and [2,5-Me_2-3,4-Ph_2(η^5-C_4CNHPh)]Ru(CO)$_2$OTf (**9-OTf**). Reaction of **9-OTf** with H_2 and base led to the re-formation of **9-H**. These reactions provide the transformations required for a catalytic cycle for hydrogenation of aldehydes.

Introduction

Homogeneous catalytic reduction of polar functional groups mediated by transition-metal complexes has emerged as an alternative to stoichiometric reduction by metal hydrides such as $LiAlH_4$ and $NaBH_4$.[1] Interest in this area has been spurred by development of highly efficient catalysts for the selective hydrogenation of ketones and aldehydes.[2] For example, Noyori's chiral catalyst [$RuCl_2$\{(*S*)-tolbinap\}\{(*S*,*S*)-1,2-diphenylethylenediamine\}] (**1**) hydrogenates ketones with high levels of reactivity, chemoselectivity, and enantioselectivity.[3]



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Several years ago, Shvo discovered that the diruthenium complex **2** (R = Ph) was an efficient ketone hydrogenation catalyst at 145 °C.[4] The active reducing agent in this catalytic system is the hydroxycyclopentadienyl ruthenium hydride **3-H** (R = Ph). The presence of an electronically coupled acidic OH group and a ruthenium hydride in the same molecule appears to be the key to the high reactivity of **3-H**.[5] Bäckvall[6] and Park[7] have used the Shvo catalyst **2** to interconvert enantiomeric alcohols via reversible dehydrogenation in tandem with enzymatic conversion of one enantiomer to a single enantiomer of an ester. This tandem process accomplishes the dynamic kinetic resolution of secondary alcohols.

Recently, we investigated the mechanism of the reaction of **4-H** (R = Tol) with benzaldehyde in detail[8] and concluded that carbonyl reduction occurs outside the coordination sphere of the metal (Scheme 1). Our observation of kinetic deuterium isotope effects for both OD and RuD of **4-H** requires a mechanism involving simultaneous transfer of H^+ from OH and H^- from RuH to the aldehyde substrate. Noyori has proposed a similar mechanism involving simultaneous transfer of an acidic RuN−H and a hydridic Ru−H for reduction by **1** and related compounds.[9,10]

A striking feature of the Shvo system is that the reduction of benzaldehyde by **4-H** is rapid at low temperature (−40 to −10 °C) but catalysis with the diruthenium complex requires elevated temperature (80−150 °C). The dienone dicarbonyl intermediate generated by hydrogen transfer is trapped by ruthenium hydride **4-H** to produce the kinetically stable diruthenium complex **5** (R = Tol). The slow step involves reaction of the diruthenium complex with hydrogen.[4] In an effort to develop a more reactive catalyst, we have sought ways of blocking the formation of diruthenium complexes analogous to **5**.

(1) Fehring, V.; Selke, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1827 and references therein.
(2) Ohkuma, T.; Noyori, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 40 and references therein.
(3) Ohkuma, T.; Ooka, H.; Hashiguchi, S.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1995**, *117*, 2675.
(4) Blum, Y.; Czarkie, D.; Rahamim, Y.; Shvo, Y. *Organometallics* **1985**, *4*, 1459.
(5) For our earlier attempts to develop heterobimetallic systems capable of delivering an acidic and a hydridic hydrogen, see: (a) Casey, C. P.; Wang, Y.; Tanke, R. S.; Hazin, P. N.; Rutter, E. W., Jr. *New J. Chem.* **1994**, *18*, 43. (b) Casey, C. P. *J. Organomet. Chem.* **1990**, *400*, 205.
(6) (a) Bäckvall, J. E.; Pamies, O. *J. Org. Chem.* **2002**, *67*, 1261. (b) Bäckvall, J. E.; Huerta, F. F.; Minidis, A. B. E. *Chem. Soc. Rev.* **2001**, *30*, 321 and references therein.
(7) (a) Kim, M. J.; Choi, Y. K.; Choi, M. Y.; Kim, M. J.; Park, J. *J. Org. Chem.* **2001**, *66*, 4736. (b) Jung, H. M.; Koh, J. H.; Kim, M. J.; Park, J. *Org. Lett.* **2000**, *2*, 2487.
(8) (a) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090. (b) Casey, C. P.; Singer, S. W.; Powell, D. R. *Can. J. Chem.* **2001**, *79*, 1002.
(9) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97 and references therein.
(10) Noyori's mechanism is consistent with DFT calculations: Alonso, D. A.; Brandt, P.; Nordin, S. J. M.; Andersson, P. G. *J. Am. Chem. Soc.* **1999**, *121*, 9580.

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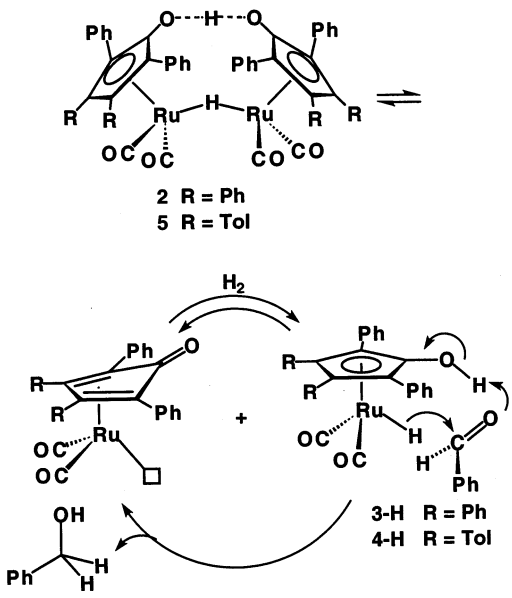
Scheme 1



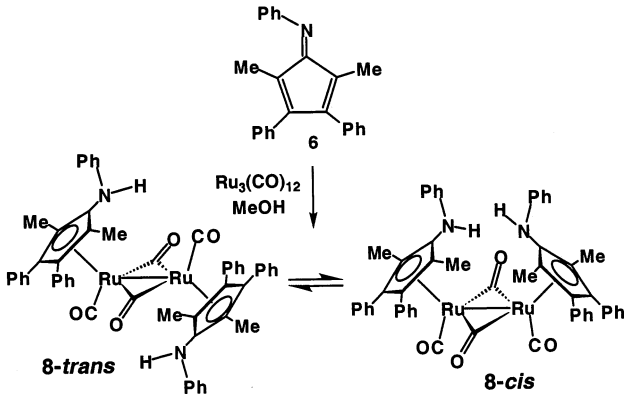
Here we present an approach to preventing formation of diruthenium complexes similar to **5** by introducing sterically large −NPh groups on the Cp ring in place of the less crowded −OH of **4-H**. We anticipated that the formation of a bridging PhN- - -H- - -NPh unit would be greatly disfavored by steric interactions and by weaker hydrogen bonding between the nitrogen centers compared to that between oxygen centers. An additional advantage of the −NHR catalysts is added flexibility in catalyst design; changing the R group on the amine will allow drastic alteration of the electronic and steric features of the catalyst.

We have found that the −NHPh unit does prevent formation of bridged complexes similar to **5** but that the lower acidity of the CpNHPh unit reduces the activity of the mononuclear hydride. A more active reducing agent was obtained by protonating the nitrogen center to give a $CpNH_2Ph^+$ complex which reduces benzaldehyde rapidly at low temperature. We have also found means of regenerating the ruthenium hydride under mild conditions and are poised to develop a new catalytic system.

