PPh_3-Substituted [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru(CO)(PPh_3)H Exhibits Slower Stoichiometric Reduction, Faster Catalytic Hydrogenation, and Higher Chemoselectivity for Hydrogenation of Aldehydes over Ketones Than the Dicarbonyl Shvo Catalyst

Charles P. Casey,* Neil A. Strotman, Sharon E. Beetner, Jeffrey B. Johnson, David C. Priebe, and Ilia A. Guzei

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Received November 1, 2005

The PPh_3-substituted hydroxycyclopentadienyl ruthenium hydride [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]-Ru(CO)(PPh_3)H (**1**) stoichiometrically reduces aldehydes and ketones in the presence of a pyridine trap to produce alcohols and the ruthenium pyridine complex **5**, with a rate law that is dependent only on [aldehyde] and [**1**]. The observation of deuterium kinetic isotope effects on substitution of the acidic and hydridic protons of **1** are consistent with concerted transfer of hydrogen to aldehydes during reduction. **1** catalytically hydrogenates aldehydes under mild temperature and pressure conditions. While the Shvo catalyst **2** shows little activity under these conditions, it surpasses **1** at elevated temperatures and pressures. **1** shows high chemoselectivity for catalytic hydrogenation of aldehydes over ketones, while **2** is much less selective.

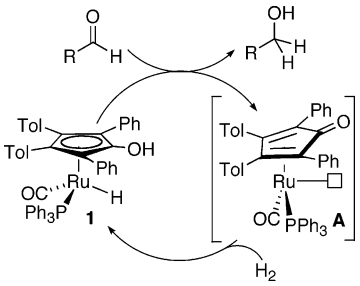
Introduction

In the accompanying paper,[1] we reported the synthesis of the phosphine-substituted hydroxycyclopentadienyl ruthenium hydride [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru(CO)(PPh_3)H (**1**) and demonstrated its ability to catalytically hydrogenate benzaldehyde. The catalytic cycle for hydrogenation of benzaldehyde with **1** appears to be straightforward and involves aldehyde reduction by **1** to generate alcohol and the unsaturated intermediate **A**, followed by reaction of **A** with H_2 to regenerate the active reducing species **1** (Scheme 1).

Catalyst **1** avoids the major weakness of the Shvo diruthenium catalyst **2**, which must dissociate to the monoruthenium hydride **3**, this being the active reducing agent (Scheme 2).[2] High temperature is required for dissociation of **2** to **3** and unsaturated intermediate **B**, and high H_2 pressure is needed to efficiently convert **B** to **3**. These conditions preclude catalysis under mild conditions. The steric bulk of the phosphine ligand of **1** apparently inhibits the formation of related diruthenium species and enables catalysis at lower temperature and hydrogen pressure.

Here we report experiments that establish the mechanism of reversible stoichiometric aldehyde reduction by **1**. The rate of stoichiometric reduction of aldehydes by **1** is within experimental error of the rate of hydrogenation of aldehydes catalyzed by **1**. While the rate of stoichiometric reduction of benzaldehyde by **1** is much slower than by dicarbonyl hydride **3**, the rates of hydrogenation of aldehydes catalyzed by **1** are similar to those of the Shvo dicarbonyl ruthenium system (**2** ⇔ **3**). The catalytic rates of the two systems are compared at different temperatures and pressures. High chemoselectivity for reduction of aldehydes over ketones was seen in both stoichiometric and catalytic reactions of **1**.

Scheme 1



Results

PPh_3 Trapping Studies. After determining that the stoichiometric reduction of aldehydes by **1** required a trap to coordinate to the unsaturated intermediate **A**,[1] we attempted to employ PPh_3 as a trap to measure the rate of aldehyde reduction. Previously, PPh_3 was employed successfully as an irreversible trap in the reduction of benzaldehyde by **3**. The reaction of **1** with a large excess of *p*-tolualdehyde and PPh_3 in toluene led to the isolation of the bis(phosphine) trapping product [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]Ru(PPh_3)$_2$(CO) (**4**) as a bright yellow powder, which was characterized by spectroscopy and by X-ray crystallography (Scheme 3, Figure 1).

When the reaction of **1** (10.5 μM) with excess *p*-tolualdehyde (0.105 M) and excess PPh_3 (0.100 M) in toluene-d_8 at 26 °C was monitored by ^{1}H NMR spectroscopy, the partial disappearance of **1** and the appearance of **4** and 4-methylbenzyl alcohol were observed (Figure 2, Table 1). Disappearance of **1** followed a pseudo first-order approach to equilibrium with $k_{\rightarrow eq(obs)} = 1.36 \times 10^{-3}$ s^{-1}.[3] At double the concentration of *p*-tolualdehyde

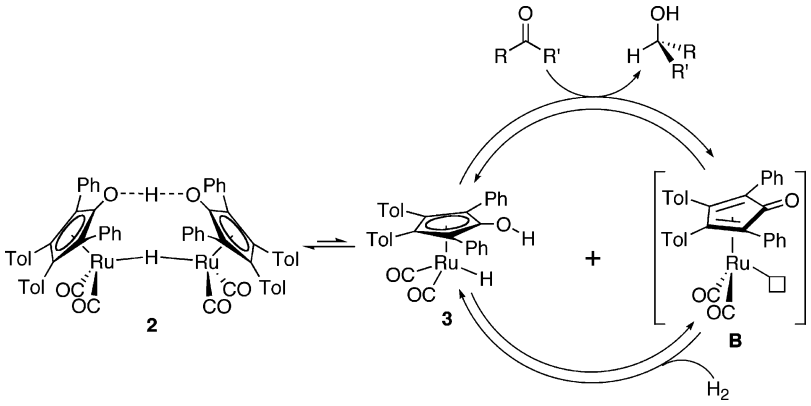
* To whom correspondence should be addressed. E-mail: casey@chem.wisc.edu.

(1) Casey, C. P.; Strotman, N. A.; Beetner, S. E.; Johnson, J. B.; Priebe, D. C.; Vos, T. E.; Khodavandi, B.; Guzei, I. A. *Organometallics* **2006**, *25*, 1236.

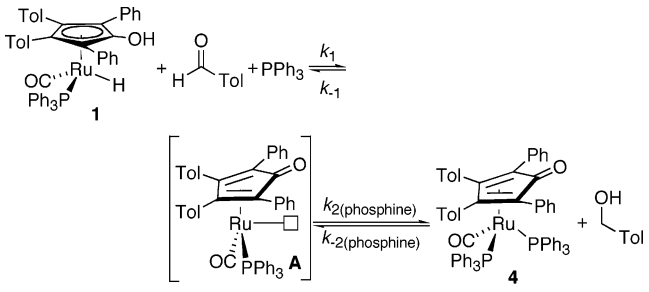
(2) (a) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. *J. Am. Chem. Soc.* **1986**, *108*, 7400. (b) Menashe, N.; Shvo, Y. *Organometallics* **1991**, *10*, 3885. (c) Menashe, N.; Salant, E.; Shvo, Y. *J. Organomet. Chem.* **1996**, *514*, 97.

10.1021/om050939z CCC: $33.50
Publication on Web 01/25/2006

Scheme 2



Scheme 3



$K_{eq} = (k_1 k_{2(phosphine)})/(k_{-1} k_{-2(phosphine)}) = ([\mathbf{4}][RCH_2OH])/([\mathbf{1}][RCHO][PPh_3])$

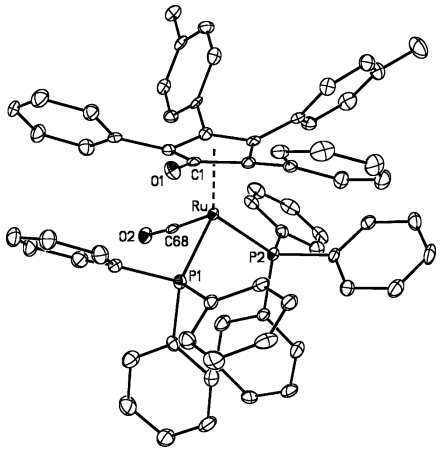


Figure 1. X-ray crystal structure of **4**.

