Syntheses and Characterization of Hydrotris(1-pyrazolyl)borate Dihydrogen Complexes of Ruthenium and Their Roles in Catalytic Hydrogenation Reactions

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A series of new hydrotris(1-pyrazolyl)borate complexes of ruthenium were synthesized. Reaction of $RuCl(HB(pz)_3)(PPh_3)_2$ with $NaBH_4$ in ethanol produced the yellow monohydride complex $RuH(HB(pz)_3)(PPh_3)_2$. Protonation of the monohydride complex $RuH(HB(pz)_3)(PPh_3)_2$ with $HBF_4 \cdot Et_2O$ in dichloromethane gave the molecular dihydrogen complex $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$. Reactions of the dihydrogen complex $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$ with L (L = CH_3CN, H_2O, N_2) produced the adducts $[Ru(HB(pz)_3)(PPh_3)_2(L)]BF_4$. The dihydrogen complex $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$ could be regenerated by reactions of $[Ru(HB(pz)_3)(PPh_3)_2(L)]BF_4$ (L = CH_3CN, H_2O) with pressurized H_2. Deprotonation of the molecular dihydrogen complex $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$ occurred with NEt_3 or H_2O under hydrogen pressure. Treatment of $RuCl(HB(pz)_3)(PPh_3)_2$ with $LiBF_4$ in acetonitrile produced the bis-solvento complex $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)_2]BF_4$. Heating a THF/$CH_3CN$ (9/1) solution of $RuCl(HB(pz)_3)(PPh_3)_2$ at 60 °C led to the formation of $RuCl(HB(pz)_3)(PPh_3)(CH_3CN)$. Reaction of $RuCl(HB(pz)_3)(PPh_3)(CH_3CN)$ with $NaBH_4$ in THF produced the yellow monohydride complex $RuH(HB(pz)_3)(PPh_3)(CH_3CN)$. Acidification of the monohydride with $HBF_4 \cdot Et_2O$ yielded $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)(H_2)]BF_4$. Both complexes $[Ru(HB(pz)_3)(PPh_3)_2(CH_3CN)]BF_4$ and $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)_2]BF_4$ were found to be active catalysts for the hydrogenation of olefins in either anhydrous or hydrous THF. Enhanced catalytic activities were observed in the presence of water or NEt_3. In addition, deuterium was incorporated into the catalytic hydrogenation products when D_2O was present in the reaction mixture. The enhanced catalytic activity in the presence of water, and incorporation of deuterium in the hydrogenation products, could be best explained with mechanisms which involve dihydrogen complexes.

Introduction

Since the seminal discovery of the first isolable dihydrogen complex by Kubas and co-workers in 1984,[1] there has been intense interest in this interesting class of compounds.[2] Dihydrogen complexes have several distinctive properties that are important in the rationalization of some important steps of catalytic cycles and in the development of new catalytic systems, although these aspects have not been widely explored. Dihydrogen complexes have been used as precursors or catalysts in catalytic hydrogenation and hydrosilylation[3] and H/D and proton exchange reactions.[4−10]

Most of the reported dihydrogen complexes involved in catalytic hydrogenation have both M(H_2) and M−H functional groups. In these catalytic systems, the H_2 ligand usually serves as a good leaving group to provide a vacant site for substrate.[3a−d] Examples of direct involvement of dihydrogen complexes in catalytic cycles are still limited. The selective hydrogenation of 1-alkynes

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to alkenes[11] by $[Fe(H_2)H(pp_3)]^+$ [$pp_3 = P(CH_2CH_2PPh_2)_3$] provides a rare example involving an intermediate with *cis* disposed H_2 and σ-vinyl ligands. Intramolecular protonation of the adjacent vinyl ligand by an η^2-H_2 ligand produces alkenes. Probably, similar mechanisms are involved in the catalytic hydrogenation and hydrosilylation reactions using $Os(H_2)HCl(CO)(PR_3)_2$.[3c,h]