Results

***N*-Phenyl-2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienimine (6).** Since initial attempts to synthesize *N*-phenyltetraarylcyclopenta-2,4-dienimine ruthenium complexes were plagued by problems of low yield and low solubility,[11] we turned to the *N*-phenyl-2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienimine ligand (**6**) at an early stage. To determine whether the replacement of two phenyl groups by two methyl groups greatly affected the reactivity of ruthenium complexes, we measured the relative rates of reduction of benzaldehyde by [2,5-Me_2-3,4-Ph_2(η^5-C_4COH)]Ru$(CO)_2$H (**7-H**) and by [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru$(CO)_2$H (**4-H**) in THF-d_8 at −10 °C. The stoichiometric reduction of benzaldehyde by the methyl-substituted complex **7-H** was 4 times faster than by the aryl-substituted complex **4-H**.[12]

Scheme 2



N-Phenyl-2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienimine (**6**) was synthesized in 70% yield by heating 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone, aniline, and $TiCl_4$ in benzene.[13] In the ^{1}H NMR spectrum of **6**, resonances at δ 1.28 and 2.01 were seen for the methyl groups syn and anti to the *N*-phenyl group of the imine.

{[2,5-Me_2-3,4-Ph_2(η^5-C_4CNHPh)]Ru(CO)(μ-CO)}$_2$ (8). Reaction of **6** and Ru_3CO_{12} in refluxing MeOH for 1 day led to precipitation of **8-trans** as an orange powder in 55% yield (Scheme 2). The structure of **8-trans** was established by X-ray crystallography (Figure 1; crystal data and structure refinement details are given in Table 1).

Spectroscopic studies are consistent with the solid being pure **8-trans**, which dissolves to give solutions of equilibrating mixtures of **8-trans** and **8-cis**. The infrared spectrum of solid **8-trans** as a Nujol mull has only two strong bands at 1946 and 1752 cm^{-1} for its terminal and bridging CO's. However, in CH_2Cl_2 solution, two terminal CO bands at 2021 (s) and 1963 (vs) cm^{-1} and a bridging CO band at 1769 cm^{-1} are seen for a mixture of **8-trans** and **8-cis** isomers. The ^{1}H NMR spectrum in CD_2Cl_2 at −70 °C shows a 5:1 mixture of isomers with $CpCH_3$ resonances at δ 1.78 and 1.87; at −40 °C, these resonances are still sharp but in a 3:1 ratio; at room temperature, a single sharp coalesced resonance is seen at δ 1.87 for a rapidly interconverting mixture of **8-trans** and **8-cis**. The ^{13}C NMR spectrum in CD_2Cl_2 at −70 °C shows a 5:1 mixture of isomers and also reveals an additional dynamic process that interchanges the terminal and bridging CO's of **8-trans**. Sharp resonances are seen for the bridging (δ 256.1) and terminal (δ 200.6) resonances of **8-cis**, while broad ($\omega_{1/2}$ > 100 Hz) resonances are seen for the bridging (δ 258.6) and terminal (δ 200.6) resonances of **8-trans**.

The very rapid interconversion of the bridging and terminal carbonyls of the trans isomer, the somewhat slower interconversion of cis and trans isomers, and the

(11) Park has made an *N*-isopropyltetraarylcyclopenta-2,4-dienimine ruthenium chloride complex by heating $Ru_3(CO)_{12}$ and the corresponding imine in $CHCl_3$: Choi, J. H.; Kim, Y. H.; Nam, S. H.; Shin, S. T.; Kim, M. J.; Park, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 2373.

(12) k_{obs} = 0.50 × 10^{-3} s^{-1} at 0.8 M of benzaldehyde in THF-d_8 at −10 °C for [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru$(CO)_2$H (**4-H**); k_{obs} = 1.9 × 10^{-3} s^{-1} at 0.8 M of benzaldehyde in THF-d_8 at −10 °C for [2,5-Me_2-3,4-Ph_2(η^5-C_4COH)]Ru$(CO)_2$H (**7-H**).

(13) When imine synthesis was attempted by dehydration of 2,5-dimethyl-3,4-diphenylcyclopenta-2,4-dienone and aniline using azeotropic distillation of toluene, only a 25% yield of **6** was obtained after 10 days.

Table 1. Crystal and Structure Refinement Data for 4-Cl, 8-trans, 9-Cl, and 9-OTf

	4-Cl	**8**-trans	**9**-Cl	**9**-OTf
mol formula	$C_{33}H_{25}ClO_3Ru$	$C_{54}H_{44}N_2O_4Ru_2$	$C_{27}H_{22}ClNO_2Ru\cdot 0.5CH_2Cl_2$	$C_{28}H_{22}F_3NO_5RuS$
fw	606.05	987.05	571.44	642.60
color, shape	yellow, prism	orange, prism	yellow, prism	yellow, plate
dimens (mm)	0.46 × 0.32 × 0.24	0.43 × 0.34 × 0.26	0.31 × 0.24 × 0.15	0.38 × 0.28 × 0.08
temp (K)	133(2)	173(2)	173(2)	100(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73
cryst syst	triclinic	rhombohedral	monoclinic	triclinic
space group	$P\bar{1}$	$R\bar{3}$	$P2/n$	$P\bar{1}$
a (Å)	11.1279(3)	30.726(2)	14.2002(6)	12.2553(11)
b (Å)	12.1118(3)	30.726(2)	12.4984(6)	12.5502(11)
c (Å)	12.1881(3)	12.3601(11)	15.4984(7)	17.7033(16)
α (deg)	105.520(2)	90	90	82.203(2)
β (deg)	109.349(2)	90	116.931(1)	74.237(2)
γ (deg)	106.600(2)	120	90	88.393(2)
V (Å^3)	1360.92(6)	10106.0(13)	2450.21(19)	2596.1 (4)
Z	2	9	4	4
ρ_{calcd} (Mg m^{-3})	1.479	1.460	1.549	1.644
abs coeff (mm^{-1})	0.707	0.721	0.883	0.746
F(000)	616	4518	1156	1296
θ range (deg)	2.81−29.15	1.33−26.38	1.63−26.39	1.90−26.39
total no. of data	15 447	11 714	20 429	21 281
no. of unique data	6467 (R(int) = 0.0347)	4495 (R(int) = 0.0424)	5012 (R(int) = 0.0319)	10 497 (R(int) = 0.0537)
abs cor	empirical with SADABS			
max and min transmission	0.746 and 0.633	0.835 and 0.747	0.879 and 0.771	0.943 and 0.765
no. of data/restraints/params	6467/0/343	4495/0/284	5012/0/295	10 497/0/707
GOF	1.028	1.001	1.057	1.026
R indices	R1= 0.0213	R1 = 0.0473	R1 = 0.0307	R1 = 0.0483
	wR2 = 0.0564	wR2 = 0.1031	wR2 = 0.0723	wR2 = 0.1187

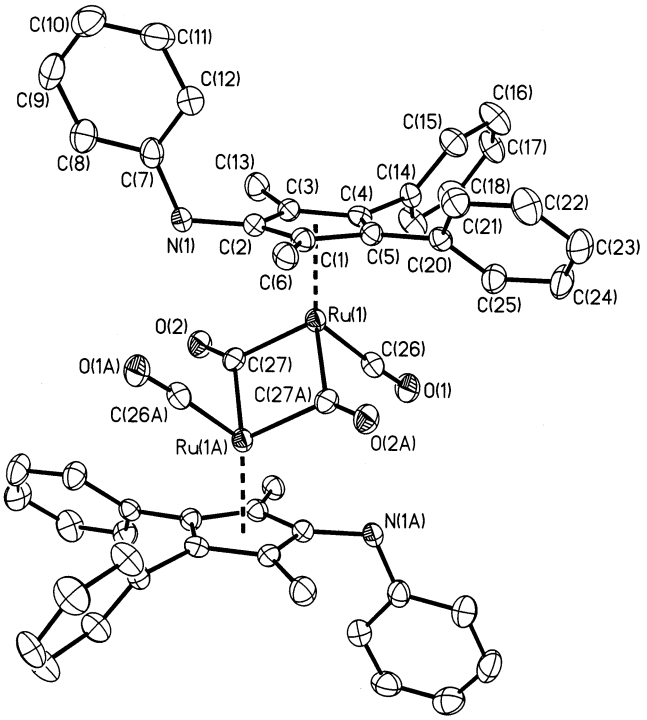
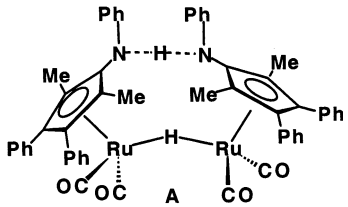