(0.205 M), $k_{\rightarrow eq(obs)}$ increased to 2.39×10^{-3} s^{-1}. Thus, the rate of approach to equilibrium is approximately first order in aldehyde. At higher phosphine concentrations, the equilibrium was shifted more toward **4** and alcohol. The equilibrium constant is $K_{eq} = (k_1 k_{2(phosphine)})/(k_{-1} k_{-2(phosphine)}) = ([\mathbf{4}][alcohol])/([\mathbf{1}][aldehyde][PPh_3]) = 0.81$ M^{-1}.[4]

Because the reaction does not go to completion, it is difficult to accurately determine the second-order rate constant for reduction of aldehyde by **1** (k_1 in Scheme 3). However, the initial rate allows estimation of k_1, because at early reaction time the concentration of product alcohol is so low that PPh_3 traps intermediate **A** almost every time it is formed. In agreement with efficient trapping by PPh_3 early in the reaction, the initial rates were independent of $[PPh_3]$.[5]

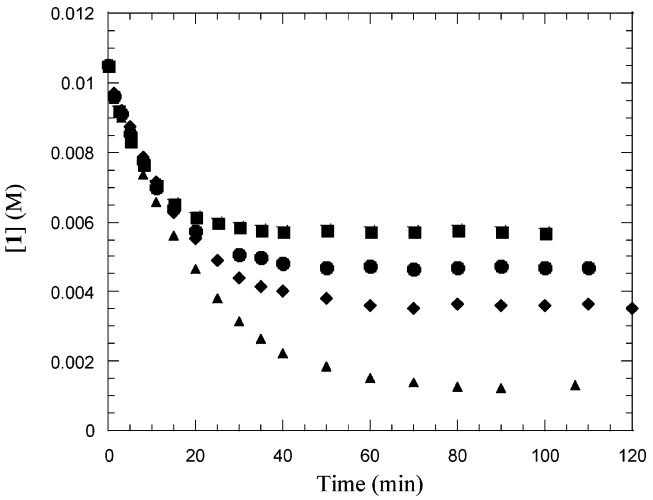


Figure 2. Plot of [**1**] versus time for reduction of *p*-tolualdehyde (0.105 M) by **1** (10.5 mM) in the presence of PPh_3 in toluene-d_8 at 26 °C. $[PPh_3]_0 = 0.050$ M (■), 0.100 M (●), 0.200 M (▲), 0.500 M (▲).

Table 1. Effect of $[PPh_3]_0$ on Equilibrium Position and Rate of Approach to Equilibrium for Stoichiometric Reduction of *p*-Tolualdehyde by 1 (10.5 mM) in Toluene-d_8 at 26 °C

$[RCHO]_0$ (M)	$[PPh_3]_0$ (M)	% Ru as **1** at eq	K_{eq} (M^{-1})	$k_{\rightarrow eq(obs)}$ (10^{-3} s^{-1})	$k_{\rightarrow eq(obs)}/[RCHO]_0$ (10^{-2} M^{-1} s^{-1})	$k_1 = k_{initial(obs)}/[RCHO]_0$ (10^{-3} M^{-1} s^{-1})
0.105	0.050	55	0.88	1.95	1.86	8.4
0.105	0.100	44	0.79	1.36	1.30	7.1
0.210	0.100	32	0.82	2.39	1.14	7.7
0.105	0.200	33	0.74	1.05	1.10	6.6
0.105	0.500	13	1.33	0.83	0.79	7.0

Pyridine Trapping Studies. Since PPh_3 was not an adequate trap for unsaturated intermediate **A**, we turned to pyri-

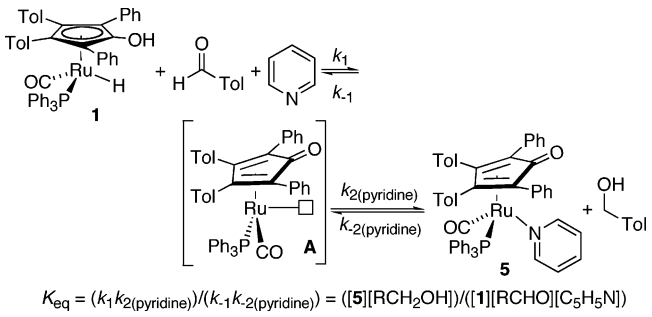
(3) All rate constants were derived from nonlinear least-squares fits of data using the following equation for an approach to equilibrium: $[\mathbf{1}]_t = [\mathbf{1}]_\infty + ([\mathbf{1}]_0 - [\mathbf{1}]_\infty)e^{-(k_{\rightarrow eq(obs)})t}$.

(4) The first four entries in Table 1 were used in determining K_{eq}. The other value is an outlier and contains substantial error due to inaccuracy in the measurement of [**1**] due to its low equilibrium concentration. If the percent Ru as **1** were 17% rather than the 13% measured, then a K_{eq} value of 0.84 would be obtained, which is consistent with the values for entries 1−4.

(5) The slope of the plots in Figure 2 at time zero provide a measure of $k_{initial(obs)}$. An approximate value of k_1 ($\sim 7.3 \times 10^{-3}$ M^{-1} s^{-1}) was obtained from $k_{initial(obs)}/[RCHO]$. Notice that $k_{\rightarrow eq(obs)}/[RCHO]$ approaches the second-order rate constant $k_1 = k_{initial(obs)}/[RCHO]$ as the phosphine concentration is increased because a greater fraction of intermediate **A** is converted into **4** at higher phosphine concentration. At lower phosphine concentration, the rate of approach to equilibrium exceeds the rate of formation of **4**. For example, if the equilibrium ratio of **1** to **4** is 1, then every time 1 mol of **1** is converted to 1 mol of **4**, 2 mol has reached equilibrium. In Table 1, as the percent Ru as **1** at equilibrium decreases, $k_{\rightarrow eq(obs)}/[RCHO]$ decreases and approaches k_1.

(6) Casey, C. P.; Singer, S. W. Unpublished results.

Scheme 4



$K_{eq} = (k_1k_{2(pyridine)})/(k_{-1}k_{-2(pyridine)}) = ([\mathbf{5}][RCH_2OH])/([\mathbf{1}][RCHO][C_5H_5N])$

dine as a possibly more efficient trap because it is less bulky than PPh_3 and has been shown to form a stable related $Ru(CO)_2$ complex.[6] The reaction of **1** with excess *p*-tolualdehyde and excess pyridine in toluene-d_8 went to completion. After 3 h, ^{1}H NMR spectroscopy showed quantitative conversion to 4-methylbenzyl alcohol and a new ruthenium pyridine complex with inequivalent tolyl resonances at δ 1.83 and 1.72 (Scheme 4). The pyridine complex [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]Ru(PPh_3)(CO)(NC_5H_5) (**5**) was isolated as a bright yellow crystalline solid and characterized by spectroscopy and by X-ray crystallography (Figure 3).

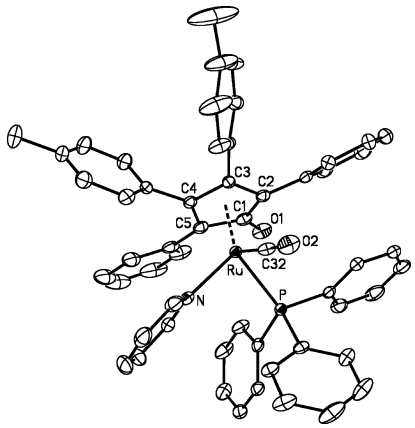


Figure 3. X-ray crystal structure of **5**.

When the reaction of **1** (0.0105 M) with excess *p*-toluladehyde (0.105 M) in the presence of excess pyridine (0.105 M) in toluene-d_8 at 26 °C was monitored by ^{1}H NMR spectroscopy, **1** underwent pseudo first-order decay accompanied by the growth of pyridine complex **5** and of 4-methylbenzyl alcohol. Pyridine proved to be an efficient trap, and complete conversion of **1** to **5** was observed. First-order dependence on aldehyde concentration and zero-order dependence on pyridine concentration were observed (Table 2), establishing the rate law $-d[\mathbf{1}])/dt = d[\mathbf{5}]/dt = k_1[\mathbf{1}][p\text{-tolualdehyde}][C_5H_5N]^0$. This rate law is consistent with rate-limiting transfer of hydrogen from **1** to aldehyde to give alcohol and the coordinatively unsaturated intermediate **A**, followed by rapid trapping of **A** by pyridine.[7] The second-order rate constant (k_1, Scheme 4) for reduction of *p*-tolualdehyde by **1** was obtained from a least-squares fit of the plot of k_{obs} (s^{-1}) versus [RCHO]; $k_1 = (6.84 \pm 0.37) \times 10^{-3}$ M^{-1} s^{-1}.[8] This is similar to the approximate rate constant (7.3×10^{-3} $M^{-1}s^{-1}$) estimated from the initial rate of reduction of *p*-tolualdehyde by **1** in the presence of PPh_3 and demonstrates that neither the identity of the trap nor its concentration affect the rate of aldehyde reduction.

Deuterium Kinetic Isotope Effects on Reduction of Aldehydes by 1. In our earlier studies of the reduction of benzaldehyde by the dicarbonyl hydride **3**, we found significant primary deuterium kinetic isotope effects for both OH and RuH,[9] which provided evidence for concerted transfer of a hydride and a proton to aldehyde during the rate-limiting step.

Table 2. Rate of Reduction of *p*-Tolualdehyde by 1 (0.0105 M) in the Presence of Pyridine in Toluene-d_8 at 26 °C

$[RCHO]_0$ (M)	$[pyridine]_0$ (M)	k_{obs} (10^{-4} s^{-1})	k_1 (10^{-3} M^{-1} s^{-1})
0.105	0.105	5.91	5.63
0.105	0.210	6.35	6.05
0.210	0.105	14.2	6.76
0.315	0.105	20.3	6.44

Table 3. Deuterium Kinetic Isotope Effects on Reduction of *p*-Tolualdehyde by Isotopologues of 1 in Toluene-d_8

k_{RuHOH}/k_{RuDOH}	1.8 ± 0.1
k_{RuHOH}/k_{RuHOD}	1.9 ± 0.1
k_{RuHOH}/k_{RuDOD}	3.3 ± 0.1
k_{RuHOD}/k_{RuDOD}	1.8 ± 0.1
k_{RuDOH}/k_{RuDOD}	1.9 ± 0.1

^{1}H NMR spectroscopy was used to monitor the reaction of the isotopologues of **1** (10.8 μM) with excess *p*-tolualdehyde (0.215 M) in the presence of excess pyridine (0.108 M) in toluene-d_8 at 26 °C.[10] The nonlinear least-squares fits of the plots of [**1**] versus time gave rate constants of $k_1 = 6.76 \times 10^{-3}$ M^{-1} s^{-1} for **1**, $k_1 = (3.80 \pm 0.23) \times 10^{-3}$ M^{-1} s^{-1} for **1-RuDOH**, $k_1 = (3.64 \pm 0.13) \times 10^{-3}$ M^{-1} s^{-1} for **1-RuHOD**, and $k_1 = (2.05 \pm 0.03) \times 10^{-3}$ M^{-1} s^{-1} for **1-RuDOD**. Table 3 shows the kinetic isotope effects derived for substitution of deuterium for hydrogen at the acidic and hydridic sites of **1**.

The product of each individual isotope effect for substitution of the hydroxyl proton or the hydride proton is $1.8 \times 1.9 = 3.4 \pm 0.2$, which is within error of the doubly labeled kinetic isotope effect (3.3 ± 0.1). This indicates that reduction of *p*-tolualdehyde by **1** occurs by a mechanism involving transfer of the hydroxyl proton and hydride in a concerted fashion. The magnitude of these kinetic isotope effects is similar to those seen for benzaldehyde reduction by dicarbonyl hydride **3** in dry toluene ($k_{RuHOH}/k_{RuHOD} = 1.38 \pm 0.08$, $k_{RuHOH}/k_{RuDOH} = 2.65 \pm 0.18$, $k_{RuHOH}/k_{RuDOD} = 3.63 \pm 0.25$).[9b]

Isotope Scrambling between Aldehydes and Alcohols Mediated by 1. It is interesting to note that although pyridine is an efficient trap for unsaturated intermediate **A**, it reversibly dissociates from **5**. Following the reduction of *p*-tolualdehyde by **1-RuDOD** in the presence of pyridine, toluene-d_8 was evaporated after 2.5 h and was replaced with protio toluene. The ^{2}H NMR spectrum showed the majority of deuterium derived from the hydride in the benzylic position of 4-methylbenzyl alcohol (δ 4.34, 92%) and only a small portion in the aldehydic position of excess *p*-tolualdehyde (δ 9.68, 8%). After

(7) The observed rate law is consistent with that derived from this mechanism using a steady-state approximation. See the Supporting Information.

(8) The average of the four independently determined k_1 values is 6.22×10^{-3} M^{-1} s^{-1}.

(9) (a) Our group measured deuterium kinetic isotope effects on reduction of benzaldehyde by **3** in wet THF ($k_{RuHOH}/k_{RuHOD} = 2.2 \pm 0.1$, $k_{RuHOH}/k_{RuDOH} = 1.5 \pm 0.2$, $k_{RuHOH}/k_{RuDOD} = 3.6 \pm 0.3$).[9b] The product (3.3) of these individual isotope effects is within error of the kinetic isotope effect of that seen for the doubly labeled isotopologue of **3**. The kinetic isotope effects were somewhat different in dry THF ($k_{RuHOH}/k_{RuHOD} = 1.30 \pm 0.02$, $k_{RuHOH}/k_{RuDOH} = 2.60 \pm 0.09$, $k_{RuHOH}/k_{RuDOD} = 3.38 \pm 0.19$).[9c] In dry toluene, we also measured kinetic isotope effects on the reduction of benzaldehyde by **3** ($k_{RuHOH}/k_{RuHOD} = 1.38 \pm 0.08$, $k_{RuHOH}/k_{RuDOH} = 2.65 \pm 0.18$, $k_{RuHOH}/k_{RuDOD} = 3.63 \pm 0.25$).[9c] Again, the doubly labeled kinetic isotope effect was within error of the product of the individual isotope effects (3.66). (b) Casey, C. P.; Singer, S. W.; Powell, D. R.; Hayashi, R. K.; Kavana, M. *J. Am. Chem. Soc.* **2001**, *123*, 1090. (c) Casey, C. P.; Johnson, J. B. *Can. J. Chem.* **2005**, *83*, 1339.

(10) For the preparation of **1-RuDOD**, **1-RuHOD**, and **1-RuDOH**, see ref 1.

Table 4. Temperature Dependence of Reduction of Benzaldehyde by 1 in Toluene-d_8

temp (K)	$[RCHO]_0$ (M)	$[pyridine]_0$ (M)	k_{obs} (10^{-4} s^{-1})	k_1 (10^{-3} M^{-1} s^{-1})
277	0.210	0.210	4.16	1.98
289	0.157	0.210	8.14	5.19
299	0.105	0.210	8.86	8.44
309	0.167	0.210	27.9	16.7

3 days, ^{2}H NMR spectroscopy showed 88% of the deuterium in the more abundant *p*-tolualdehyde and 12% in 4-methylbenzyl alcohol. This isotopic exchange requires both reversible pyridine dissociation from **5** and reversible dehydrogenation of 4-methylbenzyl alcohol by **A**.

Activation Parameters for Reduction of Benzaldehyde by 1. The temperature dependence of the rate of reduction of benzaldehyde by **1** using pyridine as the trap was measured between 4 and 36 °C (Table 4) to obtain activation parameters: $\Delta H^{\ddagger} = 10.5 \pm 0.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = -32.9 \pm 2.4$ eu.[11] This large negative entropy of activation is characteristic of bimolecular reactions and is consistent with a highly ordered transition state involving association of **1** and benzaldehyde.

The activation parameters for reduction of benzaldehyde by dicarbonyl hydride **3** ($\Delta H^{\ddagger} = 13.0 \pm 1.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.0 \pm 5.1$ eu) were determined earlier from rate measurements between −49 and −26 °C.[9b] These activation parameters allow extrapolation of the rate constant to higher temperatures ($k_1 = 1.25$ M^{-1} s^{-1} at 4 °C and 7.74 M^{-1} s^{-1} at 26 °C). Therefore, stoichiometric reduction of benzaldehyde by the phosphine-substituted hydride **1** is much slower than by the dicarbonyl hydride **3**. At 4 °C, **1** is 630 times slower than **3**, and at 26 °C, it is 920 times slower.

Electronic Effect of Para Substitution on the Rate of Benzaldehyde Reduction. The rates of reduction of para-substituted benzaldehydes by **1** were investigated by ^{1}H NMR spectroscopy. The stoichiometric reduction of *p*-anisaldehyde (0.210 M) by **1** (10.5 mM) in the presence of pyridine (0.210 M) in toluene-d_8 at 26 °C was followed by the disappearance of **1** and the appearance of **5** and 4-methoxybenzyl alcohol (δ 4.49, 3.36). Pseudo first-order decay of **1** ($k_{obs} = 7.12 \times 10^{-4}$ s^{-1}, $k = (3.39 \pm 0.03) \times 10^{-3}$ M^{-1} s^{-1}) was seen. Similarly, reduction of *p*-nitrobenzaldehyde (5.0 mM) by **1** (1.0 mM) in the presence of pyridine (0.020 M) in toluene-d_8 at 26 °C was monitored by following the disappearance of **1** and the appearance of **5** and *p*-nitrobenzyl alcohol (δ 4.06): $k_{obs} = 1.42 \times 10^{-3}$ s^{-1}, $k = (2.85 \pm 0.14) \times 10^{-1}$ M^{-1} s^{-1}.