Figure 1. X-ray structure of {[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNHPh)]Ru(CO)(μ-CO)}$_2$ (**8-*trans***). Selected bond lengths (Å) and angles (deg): Ru(1)−C(1), 2.297(4); Ru(1)−C(2), 2.301(4); Ru(1)−C(3), 2.233(4); C(1)−N(1), 1.414(5); Ru(1)−Ru(1A) 2.7499(7); Ru(1)−C(27)−Ru(1A), 84.81(19); C(27)−Ru(1)−C(27A), 95.2(2); C(26)−Ru(1)−C(27), 92.45(18).

observation of only the trans isomer in the solid state has been seen for [CpRu(CO)$_2$]$_2$, [CpFe(CO)$_2$]$_2$, and other related complexes.[14]

Our synthesis of **8** demonstrates the success of our strategy of employing sterically encumbered nitrogen-substituted Cp ruthenium complexes to prevent formation of diruthenium complex **A**, which is analogous to the kinetically sluggish diruthenium complex **2** of Shvo. It should be noted that dimer **8** is an isomer of **A**.



Never observed

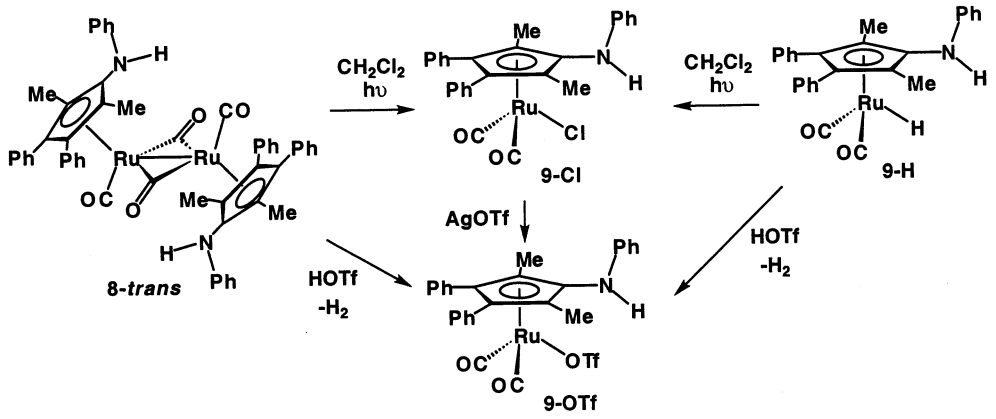
[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNHPh)]Ru(CO)$_2$Cl (9-Cl) from Reaction of 8 with Chlorinated Solvents. Dimer **8** is stable to air as a solid and is stable for days in solution under nitrogen in nonhalogenated solvents. **8** is stable in CH_2Cl_2 and CD_2Cl_2 for days in the dark but reacts with CH_2Cl_2, CD_2Cl_2, or $CHCl_3$ in ambient light over 4−6 h to form the aminocyclopentadienyl ruthenium chloride **9-Cl** (Scheme 3). The structure of **9-Cl** was determined spectroscopically and confirmed by X-ray crystallography (Figure 2; crystal data and structure refinement details are given in Table 1). This chlorination is analogous to the photochemical conversion of [CpRu(CO)$_2$]$_2$ (**10**) in halogenated solvents to CpRu(CO)$_2$X (X = I, Cl, Br).[15]

[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNHPh)]Ru(CO)$_2$OTf (9-OTf) was most readily prepared by reaction of **9-Cl** with 1.2 equiv of AgOTf in CH_2Cl_2 at room temperature (Scheme 3). The conversion from **9-Cl** to **9-OTf** was quantitative by ^{1}H NMR spectroscopy. **9-OTf** was also

(14) (a) Adams, R. D; Cotton, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6589. (b) Cotton, F. A. *Inorg. Chem.* **2002**, *41*, 643 and references therein. (c) Dyke, A. F.; Knox, S. A. R.; Mead, K. A.; Woodward, P. *J. Chem. Soc., Chem. Commun.* **1981**, 861.

(15) Eisenstadt, A.; Tannenbaum, R.; Efraty, A. *J. Organomet. Chem.* **1981,** *221*, 317.

Scheme 3



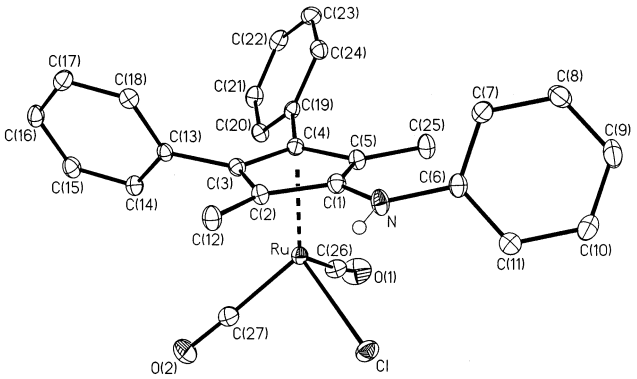


Figure 2. X-ray structure of [2,5-Me_2-3,4-Ph_2(η^5-C_4CNHPh)]-Ru(CO)$_2$Cl (**9-Cl**). Selected bond lengths (Å) and angles (deg): Ru−C(1), 2.375(2); Ru−C(2), 2.250(2); Ru−C(3), 2.182(2); Ru−Cl, 2.4362(6); N−C(1), 1.361(3); C(26)−Ru-(1)−C(27), 92.75(11); C(26)−Ru(1)−Cl, 92.56(7).

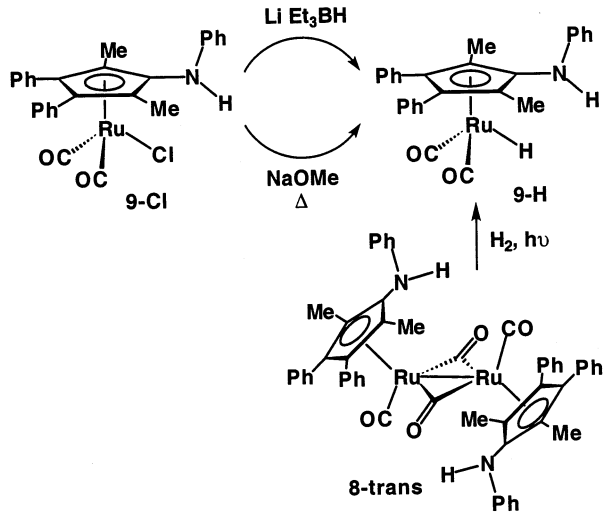
prepared by addition of 2.1 equiv of triflic acid to the dimer **8** in CH_2Cl_2 at room temperature. **9-OTf** was characterized by spectroscopy and by X-ray crystallography (see the Supporting Information). Two equal-intensity IR bands were seen at 2043 and 1994 cm^{-1}. The ^{13}C NMR spectrum had a resonance for CO at δ 198.4.