Using the rates of reduction of *p*-anisaldehyde, *p*-tolualdehyde, benzaldehyde, and *p*-nitrobenzaldehyde by **1**, a Hammett plot of $\log(k_X/k_H)$ vs σ, where X is the para substituent of the benzaldehyde, was constructed (Table 5, Figure 4).[12] This plot gave a ρ value of $+1.77 \pm 0.08$ ($R^2 = 0.99639$), which is smaller than that obtained for reduction of substituted benzaldehydes by $NaBH_4$ ($\rho = +3.8$)[13] but is similar to ρ values for reduction of substituted acetophenones by $NaBH_4$ ($\rho = +3.06$, $+2.02$)[14,15] and reduction of substituted benzophenones by $LiAlH_4$ ($\rho = +1.95$).[16]

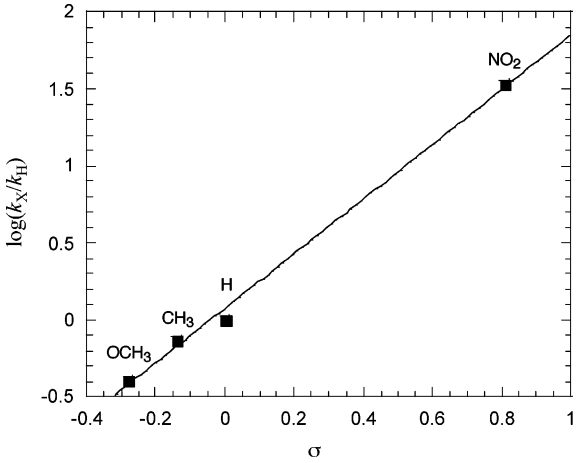


Figure 4. Hammett plot of $\log(k_X/k_H)$ vs σ for stoichiometric reductions of para-substituted benzaldehydes by **1** in toluene-d_8 at 26 °C.

Table 5. Effects of Para Substitution on Rates of Benzaldehyde Reduction by 1 in Toluene-d_8 at 26 °C

substituent (X)	σ	k (10^{-3} M^{-1} s^{-1})	$\log(k_X/k_H)$
OCH_3	−0.28	3.39	−0.396
CH_3	−0.14	6.22	−0.133
H	0	8.44	0
NO_2	0.81	285	1.53

Slow Reduction of Acetophenone by 1. Reduction of acetophenone by **1** proceeds much more slowly than reduction of benzaldehyde. Two solutions of **1** (5.20 μM), acetophenone (0.709 M), and pyridine (0.352 or 0.709 M) in toluene-d_8 at 69 °C were monitored by ^{1}H NMR spectroscopy over 74 h (>4 half-lives). The disappearance of **1** was accompanied by the formation of pyridine complex **5** and 1-phenylethanol. The reaction followed pseudo first-order kinetics and showed no dependence on [pyridine]: $k_{obs} = 1.12 \times 10^{-5}$ s^{-1} at 0.352 M pyridine and $k_{obs} = 1.14 \times 10^{-5}$ s^{-1} at 0.709 M. The second-order rate constant for reduction of acetophenone by **1** at 69 °C ($k_1 = 1.61 \times 10^{-5}$ M^{-1} s^{-1}) is approximately 520 times smaller than for benzaldehyde reduction at the much lower temperature of 26 °C. The activation parameters determined for reduction of benzaldehyde by **1** allow extrapolation of the rate constant to 69 °C ($k_1 = 8.97 \times 10^{-2}$ M^{-1} s^{-1}). Therefore, stoichiometric reduction of benzaldehyde by the phosphine-substituted hydride **1** is about 5600 times faster than the reduction of acetophenone at 69 °C. **1** shows remarkably high chemoselectivity for reduction of aldehydes over ketones.

Oxidation of 4-Methylbenzyl Alcohol by 5. This process is the microscopic reverse of the reduction of *p*-tolualdehyde by **1** using a pyridine trap and is an equilibrium process. When a solution of pyridine complex **5** and 4-methylbenzyl alcohol in toluene-d_8 was monitored by ^{1}H NMR spectroscopy at 26 °C over 90 min, formation of *p*-tolualdehyde and the phosphine-substituted hydride **1** was observed (Scheme 4). The approach to an equilibrium between **5** and **1** was observed ($K_{eq} = (k_1 k_{2(pyridine)})/(k_{-1} k_{-2(pyridine)}) = \{[\mathbf{5}][alcohol]\}/\{[\mathbf{1}][aldehyde][C_5H_5N]\} = 6.8 \times 10^2$ M^{-1}) (Table 6).

Complete conversion to ruthenium hydride **1** was seen only at a very low concentration of **5** (1.10 mM) and a very high

(11) For stoichiometric reduction of benzaldehyde by **3** in toluene, the activation parameters were $\Delta H^{\ddagger} = 13.0 \pm 1.8$ kcal mol^{-1} and $\Delta S^{\ddagger} = -11.0 \pm 5.1$ eu.[9c] We do not fully understand why the entropy of activation for **1** is much more negative than for **3**. It may be that the steric bulk of the PPh_3 ligand makes the conformation of **1** required for transfer of hydrogen much more crowded and constrained than the major conformation in solution.

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

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

(14) Bowden, K.; Hardy, M. *Tetrahedron* **1966**, *22*, 1169.

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

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

Table 6. Equilibrium Position and Rate of Approach to Equilibrium for Oxidation of 4-Methylbenzyl Alcohol by 5 in Toluene-d_8 at 26 °C

$[5]_0$ (mM)	$[\text{alcohol}]_0$ (mM)	[**1**]:[**5**] at equilibrium	k_{obs} (10^{-3} s^{-1})
4.34	34.3	3.5:1	0.67
4.36	173	15.5:1	0.93
1.10	173	1:0	1.21
1.10	325	1:0	1.21

concentration of 4-methylbenzyl alcohol (173 and 325 mM). In these two experiments, identical rate constants were observed ($k_{obs} = (1.21 \pm 0.07) \times 10^{-3}$ s^{-1}). Under these conditions, the reaction rate is independent of alcohol concentration and the rate law is $-d[\mathbf{5}]/dt = d[\mathbf{1}]/dt = k_{-2(pyridine)}[\mathbf{5}][\text{alcohol}]^0$. That is, $k_{obs} = k_{-2(pyridine)}$, the rate constant for pyridine dissociation from **5** to give unsaturated intermediate **A**.[17]

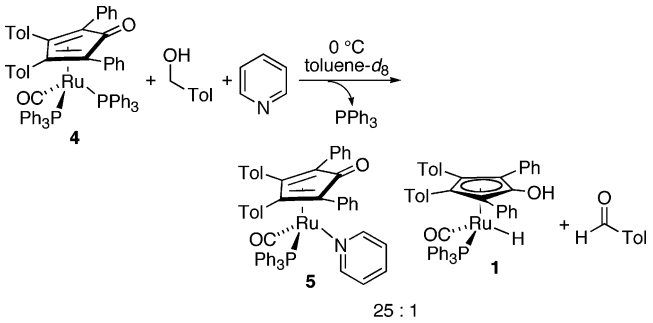
Using the rate constants k_1 and $k_{-2(pyridine)}$ and the equilibrium expression $K_{eq} = (k_1k_{2(pyridine)})/(k_{-1}k_{-2(pyridine)})$, we calculated that the rate constant for reaction of unsaturated intermediate **A** with pyridine to give **5** is about 120 times greater than that for its reaction with alcohol to give **1** ($k_{2(pyridine)}/k_{-1} \approx 120$).[18]

Oxidation of 4-Methylbenzyl Alcohol by 4. The rate of oxidation of 4-methylbenzyl alcohol by the bis(phosphine) complex **4** was much faster than oxidation by pyridine complex **5** and was too rapid to measure at 26 °C. However, at −2 °C, the rate of reaction of **4** (0.843 mM) with 4-methylbenzyl alcohol (12.7 or 25.3 mM) was readily measured by ^{1}H NMR spectroscopy ($k_{obs} = 5.7 \times 10^{-4}$ s^{-1} and $k_{obs} = 5.9 \times 10^{-4}$ s^{-1}, respectively). The rate was independent of alcohol concentration, which establishes the rate law as $-d[\mathbf{4}]/dt = d[\mathbf{1}]/dt = k_{-2(phosphine)}[\mathbf{4}][\text{alcohol}]^0$. This is consistent with rate-limiting dissociation of phosphine from **4** and rapid trapping of intermediate **A** by alcohol ($k_{obs} = k_{-2(phosphine)}$) (Scheme 3).

Using an estimate of the rate constant for dissociation of phosphine from **4** at 26 °C of $k_{-2(phosphine)} = 0.019$ s^{-1},[19] assuming that the rate constant for reduction of aldehyde by **1** (k_1) is the same as that obtained from pyridine trapping, and using the K_{eq} value measured earlier, the ratio of rate constants for reaction of **A** with PPh_3 and with alcohol was calculated to be $k_{2(phosphine)}/k_{-1} = 2.3$ (Scheme 3).

Competition between Reactions of 4 with Pyridine and with Alcohol. An independent measure of the partitioning of unsaturated intermediate **A** between reaction with pyridine and with alcohol was obtained from the reaction of the bis(phosphine) complex **4** (0.646 mM) with pyridine (24.3 mM) and 4-methylbenzyl alcohol (24.3 mM) at 0 °C (Scheme 5). Under these conditions, complex **4** readily loses phosphine to give the unsaturated intermediate **A**, but the two potential products **1** and **5** are stable. ^{1}H NMR spectroscopy showed complete disappearance of **4** within 50 min and 96% conversion to pyridine complex **5** and ∼4% conversion to ruthenium hydride **1**. Therefore, the ratio of rate constants for partitioning of unsaturated intermediate **A** between reaction with pyridine to give **5** and with alcohol to give **1** is estimated to be $k_{2(pyridine)}/k_{-1} \approx 25$.

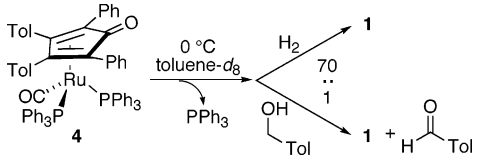
Scheme 5



Since k_{-1}, the rate constant for reaction of **A** with alcohol is the same in both the phosphine and pyridine systems, we calculate that pyridine ($k_{2(pyridine)}/k_{-1} = 25$) traps intermediate **A** approximately 11 times faster than PPh_3 ($k_{2(phosphine)}/k_{-1} = 2.3$). Pyridine is an overall better trap for unsaturated species **A**, because it traps ∼11 times more quickly than phosphine and dissociates ∼16 times less rapidly from **5** than phosphine dissociates from **4**.

Competition between Reactions of 4 with H_2 and with Alcohol. The relative rates of reaction of alcohol and H_2 with unsaturated intermediate **A** generated from precursor **4** were determined in a competition experiment. A solution of 4-methylbenzyl alcohol (38.2 mM) and **4** (1.34 mM) in toluene-d_8 was prepared in a resealable NMR tube below −78 °C and placed under 1 atm of H_2 at −196 °C (∼3.5 atm at 0 °C). The solution was thawed and shaken at −78 °C, and the tube was placed in an NMR spectrometer cooled to 0 °C. After 26 min, ^{1}H NMR spectroscopy employing a long relaxation delay showed complete disappearance of **4** and appearance of **1** (δ 1.87) and *p*-tolualdehyde (δ 9.62, 1.965) in a 6.7:1 ratio along with H_2 (3.2 mM, δ 4.52)[20] (Scheme 6). On the basis of the ratios of the reaction of **4** with H_2 and alcohol (5.7:1) and the ratio of concentrations of H_2 and alcohol (1:12), the rate constant for reaction of unsaturated intermediate **A** with H_2 was calculated to be ∼70 times greater than that for reaction with 4-methylbenzyl alcohol.

Scheme 6



Equilibrium between 4 and 5. After 16 h, ^{1}H NMR spectroscopy of a solution prepared from **5** (1.22 mM) and PPh_3 (0.302 M) showed a 1.8:1 equilibrium mixture of **4** and **5** (K_{eq}

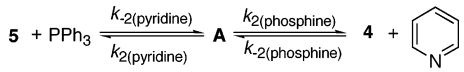
(17) This rate law is consistent with that obtained from a steady-state approximation for this reaction (see the Supporting Information).

(18) We believe that this value contains considerable error due to the different conditions used to determine k_1, $k_{-2(pyridine)}$, and K_{eq}. Two additional experiments, shown later, independently demonstrate ratios of $k_{2(pyridine)}/k_{-1}$ of 25 and 28.

(19) The rate constant for phosphine dissociation from **4** ($k_{-2(phosphine)}$) was estimated by extrapolation of a rate constant determined at −2 °C. The rate constant (5.8×10^{-4} s^{-1}) determined at −2 °C indicates that, for this process, $\Delta G^{\ddagger} = 19.86$ kcal mol^{-1}. Since phosphine dissociation is a unimolecular process, we expect $\Delta S^{\ddagger} \approx 0$. Assuming $\Delta S^{\ddagger} = 0$, then $\Delta H^{\ddagger} = 19.86$ kcal mol^{-1} and the caluclated rate constant at 26 °C is $k_{-2(phosphine)} = 0.019$ s^{-1}. If we assume that $\Delta S^{\ddagger} = +5$ eu, then $\Delta H^{\ddagger} = 21.22$ kcal mol^{-1} and $k_{-2(phosphine)} = 0.024$ s^{-1} at 26 °C. If we assume that $\Delta S^{\ddagger} = -5$ eu, then $\Delta H^{\ddagger} = 18.50$ kcal mol^{-1} and $k_{-2(phosphine)} = 0.015$ s^{-1} at 26 °C.

(20) (a) This solution contained 3.2 mM H_2 at the end of the reaction; however, the starting concentration could have been as high as 4.5 mM if no additional H_2 dissolved throughout the reaction. The solubility of H_2 in toluene at 1 atm at 0 °C has been measured (2.46 mM,[20b] 2.396 mM[20c]), and extrapolation to ∼3.5 atm of H_2 gives a solubility of ∼9 mM. This suggests that our solution (3.2 mM H_2) was not saturated with H_2, since the NMR tube was only shaken well below 0 °C, where the H_2 pressure and solubility were lower. Once the NMR sample reached 0 °C, little additional H_2 would be expected to dissolve without shaking. (b) Cook, M. W.; Hanson, D. N.; Alder, B. J. *J. Chem. Phys.* **1957**, *26*, 748. (c) Waters, J. A.; Mortimer, G. A.; Clements, H. E. *J. Chem. Eng. Data* **1970**, *15*, 174 (d) Hydrogen and Deuterium. *Solubility Data Series*; Young, C. L., Ed.; Pergamon Press: Oxford, 1981; Vol. 5/6.

Scheme 7



$K_{eq} = (k_{-2(pyridine)}k_{2(phosphine)})/(k_{2(pyridine)}k_{-2(phosphine)}$
$= ([\mathbf{4}][pyridine])/([\mathbf{5}][PPh_3])$

Table 7. Comparison of Rates of Hydrogenation of Benzaldehyde (0.97 M) by Catalyzed 2 (2.4−5.2 mM) and 1 (5−8 mM) at Varying Temperatures and H_2 Pressures in Toluene[22]

entry	temp (°C)	$p(H_2)$ (atm)	$k_{obs}/(2[\mathbf{2}]_0)$ (10^{-3} M^{-1} s^{-1})	$k_{obs}/[\mathbf{1}] = k$ (10^{-3} M^{-1} s^{-1})
1	22	2.5	0.33[a]	6.7[a]
2	22	35	0.91	7.0
3	35	35	6.3	15
4	45	11	9.3	29
5	45	35	12	29
6	45	55	26	31
7	60	35	95	62

[a] These hydrogenations of benzaldehyde (0.59 M) in toluene-d_8 were run in NMR tubes in a mechanical shaker and were periodically monitored by ^{1}H NMR spectroscopy.

$= ([\mathbf{4}][pyridine])/([\mathbf{5}][PPh_3]) = (k_{-2(pyridine)}/k_{2(pyridine)})(k_{2(phosphine)}/k_{-2(phosphine)}) = 5.1 \times 10^{-3}$) (Scheme 7). Using the previously obtained values of $k_{-2(pyridine)}$, which is the rate constant for loss of pyridine from **5**, and $k_{-2(phosphine)}$, which is the rate constant for loss of PPh_3 from **4**, we determined the relative reactivities of pyridine and PPh_3 toward unsaturated intermediate **A** ($k_{2(pyridine)}/k_{2(phosphine)} = 12$). This implies that pyridine traps intermediate **A** ∼28 times faster than does 4-methylbenzyl alcohol, which is consistent with a ratio of 25 obtained earlier by a direct competition experiment.