[2,5-Me_2-3,4-Ph_2(η^5-C_4CNHPh)]Ru(CO)$_2$H (9-H) is an analogue of the hydroxycyclopentadienyl ruthenium hydride **3-H**, the active species in the catalytic reduction of aldehydes to alcohols with the Shvo catalyst. It was crucial to prepare **9-H** and to determine whether substitution of −NHPh for −OH still allowed ligand-assisted hydride transfer. The critical **9-H** complex was synthesized by three different routes (Scheme 4).

UV photolysis of the dimer **8** in THF-d_8 under 2 atm of H_2 led to the formation of hydride **9-H**. The photolysis was followed by ^{1}H NMR spectroscopy; a ruthenium hydride resonance grew in at δ −10.12 along with resonances at δ 2.04 ($CpCH_3$) and 7.13 (NH). **9-H** was formed in >95% yield and was used without further purification. Solutions of **9-H** in a variety of solvents were easily prepared by evaporation of THF under high vacuum followed by redissolving in a new solvent. **9-H** was also formed by reaction of **9-Cl** with either lithium triethylborohydride or sodium methoxide.

^{13}C NMR and IR spectroscopy confirmed the structure assignment of **9-H**. In the ^{13}C NMR spectrum of **9-H**, the resonance for the Cp ring carbon (C1) at δ 109.9 is indicative of very little carbon−nitrogen double-bond

Scheme 4



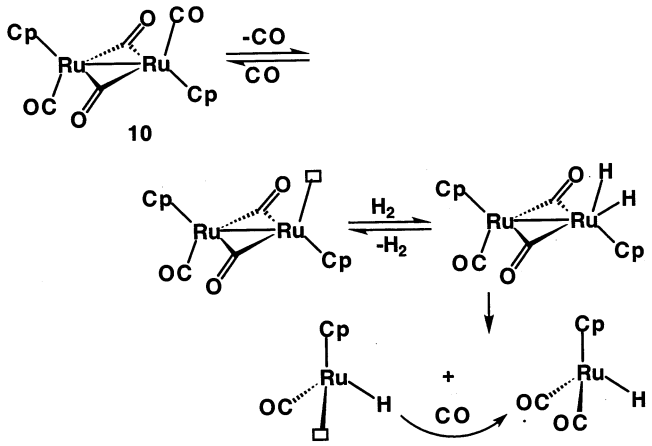
character and η^5-Cp binding. In the IR spectrum, two CO stretching bands of equal intensity appeared at 2016 and 1954 cm^{-1}. These bands occurred at frequencies lower than those of the corresponding chloride **9-Cl** (2043, 1992 cm^{-1}).

In related work, the UV photolysis of [CpRu(CO)$_2$]$_2$ (**10**) under 10−20 atm of H_2 produced CpRu(CO)$_2$H in a reaction strongly inhibited by 2−5 atm of CO.[16] A mechanism involving CO dissociation from **10**, oxidative addition of H_2, and reductive elimination of CpRu-(CO)$_2$H was proposed (Scheme 5). To determine whether the conversion from **8** to **9-H** might occur by a similar mechanism, we studied possible CO inhibition. Side-by-side tubes containing THF-d_8 solutions of **8** under either 1 atm of H_2 or 1 atm of a 1:1 mixture of H_2 and CO were photolyzed. Somewhat *greater* conversion to **9-H** was found in the presence of CO (63% vs 27% after 30 min) but was accompanied by the formation of a total of 15% of two additional unidentified species with ^{1}H NMR methyl resonances at δ 1.96 and 1.89. The failure to see CO inhibition of the formation of **9-H** indicates that it is formed by a different mechanism than the conversion of **10** to CpRu(CO)$_2$H. One possible mechanism involves photochemical cleavage of the Ru−Ru bond of **8** and reaction of monomeric species with H_2.

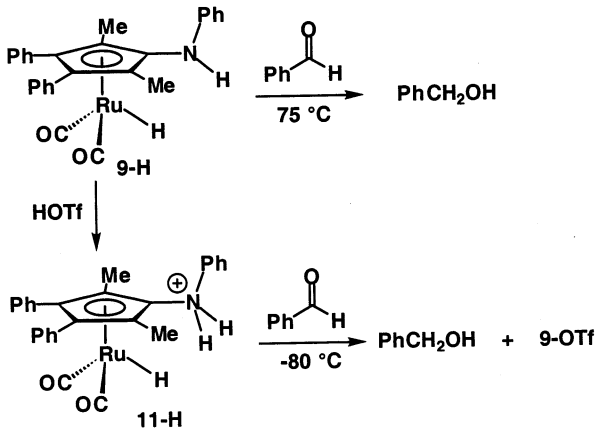
Under 1 atm of H_2, solutions of **9-H** in THF-d_8 were stable for weeks at room temperature. In the absence

(16) Bitterwolf, T. E.; Linehan, J. C.; Shade, J. E. *Organometallics* **2000**, *19*, 4915.

Scheme 5



Scheme 6



of H_2, a solution of **9-H** in THF-d_8 underwent about 20% decomposition over 36 h at 85 °C to produce an unidentified black solid, but none of dimer **8**. While solutions of **9-H** in THF-d_8 were photostable, solutions in CD_2Cl_2 under ambient light were converted to **9-Cl** within 1 h. Similar photoconversion of $CpRu(CO)_2H$ to $CpRu(CO)_2Cl$ in halogenated solvents has been reported.[17]

Low Acidity of 9-H. For the aminocyclopentadienyl ruthenium hydride **9-H** to act as an effective reducing agent for aldehydes, the −NH function needs to be acidic enough to protonate the carbonyl oxygen as hydride is being delivered from ruthenium. We therefore set out to determine the acidity of **9-H** and to compare its acidity to that of the related hydroxycyclopentadienyl ruthenium hydride **4-H**, which we had measured in CH_3CN.[8a] When the base 1,1,3,3-tetramethylguanidine (**TMG**, pK_a = 23.3 in CH_3CN) was added to a solution of **9-H** in CH_3CN, only a small decrease in the IR bands of **9-H** and no new IR peaks assignable to a deprotonated species were seen. This establishes that the pK_a value of the NHPh unit of **9-H** is greater than 25.

The NHPh unit is therefore substantially less acidic than the OH unit of the hydroxycyclopentadienyl ruthenium hydride **4-H** (pK_a = 17.5 in CH_3CN).[8a] To more quantitatively assess the difference in acidity between the −NHPh and −OH groups on Cp ruthenium systems, we compared the acidities of the more acidic chloride complexes **9-Cl** and [2,5-Ph_2-3,4-Tol(η^5-C_4COH)]Ru-$(CO)_2$H (**4-Cl**). Using Norton's IR method for determination of the pK_a of metal carbonyl hydrides in CH_3CN, **TMG** was added to a solution of **9-Cl** in CH_3CN; new IR peaks at 1990 and 1920 cm^{-1} for the deprotonated species grew in, and peaks at 2040 and 1991 cm^{-1} for **9-Cl** diminished. The pK_a of the amine group of **9-Cl** was determined to be 25.0 ± 0.2. Similarly, the pK_a of **4-Cl** in CH_3CN was determined to be 12.0 ± 0.2 by measuring the extent of deprotonation with pyridine (pK_a = 12.3 in CH_3CN). The NHPh group of **9-Cl** is therefore 13 pK_a units less acidic than the OH group of **4-Cl**.[18] The pK_a of the −OH unit of hydride **4-H** is 5.5 units greater than that of chloride **4-Cl**. If the difference between the pK_a of the −NHPh units of hydride **9-H** and chloride **9-Cl** is the same as the 5.5 pK_a unit difference between the acidities of the corresponding −OH compounds **4-H** and **4-Cl**, then the pK_a of the −NHPh unit of hydride **9-H** is estimated to be about 30.[19]