Stoichiometric Reduction of an Imine by 1. When the reaction of **1** (12.6 mM) with excess PhN═CHPh (0.500 M) and excess pyridine (0.500 M) in toluene-d_8 at 70 °C was monitored by ^{1}H NMR spectroscopy over 30 min, disappearance of **1** and appearance of **5** and *N*-phenylbenzylamine was seen ($k_{obs} = 2.23 \times 10^{-3}$ s^{-1}, $k_1 = (4.46 \pm 0.05) \times 10^{-3}$ M^{-1} s^{-1}). With half the pyridine concentration (0.272 M) and nearly identical concentrations of **1** (0.0131 M) and PhN═CHPh (0.564 M), similar rates were observed ($k_{obs} = 2.64 \times 10^{-3}$ s^{-1}, $k_1 = (4.69 \pm 0.13) \times 10^{-3}$ M^{-1} s^{-1}).

The rate constant for reduction of benzaldehyde by **1** at 70 °C was calculated from the activation parameters to be $k_1 = 9.4 \times 10^{-2}$ M^{-1} s^{-1}, which is ∼21 times greater than the rate constant for reduction of the imine PhN═CHPh. In stark contrast, the analogous dicarbonyl complex **3** stoichiometrically reduced MeN═CHPh 26 times faster than benzaldehyde.[9b]

Comparison of Benzaldehyde Hydrogenation Catalysts 1 and 2. The rates of hydrogenation of benzaldehyde (0.97 M) catalyzed by **1** were monitored by in situ IR spectroscopy and demonstrated first-order disappearance of benzaldehyde. The rate of benzaldehyde hydrogenation catalyzed by **1** was independent of H_2 pressure (Table 7, entries 1 and 2 and entries 4−6) and had a relatively moderate dependence on temperature (Table 7, entries 2, 5, and 7; about 9 times faster at 60 °C than at 22 °C). The rates of hydrogenation of benzaldehyde (0.97 M) catalyzed by **2** (2.4−5.2 mM) also showed first-order disappearance of benzaldehyde. In contrast to catalysis by **1**, the rate of benzaldehyde hydrogenation catalyzed by the Shvo catalyst system **2** ⇔ **3** depends on the H_2 pressure, but not in a simple first-order manner[21] (Table 7, entries 4−6, about 3 times faster at 5 times the pressure).

Under 35 atm of H_2 pressure at 22 °C, benzaldehyde hydrogenation catalyzed by **1** was more than 8 times faster than catalysis by **2** ⇔ **3** (Table 7, entry 2). However, when the temperature was increased to 45 °C, the rate difference decreased to about 2-fold (Table 7, entry 5). At 60 °C, a reversal of relative rates was seen and **2** ⇔ **3** became about 1.5 times faster than **1** (Table 7, entry 7). Thus, catalysis by **2** ⇔ **3** (∼100 acceleration between 22 and 60 °C) shows a much steeper temperature dependence than catalysis by **1** (∼9 acceleration between 22 and 60 °C).

The activation parameters determined from the rates of benzaldehyde hydrogenation catalyzed by **1** between 22 and 60 °C (Table 7, entries 2, 3, 5, and 7, $\Delta H^{\ddagger} = 10.7 \pm 0.3$ kcal mol^{-1} and $\Delta S^{\ddagger} = -32.1 \pm 1.9$ eu) were within experimental error of the activation parameters obtained for stoichiometric benzaldehyde reduction by **1** ($\Delta H^{\ddagger} = 10.5 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -32.9 \pm 2.4$ eu, vide supra). This provides evidence for a catalytic cycle with rate-limiting aldehyde reduction followed by rapid reaction of the unsaturated intermediate **A** with H_2.

A catalytic cycle in which **A** reacts with H_2 to regenerate **1** much more rapidly than it back-reacts with alcohol to regenerate aldehydes is supported by the observation of no product inhibition: plots of ln[PhCHO] vs time were linear to greater than 90% reaction, at which point [$PhCH_2OH$] is relatively high (∼0.9 M). Additionally, when catalytic hydrogenation of benzaldehyde (0.97 M) by **1** (5.0 mM) under H_2 (35 atm) at 45 °C was carried out in the presence of benzyl alcohol (0.718 M, initial concentration), a rate constant of $k = 3.0 \times 10^{-2}$ M^{-1} s^{-1} was obtained, which is essentially the same as that observed when there was no benzyl alcohol present initially (Table 7, entry 5). These catalytic results are in accord with the partitioning experiment shown in Scheme 6, which established that the rate constant for reaction of **A** with H_2 at 0 °C is 70 times greater than for reaction with 4-methylbenzyl alcohol.

Chemoselective Catalytic Hydrogenation of Benzaldehyde over Acetophenone. Even at 80 °C, the rate of hydrogenation of acetophenone catalyzed by **1** was too slow to measure accurately. Therefore, the selectivity for hydrogenation of aldehydes over ketones was measured through direct competition experiments. Hydrogenation of a mixture of benzaldehyde (0.19 M) and acetophenone (0.67 M) by **1** (5.7 mM) under 35 atm of H_2 at 60 °C in toluene was monitored by in situ IR spectroscopy. After 1 h, catalyst **1** had hydrogenated 89.4% of the benzaldehyde and only 0.2% of the acetophenone, corresponding to a 1200:1 selectivity difference favoring the aldehyde.[23]

For comparison, under similar conditions catalyst **2** ⇔ **3** (7.4 mM) hydrogenated 92.7% of the benzaldehyde and 6.6% of the acetophenone after 36 min, corresponding to a 40:1 selectivity difference favoring the aldehyde. Catalyst **1** is far more selective for reduction of aldehydes over ketones than is catalyst **2** ⇔ **3**.

Discussion

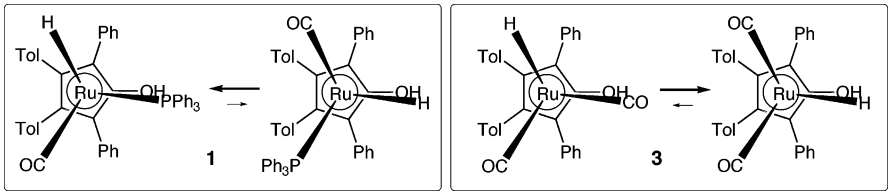
Our efforts to develop a more active catalyst related to the Shvo catalyst have focused on destabilizing unreactive diruthenium species analogous to **2**, which must dissociate to the monoruthenium hydride **3**, the active reducing agent (Scheme

(21) Whenever the catalyst system **2** ⇔ **3** is employed, the concentration reported is that of the diruthenium precatalyst **2** and is equal to half the total ruthenium concentration.

(22) The concentration of **2** is multiplied by 2 for comparison with monoruthenium species **1**, since **2** is a diruthenium species; therefore, 2[**2**] = [Ru].

(23) The relative reactivity was calculated using the following equation: $k_{benzaldehyde}/k_{acetophenone} = \{\ln[RCHO]_{initial} - \ln[RCHO]_{final}\}/\{\ln[RC(O)R']_{initial} - \ln [RC(O)R']_{final}\}$.

Scheme 8



2). High temperature is required for rapid dissociation of **2** to **3** and unsaturated intermediate **B**, and high H_2 pressure is needed to efficiently convert **B** to **3**. Catalysis with the new PPh_3-substituted complex **1** has been shown to involve only the active reducing agent **1** and an unseen unsaturated intermediate **A**, successfully avoiding unproductive diruthenium species not directly involved in the catalytic cycle (Scheme 1).

Slower Stoichiometric Reduction of Aldehydes by the PPh_3-Substituted Shvo Analogue 1. The reduction of benzaldehyde by **1**, using pyridine as a trap, occurs at moderate rates in toluene at room temperature, while reduction by the all-carbonyl hydride **3** occurs at comparable rates at −40 °C. We estimate that reduction of benzaldehyde at 26 °C by **3** occurs 900 times faster than reduction by **1**.

We suggest that three factors contribute to the lower reactivity of **1**. First, the steric bulk of the PPh_3 ligand may hinder the approach of aldehydes (and, to a greater degree, ketones) to **1**. Second, PPh_3 raises the energy of the conformation of **1** needed for reduction. In the X-ray crystal structure of the ruthenium hydride **1**, the bulky PPh_3 lies almost directly below the hydroxyl group on Cp (P−Ru−C−OH dihedral angle 8.9°).[1] However, concerted hydrogen transfer requires a conformation of **1** in which hydride lies approximately beneath the hydroxyl group (Scheme 8). This conformation has unfavorable steric interactions between PPh_3 and the aryl groups of the hydroxycyclopentadienyl ligand.[24] In contrast, the X-ray crystal structure of the chloride analogue of all-carbonyl complex **3**, bearing a chloride in place of the hydride, has a solid-state conformation where the chloride is beneath the hydroxyl group.[25]

Third, the electron donor PPh_3 ligand lowers the acidity of the CpOH group of **1** ($pK_a = 20.7$ in CH_3CN) compared to that of **3** ($pK_a = 17.5$). Since **1** has been shown to react by simultaneous transfer of both the acidic and hydridic hydrogens, the significantly lower acidity should slow hydrogen transfer. Earlier we found that a less acidic CpNHPh complex reduced benzaldehyde much more slowly than **3** and required heating to 75 °C, while a more acidic $CpNH_2Ph^+$ complex reduced benzaldehyde at −80 °C.[26] The PPh_3 ligand would also be expected to increase the hydride donor ability of **1**, accelerating hydride transfer. The hydrogen transfer process seems to be more sensitive to changes in the acidity of the CpOH unit than to the hydricity of the RuH unit.

Faster Catalytic Hydrogenation of Aldehydes under Mild Conditions by PPh_3 Substituted Shvo Analogue 1. Catalyst **1** offers advantages for hydrogenation of aldehydes at room temperature and easily achievable pressures (2.5 atm). Under these conditions, catalysis by **1** is more than 20 times faster than by **2** ⇔ **3** (Table 7). Since the rate of catalysis by **2** ⇔ **3** has a steeper temperature dependence than catalysis by **1**, a crossover in relative rates occurs as the temperature is increased, and at 60 °C under 35 atm of H_2, the **2** ⇔ **3** system is 1.5 times faster than **1** (Figure 5). In addition, catalysis of aldehyde hydrogenation by **1** is independent of H_2 pressure, but catalysis by **2** ⇔ **3** is accelerated at higher pressure. Therefore, if high temperature and high pressure are acceptable conditions, the **2** ⇔ **3** hydrogenation catalyst is preferable because of its faster rates under these conditions.

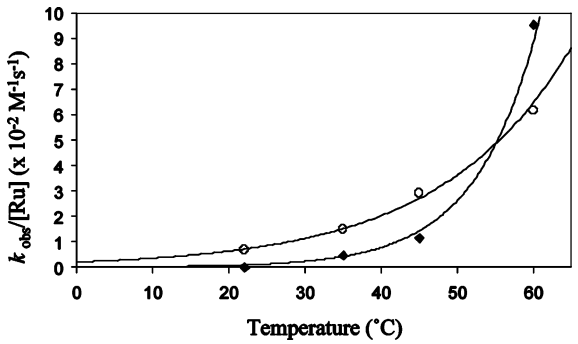


Figure 5. Plot of k_{obs}/[Ru] vs temperature for catalytic hydrogenation of benzaldehyde by **1** (○, 5.2−8.0 mM) and **2** ⇔ **3** (◆, 2.4−5.2 mM) in toluene under 35 atm of hydrogen.

Why is there a steeper temperature dependence for catalysis by **2** ⇔ **3** than by **1**? It is probably related to the fact that the rate-determining step for hydrogenation catalyzed by **1** is a second-order process ($\Delta H^{\ddagger} = 10.7$ kcal mol^{-1}, $\Delta S^{\ddagger} = -32.1$ eu), while the first-order dissociation of the diruthenium complex **2** ($\Delta H^{\ddagger} = 21.6$ kcal mol^{-1}, $\Delta S^{\ddagger} = -6.7$ eu)[27] to the active reducing agent **3** is at least partially rate determining. For competing first- and second-order processes, the first-order process normally has a higher $\Delta H^{\ddagger}$ value than the second-order process. Since $\Delta H^{\ddagger}$ is a measure of the temperature sensitivity of the rate of reaction, catalysis by **2** ⇔ **3** is accelerated to a greater degree at high temperature than is catalysis by **1**. Higher hydrogen pressure accelerates benzaldehyde hydrogenation catalyzed by **2** ⇔ **3**, because it favors the reaction of unsaturated species **B** with H_2 to regenerate the active reducing agent **3** over reaction with **3** to produce the inactive diruthenium species **2**. In addition, at higher hydrogen pressure and higher temperature, it is likely that a greater fraction of the ruthenium is present as the active reducing agent **3**.

Similar Rates of Stoichiometric and Catalytic Benzaldehyde Reduction. The rates of hydrogenation of benzaldehyde catalyzed by **1** are within experimental error of the rates of stoichiometric benzaldehyde reduction. For example, the stoichiometric reduction of benzaldehyde at 36 °C proceeded with a second-order rate constant of 16.7×10^{-3} M^{-1} s^{-1} and

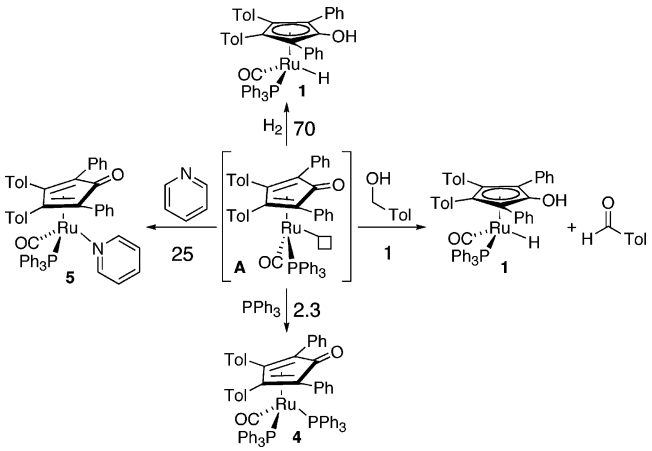
(24) A similar PPh_3−aryl interaction would be expected to destabilize and prevent formation of a phosphine-substituted diruthenium bridging hydride analogous to **2**.

(25) A crystal structure of hydride **3** has not been obtained. However, Park and co-workers obtained an X-ray crystal structure of [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru($CO)_2$Cl. The P−Ru−C−OH dihedral angle in the crystal structure of the chloride [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru(CO)-(PPh_3)Cl is 1.2°, which is similar to the 8.9° seen in hydride **1**, suggesting that hydride **3** should have a conformation similar to that of its corresponding chloride analogue [2,5-Ph_2-3,4-Tol_2(η^5-C_4COH)]Ru($CO)_2$Cl. Jung, H. M.; Choi, J. H.; Lee, S. O.; Kim, Y. H.; Park, J. H.; Park, J. *Organometallics* **2002**, *21*, 5674.

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

(27) Casey, C. P.; Johnson, J. B. Unpublished results.

Scheme 9. Relative Rates of Reaction with Unsaturated Intermediate A



catalytic reduction of benzaldehyde at 35 °C proceeded with a rate constant of 15×10^{-3} M^{-1} s^{-1}. These similar rates are consistent with mechanisms having the same rate-determining transfer of hydrogen from **1** to aldehyde in both the catalytic and stoichiometric reductions. In the catalytic cycle, turnover-limiting aldehyde reduction forms unsaturated intermediate **A**, which then rapidly reacts with H_2.

Chemoselective Reduction of Aldehydes over Ketones. While the stoichiometric reduction of benzaldehyde by **1** proceeded at a moderate rate at 26 °C, reduction of acetophenone by **1** proceeded slowly even upon heating at 69 °C. The rate of reduction of benzaldehyde at 69 °C was estimated from the activation parameters determined at lower temperature (4−36 °C) to be ∼5600 times faster than acetophenone reduction at 69 °C. For comparison, the rate of stoichiometric reduction of benzaldehyde by dicarbonyl complex **3** in toluene at 0 °C was estimated from activation parameters determined at lower temperature (−49 to −26 °C) to reduce benzaldehyde only 69 times faster than acetophenone.[9c]

The chemoselectivity for hydrogenation of aldehydes over ketones catalyzed by **1** was directly determined in internal competition experiments. Hydrogenation of mixtures of benzaldehyde and acetophenone catalyzed by **1** showed that the aldehyde was reduced about 1200 times faster than the ketone. In contrast, the dicarbonyl catalyst system **2** ⇔ **3** showed a lower chemoselectivity of 40:1 for the hydrogenation of mixtures of benzaldehyde and acetophenone.