Slow Reaction of 9-H with Benzaldehyde. In contrast to the rapid reaction of CpOH complex **4-H** with benzaldehyde at low temperature, the CpNHPh complex **9-H** did not react with benzaldehyde at room temperature. Slow reduction of benzaldehyde by **9-H** in THF-d_8 was observed by ^{1}H NMR spectroscopy at 75 °C (Scheme 6). After 8.5 h, approximately 30% of **9-H** had reacted and benzyl alcohol (δ 4.53 for CH_2O) was formed. The rate of reduction of benzaldehyde by **9-H** is approximately 10 000 times slower than by **4-H**.[20] We ruled out a fast and reversible hydrogenation of benzaldehyde by reacting **9-H** with benzaldehyde-*d* at room temperature for 2 days and finding no hydrogen incorporation into the benzaldehyde and no deuterium incorporation into **9-H.** Also, no significant difference in the rate of reduction of benzaldehyde by **9-H** was seen when the reaction was carried out under 1 atm of CO. In toluene, where the rate of reaction of **4-H** with benzaldehyde is 50 times faster than in THF, 20% reaction of **9-H** with benzaldehyde to produce benzyl alcohol (δ 4.36 for CH_2O) was seen after 2 h at 75 °C. Thus, the reaction of **9-H** with benzaldehyde in toluene is only about 2−3 times faster than in THF.

The greatly diminished reactivity of the CpNHPh complex **9-H** compared to that of the CpOH complex **4-H** is attributed to the much less acidic nature of the CpNHPh unit and the necessity for simultaneous protonation of the aldehyde oxygen as hydride is delivered from ruthenium. Protonation at nitrogen to give a cationic $CpNH_2Ph^+$ complex provides an attractive way to enhance the acidity of the NH group and to achieve rapid reduction of benzaldehyde.

Protonation of 9-H. There are two potential sites for protonation of **9-H**: the amine nitrogen to give an

(17) Morandini, F.; Consiglio, G.; Lucchini, V. *Organometallics* **1985**, *4*, 1202.

(18) This is substantially larger than the 7 pK_a unit difference between the acidities of diphenylamine (25) and phenol (18) in DMSO: Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456.

(19) Because of the very low acidity of the −NHPh unit of **9-H**, the most acidic proton in the compound may be the RuH. The pK_a of $CpRu(CO)_2H$ in CH_3CN is 20.2: Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257.

(20) Assuming a second-order rate law, 30% conversion of **9-H** in reaction with 0.8 M benzaldehyde corresponds to $k_2 \approx 1.5 \times 10^{-5}$ M^{-1} s^{-1}. Careful kinetic studies of the reduction of benzaldehyde by **4-H** between 0 °C and −15 °C gave $\Delta H^{\ddagger} = 12.0 \pm 1.5$ kcal mol^{-1} and $\Delta S^{\ddagger} = -28 \pm 5$ eu; extrapolation to 75 °C gives $k_2 \approx 1.6 \times 10^{-1}$ M^{-1} s^{-1}. While this estimate is crude, the calculated rate difference of 10^4 is large.

ammonium salt and ruthenium to give either a dihydride or a dihydrogen complex. With excess acid, both nitrogen and ruthenium might be protonated. Protonation of **9-H** with either triflic acid or $HBF_4{\cdot}OMe_2$ in CD_2Cl_2 at low temperature gave the ammonium complex {[2,5-Me_2-3,4-Ph_2(η^5-C_4CNH_2Ph)]Ru$(CO)_2H$}$^+$ (**11-H**). Triflic acid in CD_2Cl_2 was added to a solution of **9-H** in CD_2Cl_2 at −78 °C in a resealable NMR tube. The tube was shaken and immediately placed in a precooled NMR probe at −70 °C. In the ^{1}H NMR spectrum, the *N*-Ph protons moved to δ 7.5 from δ 6.71 and 6.69 in the neutral complex **9-H**; this chemical shift change is very characteristic of protonation of NPh^+ groups. The $-NH_2$ resonance of **11-H** appears at δ 11.2 as a broad singlet, and RuH is a sharp singlet at δ −10.1.[21]

Interestingly, **9-H** could not be appreciably protonated *in THF* either by triflic acid or by excess $HBF_4{\cdot}OMe_2$. Addition of THF to a CH_2Cl_2 solution of **11-H** led to deprotonation and re-formation of **9-H**. Thus, while the amine nitrogen of **9-H** can be protonated by triflic acid, the resulting ammonium complex **11-H** is a very strong acid capable of protonating THF. The high acidity of the ammonium nitrogen would be expected to greatly enhance the ability of **11-H** to reduce aldehydes.

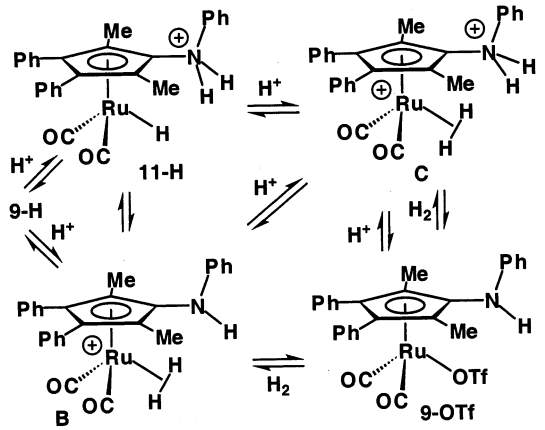
Protonation of the ruthenium triflate **9-OTf** and the ruthenium chloride **9-Cl** by excess triflic acid in CD_2Cl_2 also occurred at the NHPh group to produce {[2,5-Me_2-3,4-Ph_2(η^5-C_4CNH_2Ph)]Ru$(CO)_2$OTf}OTf (**11-OTf**) and {[2,5-Me_2-3,4-Ph_2(η^5-C_4CNH_2Ph)]Ru$(CO)_2$Cl}OTf (**11-Cl**). ^{1}H NMR spectroscopy at −70 °C showed shifts of the NPh hydrogens to higher frequency (δ 7.5 from δ 7.0) upon protonation, just as seen for **11-H**. Solutions of **11-OTf** and **11-Cl** are stable at room temperature for hours.

Reduction of Benzaldehyde with 11-H at −80 °C. In contrast to the very slow reaction of the neutral ruthenium hydride **9-H** with benzaldehyde at 75 °C, reaction of **11-H** with benzaldehyde occurred very rapidly at −80 °C (Scheme 6). A solution of benzaldehyde in CH_2Cl_2 was added to a solution of **11-H** in CD_2Cl_2 in a resealable NMR tube at −94 °C. The tube was immediately placed in a precooled NMR probe at −80 °C, and a ^{1}H NMR spectrum was obtained within 5 min. The spectrum showed complete disappearance of **11-H**. The room-temperature NMR spectrum showed resonances for benzyl alcohol at δ 4.69 (CH_2O) and for **9-OTf** at δ 1.9 ($CpCH_3$).

While **11-H** reacted with benzaldehyde very rapidly at −80 °C, no reaction between **11-H** and cyclohexene in CD_2Cl_2 was seen by ^{1}H NMR spectroscopy up to −20 °C, where decomposition of **11-H** to **9-OTf** was observed. Thus, **11-H** rapidly adds hydrogen across the polar C═O double bond of benzaldehyde but does not react with the unpolarized C═C double bond of cyclohexene.[22] Similar reactivity was seen for the hydroxycyclopentadienyl ruthenium hydride **4-H**.

Loss of Hydrogen from {[2,5-Me_2-3,4-Ph_2(η^5-C_4CNH_2Ph)]Ru$(CO)_2H$}OTf (11-H). The triflate salt of **11-H** was unstable above −25 °C and lost hydrogen to form **9-OTf**. At −25 °C, a solution of **11-H** in CD_2Cl_2, formed by addition of triflic acid to **9-H**, turned cloudy and some solid precipitated.[23] Upon being warmed to room temperature, the precipitate redissolved and **9-OTf** was observed by ^{1}H NMR spectroscopy. A few bubbles were seen, and a small resonance in the ^{1}H NMR spectrum at δ 4.6 was observed, consistent with the evolution of H_2. With only a slight excess of triflic acid present, the more basic nitrogen of **9-H** is protonated while the somewhat less basic nitrogen of **9-OTf** is not protonated.

Scheme 7



While we have not yet probed the mechanism of the decomposition of **11-H**, there are three distinct possible mechanisms that appear plausible (Scheme 7). First, a dihydrogen complex (**B**) might be formed from **11-H** by intramolecular proton transfer and then lose dihydrogen. Capture of the resulting vacant coordination site by triflate would then produce **9-OTf**. Second, the dihydrogen complex **B** might form by a series of intermolecular proton transfers mediated by triflic acid and then lose dihydrogen to give **9-OTf**. Third, the dicationic dihydrogen complex **C** might be generated by protonation of **11-H** at ruthenium with excess acid and then lose dihydrogen and a proton to give **9-OTf**.

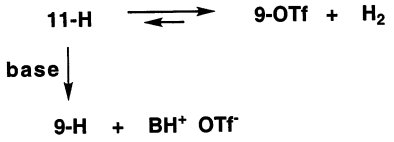
Reaction of 9-OTf with H_2 To Generate 9-H. The development of a catalytic system for the reduction of aldehydes based on the cationic **11-H** requires a means of reacting **9-OTf** with H_2 to regenerate at least small equilibrium amounts of the active reducing agent **11-H**, which can be drained off by reaction with carbonyl compounds. The rapid decomposition of the protonated ruthenium hydride **11-H** to dihydrogen and **9-OTf** suggests that the microscopic reverse, the conversion of the triflate complex to ruthenium hydride complex **11-H** under H_2, may also be a facile process. To determine whether the reaction of **9-OTf** is kinetically rapid enough to regenerate **11-H** at room temperature, we sought to trap **11-H** by a very favorable deprotona-

(21) No evidence for protonation at ruthenium was seen. This is consistent with Morris's estimate of the p*K* of $CpRu(CO)_2(\eta^2$-$H_2)^+$ in CH_2Cl_2 of −6: Morris, R. H.; Jia, G. *J. Am. Chem. Soc.* **1991**, *113*, 875.

(22) In some cases, trisubstituted and tetrasubstituted alkenes that are readily protonated can be reduced by strong acids and transition-metal hydrides: Bullock, R. M.; Song, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 8602.

(23) We speculate that the precipitate may be the bridging ruthenium hydride [{[2,5-Me_2-3,4-Ph_2(η^5-C_4CNHPh)]Ru$(CO)_2$}$_2$(μ-H)]OTf. The related BF_4 salt was apparently formed when a solution of **11-H** in CD_2Cl_2 (formed by addition of excess $HBF_4{\cdot}OMe_2$ to **9-H**) was warmed above −25 °C. ^{1}H NMR spectroscopy showed a bridging hydride resonance at δ −16.5 (1 H), a methyl resonance at δ 2.06 (12 H), and resonances for an unprotonated N−Ph group at δ 7.0−7.2. Similar hydride chemical shifts have been seen for other cationic bridging diruthenium hydrides. Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989,** *8*, 1824.

Scheme 8



tion with added base to produce the neutral hydride **9-H** (Scheme 8).

Reaction of **9-OTf** with H_2 and diisopropylethylamine in CH_2Cl_2 at room temperature led to the clean formation of **9-H**. The reaction was followed by IR spectroscopy. No reaction between diisopropylethylamine and **9-OTf** was seen until H_2 was added. Upon addition of 100 atm of H_2, IR peaks for **9-H** (2014 and 1957 cm^{-1}) grew in with a half-life of about 30 min.

The related reaction of **9-OTf** with 1 atm of H_2 in THF-d_8 was followed by ^1H NMR spectroscopy. After a few hours, the ratio **9-OTf**:**8**:**9-H** was 25:60:15, as measured by integration of the CpCH_3 ^1H NMR resonances. After 3 days, the equilibrium ratio **9-OTf**:**8**:**9-H** was <5:53:47. Apparently, THF is basic enough to drive the equilibrium toward **9-H**.

Discussion

Different Structural Types for CpOH and CpNHPh Diruthenium Complexes. We had determined that reduction of aldehydes by the hydroxycyclopentadienyl ruthenium hydride **4-H** is very rapid and that the slow step in aldehyde hydrogenations catalyzed by the diruthenium bridging hydride **5** was its reaction with H_2. In an effort to develop more active hydrogenation catalysts, we sought to prevent formation of a kinetically sluggish bridging hydride. We turned to CpNHPh systems with the anticipation that a sterically congested bridging PhN- - -H- - -NPh unit would disfavor formation of bridging hydride **A**. This strategy was successful: instead of obtaining bridging hydride **A**, the isomeric symmetric dimer **8** was obtained. The change in the type of diruthenium compound formed in going to −NHPh systems from −OH systems is attributed to both steric destabilization of **A** and to weaker hydrogen bonding between the nitrogen centers of **A** compared with the oxygen centers of **5**.

Another way of explaining why **5** and **8** have different structures involves consideration of the hypothetical monoanions of each complex. These structures have a metal−metal bond and a single proton shared by the CpO or CpNPh groups. For oxygen, the bridge should resemble a carbonyl group hydrogen-bonded to an alcohol (C═O- - -H−O); for nitrogen, the bridge involves an imine hydrogen bonded to an amine (C═NR- - -H−N). What is the most likely site of protonation for each structure? For the much more basic imine, protonation at N is expected and dimer **8** is formed. In contrast, the less basic carbonyl oxygen is not readily protonated and protonation of the Ru−Ru bond occurs to give the bridging hydride complex **5**.

Enhanced Reactivity of Acidic CpXH Complexes. Huge rate enhancements for reduction of benzaldehyde by ruthenium hydrides were observed as the acidity of the group attached to the Cp ring was increased. The CpNHPh complex **9-H** ($pK_a \approx 30$) reacted slowly with benzaldehyde at 75 °C, the CpOH complex **4-H** ($pK_a = 17.5$) reacted rapidly at −10 °C, and the $CpNH_2Ph^+$ complex **11-H** ($pK_a \approx 1$) reacted rapidly at −80 °C. These rate enhancements are consistent with our proposed concerted mechanism for aldehyde reduction, in which an acidic proton is transferred to the aldehyde oxygen as hydride is transferred from ruthenium. Clearly, the acidity of the CpOH or CpNHR group plays a central role in carbonyl reductions.

Mechanism of Aldehyde Reduction. We have proposed that the CpOH complex **4-H** reacts with aldehydes by a concerted mechanism (Scheme 1). The simultaneous transfer of a proton from OH and hydride from RuH is supported by a second-order kinetic rate law, the absence of CO inhibition, and deuterium isotope effects for both OD and RuD. A similar mechanism would be anticipated for the neutral CpNHPh complex **9-H**.