It is interesting that the selectivity of phosphine-substituted catalyst **1** is much greater for aldehydes over ketones than is catalyst **2**. Catalyst **1** contains a bulky phosphine group, which sterically interacts with incoming carbonyl compounds. In the case of benzaldehyde, there is only minor steric repulsion between the aldehyde hydrogen and the phosphine, whereas in the case of acetophenone, there is a greater steric interaction between the methyl group and the phosphine.

High Kinetic Reactivity and Selectivity of Unsaturated Species A. The coordinatively unsaturated pseudo four-coordinate Ru(0) intermediate **A** is highly reactive. It is trapped reversibly by pyridine, PPh_3, and benzoic acid. It also reacts rapidly and reversibly with alcohols to dehydrogenate them and produce ruthenium hydride **1**. Most importantly, it reacts essentially irreversibly with H_2 to give **1**. We succeeded in generating **A** in the presence of pairs of reactants and measuring relative reactivities (Scheme 9). Unsaturated intermediate **A** reacts with H_2 ∼70 times more rapidly than with 4-methylbenzyl alcohol.

Experimental Section

Reduction of *p*-Tolualdehyde by 1 in the Presence of PPh_3 To Give [2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]Ru(PPh_3)$_2$(CO) (4). This process will be demonstrated with a specific example. Distilled *p*-tolualdehyde (7.4 μL, 62.9 μmol, 0.105 M) was added to a solution of **1** (100 μL (62.9 mM solution in toluene-d_8), 6.29 μmol, 10.5 mM), and PPh_3 (200 μL (0.300 M solution in toluene-d_8), 60 μmol, 0.100 M) in toluene-d_8 (0.30 mL), and the reaction was monitored by ^{1}H NMR spectroscopy over 110 min. Disappearance of a tolyl resonance for **1** (δ 1.87) and appearance of a methylene resonance of 4-methylbenzyl alcohol (δ 4.34) were used to monitor the reaction. Materials from several similar reactions were combined, additional PPh_3 was added, and toluene was evaporated. The residue was washed with pentane to give impure **4** containing PPh_3. Recrystallization from toluene/pentane at −30 °C gave bright yellow crystals of **4** suitable for X-ray crystallographic analysis. ^{1}H NMR (300 MHz, toluene-d_8): δ 1.82 (s, CpTolCH_3), 6.49 (d, J = 7.2 Hz, 4H), 6.77 (d, J = 7.5 Hz, 12H), 6.85−7.06 (m, 16 H), 7.42 (t, J = 8.7 Hz, 12H), 7.78 (d, J = 8.7 Hz, 4H). ^{1}H NMR (500 MHz, C_6D_6): δ 1.80 (s, CpTolCH_3), 6.49 (d, J = 7.0 Hz, 4H), 6.77 (t, J = 7.5 Hz, 12H), 6.88 (t, J = 7.5 Hz, 3H), 6.90−6.96 (m, 6H), 7.02−7.10 (m, 4H), 7.46 (t, J = 8.5 Hz, 12H), 7.87 (d, J = 7.0 Hz, 4H). ^{13}C{^{1}H} NMR (126 MHz, C_6D_6): δ 20.9 (2C), 80.9 (2C), 103.5 (2C), 124−139 (60C, 12 resonances), 170.5, 211.8 (t, J_{PC} = 14 Hz). ^{31}P{^{1}H} NMR (121 MHz, toluene-d_8): δ 39.0. IR (CH_2Cl_2): 1919 cm^{-1}.

[2,5-Ph_2-3,4-Tol_2(η^4-C_4CO)]Ru(PPh_3)(CO)(NC_5H_5) (5). *p*-Tolualdehyde (7.4 μL, 0.629 mmol) was added to a solution of pyridine (2.5 μL, 31.5 μmol) and **1** (6.0 mg, 7.4 μmol) in toluene-d_8. After 3 h, ^{1}H NMR spectroscopy showed quantitative conversion of **1** to pyridine complex **5**. Toluene was evaporated, and the residue was washed with pentane to give **5** as a yellow powder. Recrystallization from toluene/pentane at −30 °C gave bright yellow crystals of **5** suitable for X-ray crystallographic analysis. ^{1}H NMR (300 MHz, toluene-d_8): δ 1.72 (s, CpTolCH_3), 1.83 (s, CpTolCH_3), 6.07 (t, J = 6.9 Hz, 2H), 6.56 (m, 3H), 6.72−7.12 (m, 19H), 7.30 (t, J = 9.0 Hz, 6H), 7.52 (d, J = 7.8 Hz, 2H), 8.03 (t, J = 9.8 Hz, 4H), 8.31 (d, J = 5.4 Hz, 2H). ^{1}H NMR (500 MHz, C_6D_6): δ 1.72 (s, 3H), 1.82 (s, 3H), 6.02 (t, J = 6.5 Hz, 2H), 6.51 (t, J = 7.0 Hz, 1H), 6.56 (d, J = 7.5 Hz, 2H), 6.77 (d, J = 8.0 Hz, 3H), 6.82 (td, J = 7.5, 1.5 Hz, 6H), 6.88−6.93 (m, 5H), 7.00−7.11 (m, 5H), 7.35 (t, J = 9.0 Hz, 6H), 7.57 (d, J = 7.5 Hz, 2H), 8.13 (d, J = 7.0 Hz, 4H), 8.34 (br s, 2H). ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2): δ 21.3, 21.4, 66.9, 78.9, 100.9 (d, J_{PC} = 4 Hz), 104.8 (d, J_{PC} = 6 Hz), 125−138 (45C, 22 resonances), 158.1 (2C), 169.1, 208.7 (d, J_{PC} = 16 Hz). ^{31}P{^{1}H} NMR (121 MHz, toluene-d_8): δ 41.5. IR (CH_2Cl_2): 1917 cm^{-1}. HRMS (ESI): calcd for $C_{55}H_{45}NO_2PRu$ (M + H)$^+$, 884.2231; found, 884.2253.

Reduction of *p*-Tolualdehyde by 1 in the Presence of Pyridine. This process will be demonstrated with a specific example. A solution of **1** (100 μL (0.0629 M solution in toluene-d_8), distilled *p*-tolualdehyde (7.4 μL, 62.9 μmol, 0.105 M), 6.29 μmol, 10.5 mM) and pyridine (5.1 μL, 62.9 μmol, 0.105 M) in toluene-d_8 (0.50 mL) was monitored by ^{1}H NMR spectroscopy over 120 min. Disappearance of a tolyl resonance for **1** (δ 1.87) and appearance of a methylene resonance of 4-methylbenzyl alcohol (δ 4.34) and a tolyl resonance of **5** (δ 1.72) were used to monitor this reaction.

In Situ IR Spectroscopic Monitoring of Hydrogenation of Benzaldehyde Catalyzed by 1. This procedure will be illustrated with a specific example. A toluene solution (5.1 mL) containing benzaldehyde (0.5 mL, 4.9 mmol, 0.97 M) and **1** (25.0 mg, 0.031 mmol, 6.1 mM, 0.6 mol %) was prepared in a high-pressure vessel equipped with an attenuated total reflection element (ReactIR). The reaction vessel was heated to 45 °C under a nitrogen atmosphere. The vessel was flushed with H_2 three times, pressurized to 35 atm of H_2, and maintained at that pressure during the course of the hydrogenation. The hydrogenation of benzaldehyde was followed

by measuring the intensity of the CO stretching frequency of benzaldehyde (1709 cm^{-1}) every 4 min.

Acknowledgment. Financial support from the Department of Energy, Office of Basic Energy Sciences, is gratefully acknowledged. J.B.J. thanks the ACS Organic Division Emmanuil Troyansky Graduate Fellowship for support. Grants from the NSF (No. CHE-962-9688) and NIH (No. I S10 RR04981-01) for the purchase of NMR spectrometers are acknowledged.

Supporting Information Available: Text, tables, and figures detailing X-ray crystal structure data (corresponding CIF files are also given) for **4** and **5**, experimental proceduces for oxidation of 4-methylbenzyl alcohol by **4**, competition between reaction of **4** with H_2 and alcohol, reaction of **4** with 4-methylbenzyl alcohol and pyridine, reduction of acetophenone by **1** in the presence of pyridine, oxidation of 4-methylbenzyl alcohol by **5**, equilibrium between **4** and **5**, reduction of benzylideneaniline by **1** in the presence of pyridine, competition experiments between acetophenone and benzaldehyde, and derivation of anticipated rate laws for reaction of **1** with aldehyde in the presence of a trapping agent and reaction of **4** or **5** with alcohol. This material is available free of charge via the Internet at http://pubs.acs.org.

OM050939Z