For the cationic $CpNH_2Ph^+$ complex **11-H**, a stepwise mechanism needs to be considered in addition to the concerted mechanism because of the high acidity of the ammonium group. The stepwise mechanism involves reversible protonation of the aldehyde oxygen by the ammonium group, followed by a hydride transfer from ruthenium. Two-step mechanisms for "ionic hydrogenation" have been proposed by Bullock[24] and Norton[25] for reduction of ketones by the neutral metal hydrides $CpW(CO)_3H$, $CpMo(CO)_3H$, and $CpRe(NO)(PPh_3)H$, in the presence of a strong Brønsted acid (CF_3CO_2H, CF_3SO_2H). In principle, the concerted and stepwise mechanisms for reduction of aldehydes by **11-H** can be distinguished by isotope effect measurements. Unfortunately, the rate of aldehyde reduction by **11-H** is too fast to measure.

Regeneration of Ruthenium Hydride from 9-OTf and H_2. It is not clear whether base is merely driving the equilibrium between **9-OTf** and **11-H** (Scheme 8) or is playing a more active role. There are two ways that a base might play an active role (Scheme 9). Reversible dissociation of triflate, dihydrogen coordination, and deprotonation of the dihydrogen complex by base could produce **9-H**. In related chemistry, a dihydrogen complex was formed from reaction of Cp*Re(CO)(NO)OTf and H_2 at −78 °C.[26] Alternatively, the base-promoted elimination of triflic acid could produce the neutral coordinatively unsaturated species **D** that could coordinate dihydrogen and transfer a proton intramolecularly to the imine nitrogen to produce **9-H**.

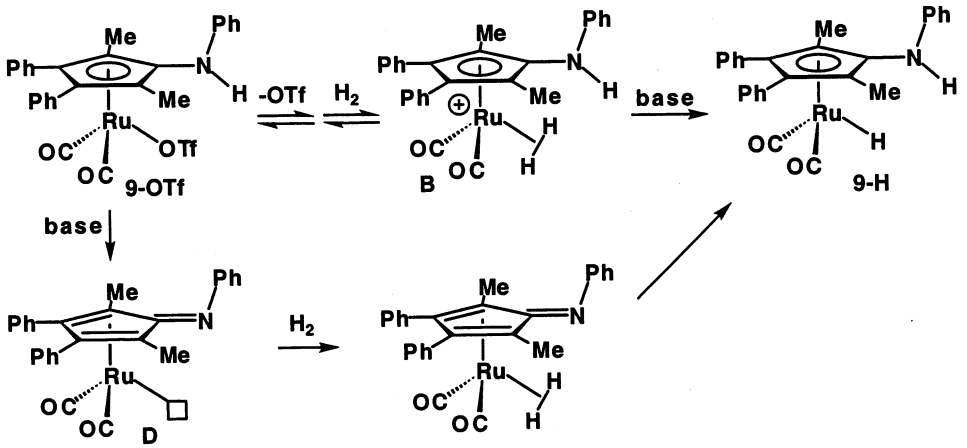
Possible Development of a Catalytic Cycle. We have demonstrated the feasibility of the two steps needed for a catalytic cycle for aldehyde hydrogenation (Scheme 10). We have shown that the cationic ruthenium hydride **11-H** rapidly reduces benzaldehyde to benzyl alcohol at −80 °C and produces the triflate **9-OTf**. This step requires strongly acidic conditions for **11-H** to remain protonated. The existence of a pathway for the regeneration of ruthenium hydride **11-H** from

(24) (a) 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. (b) Voges, M. H.; Bullock, R. M. *J. Am. Chem. Soc.* **2000**, *122*, 12594.

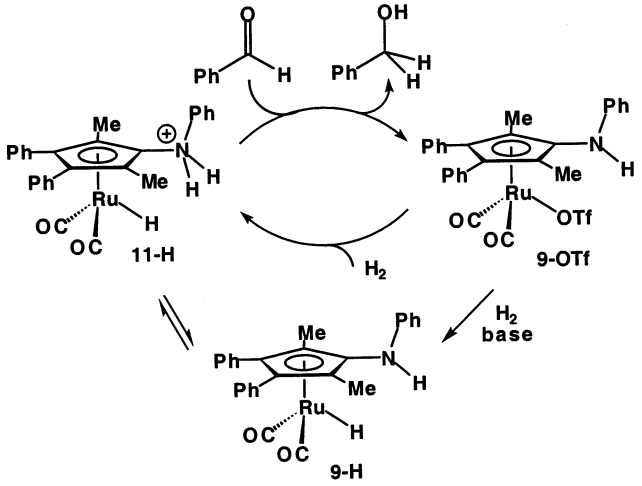
(25) (a) Smith, K. T.; Norton, J. R.; Tilset, M. *Organometallics* **1996**, *15*, 4515. (b) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778.

(26) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824.

Scheme 9



Scheme 10



reaction of H_2 with **9-OTf** was established by the observation of its facile microscopic reverse. We know this equilibrium is unfavorable for formation of **11-H** under strongly acidic conditions.

There is a second pathway for regeneration of a ruthenium hydride. In the presence of base, we have succeeded in adding H_2 to the neutral ruthenium triflate **9-OTf** to form the neutral ruthenium hydride **9-H**. Our favored explanation for this reaction is that an equilibrium between (**9-OTf** + H_2) and **11-H** (Scheme 8) is driven by base toward the ruthenium hydride **9-H**. We have not ruled out the possibility that the base is required for a more active role in the formation of **9-H**.

The cationic triflate **11-OTf** which would be the major species present under very acidic conditions is expected to have a stronger ruthenium triflate bond than neutral triflate **9-OTf**. Consequently, **11-OTf** is expected to be less reactive toward H_2 than **9-OTf**. Problems might then develop in choosing conditions for a catalytic cycle, since aldehyde reduction requires strongly acidic conditions and ruthenium hydride regeneration may require less acidic conditions. If **11-OTf** does not activate hydrogen very well, an intermediate acidity might be required to optimize catalysis. We are currently exploring the development of hydrogenation catalysts based on combination of triflic acid with the CpNHPh ruthenium compounds reported here.

Experimental Section

{[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNHPh)]Ru(CO)(μ-CO)}$_2$ (8). A suspension of $Ru_3(CO)_{12}$ (230 mg, 0.36 mmol) and **6** (387 mg, 1.15 mmol) in methanol (50 mL) was refluxed for 24 h. Filtration gave **8** as a yellow-orange precipitate, which was recrystallized from THF/pentane at −10 °C to give pure **8** (232 mg, 45%); mp 255−60 °C dec. IR (Nujol): 1947 (s), 1752 (s) cm^{-1}. ^{1}H NMR (−75 °C, CD_2Cl_2, 500 MHz): major isomer (**8-trans**), δ 1.82 (s, Me), 5.27 (s, N*H*), 6.64 (d, J = 7.5 Hz, NPh ortho), 6.75 (t, J = 7.5 Hz, NPh para), 7.10 (t, J = 7.5 Hz, NPh meta), 7.2−7.4 (aromatic); minor isomer (**8-cis**), δ 1.88 (s, Me), 5.01 (s, N*H*), 6.28 (d, J = 7.5 Hz, NPh ortho), 6.74 (t, J = 7.5 Hz, NPh para), 7.17 (t, J = 7.5 Hz, NPh meta), 7.2−7.4 (aromatic). Ratio **8-trans**:**8-cis**: at −40 °C, 3:1; at −75 °C, 5:1. ^{13}C{^{1}H} NMR (−75 °C, CD_2Cl_2, 125 MHz): major isomer (**8-trans**), δ 10.8 (Me), 102.5 (C3, C4 of Cp), 105.7 (C2, C5 of Cp), 111.1 (C1 of Cp), 114.7, 119.5, 128.4, 128.9, 130.1, 132.0 (ipso), 132.4, 145.6 (ipso), 200.7 (br s, terminal CO), 258.7 (br s, bridging CO); **8-cis** (CO resonances only), 200.7 (s, terminal CO), 256.1 (s, bridging CO). MS (electrospray ionization, CH_2Cl_2, MeOH): m/z (MNa^+) calcd for $C_{54}H_{44}O_4N_2Ru_2Na$, 1011.1, found 1011.1. Anal. Calcd for $C_{54}H_{44}N_2O_4Ru_2$ (987.08): C, 65.71; H, 4.49; N, 2.84. Found: C, 64.59; H, 4.32; N, 2.64.[27]

[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNHPh)]Ru(CO)$_2$H (9-H). A solution of **8** (14.0 mg, 0.014 mmol) in THF-d_8 (0.4 mL) in a resealable NMR tube was degassed by three successive freeze−pump−thaw cycles and placed under 1 atm of H_2 at −78 °C. The tube was irradiated with UV light (254 nm) for 30−40 h at room temperature. ^{1}H NMR spectroscopy indicated nearly quantitative formation of **9-H**. IR (THF): 2016 (s), 1957 (s) cm^{-1}. ^{1}H NMR (THF-d_8, 500 MHz): δ −10.1 (s, RuH), 2.04 (s, Me), 6.69 (d, J = 7.5 Hz, NPh para), 6.71 (t, J = 7.5 Hz, NPh ortho), 7.01 (s, NH), 7.0−7.4 (aromatic). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz): δ 11.1 (Me), 101.8 (Cp), 106.1 (Cp), 109.9 (C1 of Cp), 113.8, 118.4, 127.8, 128.2, 129.4, 132.7 (ipso), 132.8, 148.2 (ipso), 202.7 (CO). Evaporation of THF under high vacuum gave **9-H** as an oily solid which could be redissolved in a new solvent without decomposition. **9-H** decomposed over days under vacuum, and attempted recrystallizations of **9-H** were unsuccessful.

[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNHPh)]Ru(CO)$_2$OTf (9-OTf). Triflic acid (19 μL, 0.21 mmol) was added to a solution of **8** (100 mg, 0.10 mmol) in CH_2Cl_2 (6 mL). After 24 h, 3 mL of water was added. The organic layer evaporated to give **9-OTf** as a yellow solid (100 mg, 77% yield). IR (CD_2Cl_2): 2043 (s), 1994 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2, 500 MHz): δ 1.90 (s, Me), 6.52 (br s, NH), 7.0−7.4 (aromatic). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz):

(27) While the carbon analysis was low, ^{1}H and ^{13}C NMR spectroscopy indicated the compound was pure and an X-ray crystal structure was obtained on crystals of **8-trans** formed upon slow evaporation of a methanol solution.

δ 12.3 (Me), 82.2 (Cp), 102.0 (Cp), 119.7 (q, J_{C-F} = 315 Hz, CF_3), 129.9 (ipso), 125.4, 126.9, 129.2, 129.8, 130.2, 132.2, 136.5 (C1 of Cp), 139.5 (ipso), 198.4 (CO). ^{19}F NMR (CD_2Cl_2, 282 MHz): δ −76.9. MS (electrospray ionization, $CHCl_3$, MeOH): *m*/*z* ($M - OTf^+$) calcd for $C_{27}H_{22}O_2NRu$ 494.1, found 494.1. Anal. Calcd for $C_{28}H_{22}NO_5RuS$ (642.61): C, 52.33; H, 3.45; N, 2.18. Found: C, 53.68; H, 3.98; N, 2.03.[28] X-ray-quality crystals were grown by slow evaporation of a CH_2Cl_2 solution.

9-OTf was also synthesized by addition of AgOTf (10 mg, 0.039 mmol) to a solution of **9-Cl** (17 mg, 0.032 mmol) in toluene-d_8 (0.4 mL). The conversion was quantitative by NMR after 24 h.

9-OTf was also synthesized by addition of triflic acid to a solution of **9-H** in CH_2Cl_2 at −78 °C, followed by warming to room temperature. The conversion was essentially quantitative by NMR.

{[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNH$_2$Ph)]Ru(CO)$_2$OTf}OTf (11-OTf). Triflic acid (6 μL, 0.068 mmol) was added to a solution of **9-OTf** (17.1 mg, 0.027 mmol) in CD_2Cl_2 (0.4 mL) in a resealable NMR tube at −78 °C to give a solution of **11-OTf**. The NMR tube was placed into a precooled NMR probe at −70 °C. IR (CD_2Cl_2): 2082 (s), 2042 (s) cm^{-1}. ^{1}H NMR (−70 °C, CD_2Cl_2, 500 MHz): δ 2.19 (s, Me), 7.06 (d, J = 7.5 Hz, CpPh ortho), 7.31 (t, J = 7.5 Hz, CpPh meta), 7.39 (t, J = 7.5 Hz, CpPh para), 7.59 (m, 2H, NPh), 7.74 (m, 3H, NPh), 11.37 (br s, NH_2). ^{13}C{^{1}H} NMR (24 °C, CD_2Cl_2, 125 MHz): δ 11.3 (Me), 95.6 (C1 of Cp), 102.3 (Cp), 107.0 (Cp), 122.6, 126.0 (ipso), 129.7, 131.1, 131.6, 132.3, 132.8, 134.3 (ipso), 192.9 (CO). ^{19}F NMR (−70 °C, CD_2Cl_2, 470 MHz): δ −76.4, −78.5, −77.2 (HOTf).

{[2,5-Me$_2$-3,4-Ph$_2$(η^5-C$_4$CNH$_2$Ph)]Ru(CO)$_2$H}OTf (11-H). A solution of **9-H** (17.1 mg, 0.035 mmol) in THF (0.4 mL) in a resealable NMR tube was evaporated to dryness under high vacuum. CD_2Cl_2 (0.4 mL) was vacuum-transferred into the tube. Triflic acid (3.1 μL, 0.035 mmol) was added to the solution via syringe at −78 °C. The NMR tube was placed into a precooled NMR probe at −70 °C. ^{1}H NMR (−70 °C, CD_2Cl_2, 500 MHz): δ −10.13 (s, RuH), 2.22 (s, Me), 7.1−7.3 (aromatic protons), 7.53 (m, 2H, NPh), 7.58 (m, 3H, NPh), 11.16 (br s, NH_2). ^{13}C{^{1}H} NMR (−70 °C, CD_2Cl_2, 125 MHz): δ 10.6 (Me), 97.2 (C1 of Cp), 98.4 (Cp), 106.9 (Cp), 121.7, 128.0, 128.1, 129.4 (ipso), 130.6, 130.7, 132.1 (br), 135.6 (ipso), 198.8 (CO). ^{19}F NMR (−70 °C, CD_2Cl_2, 470 MHz): δ −78.2.

(28) While the carbon and hydrogen analyses were slightly high, **9-OTf** was shown to be pure by ^{1}H and ^{13}C NMR spectroscopy and X-ray crystallography.

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Supporting Information Available: Text giving general experimental methods, experimental details, and characterization data for **4-Cl**, **6**, **7-H**, **9-Cl**, **11-Cl**, figures giving original ^{1}H and ^{13}C NMR spectra of **8**, **9-H**, **9-Cl**, and **9-OTf**, text giving details of the reaction of **9-OTf** with H_2, the reduction of benzaldehyde by **7-H**, **9-H**, and **11-H**, and the pK_a determinations of **4-Cl**, **9-Cl**, and **9-H**, and tables giving X-ray crystallographic data for **4-Cl**, **8**, **9-Cl**, and **9-OTf**. This material is available free of charge via the Internet at http://pubs.acs.org.

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