During the course of our study on catalytic hydrogenation reactions with tris(1-pyrazolyl)borato complexes $[Ru(HB(pz)_3)(PPh_3)_2(CH_3CN)]BF_4$ and $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)_2]BF_4$, we observed significant enhancement of the reaction rates with added water or NEt_3. Further study revealed that the enhanced catalytic activity in the presence of water could be best explained by the involvement of the molecular dihydrogen complexes $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$ and $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)(H_2)]BF_4$, which do not have the M−H functional group. In this report, we wish to describe the synthesis and characterization of these molecular dihydrogen complexes and discuss their roles in catalytic hydrogenation reactions. Polyhydride and dihydrogen complexes supported by tris(1-pyrazolyl)borate ligands have previously been reported by several groups.[12−18]

Results

Synthesis and Characterization of $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$. The molecular dihydrogen complex $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$, **3**, was prepared according to eq 1. Reaction of $RuCl(HB(pz)_3)(PPh_3)_2$, **1**,[19] with $NaBH_4$ in ethanol produced the yellow monohydride complex $RuH(HB(pz)_3)(PPh_3)_2$, **2**. Protonation of the monohydride complex $RuH(HB(pz)_3)(PPh_3)_2$ with $HBF_4 \cdot Et_2O$ in dichloromethane gave the molecular dihydrogen complex $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$, **3**. It is interesting to note that although Cp^- and $HB(pz)_3$ are both $6e^-$ donors, protonation of the Cp^- analog of **2**, $CpRuH(PPh_3)_2$ leads to the classical dihydride complex $[CpRuH_2(PPh_3)_2]^+$.[20] This is consistent with the observation that $[Ir(H_2)H(HB(pz)_3)(PMe_3)]BF_4$ contains an η^2-H_2 ligand

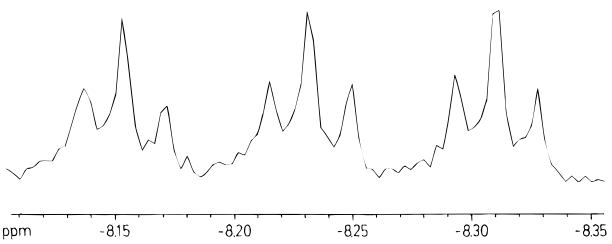
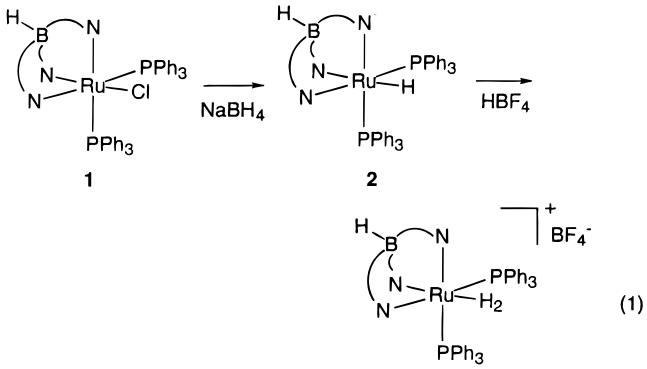


Figure 1. ^1H NMR spectrum of $[Ru(HB(pz)_3)(PPh_3)_2(HD)]BF_4$ (400 MHz, CD_2Cl_2) in the high-field region. The spectrum was obtained using an inversion-recovery experiment with a delay (τ) set to 20 ms to null the residual signal of the η^2-H_2 isotopomer.



while $[(\eta^5\text{-}C_5Me_5)IrH_3(PMe_3)]CF_3SO_3$ has the trihydride structure.[14]

The existence of the η^2-H_2 moiety in **3** was confirmed by the variable-temperature T_1 measurements and the observation of a large ^1J(HD) for the corresponding isotopomer $[Ru(HB(pz)_3)Ru(PPh_3)_2(HD)]BF_4$. The ^1H NMR spectrum of **3** in CD_2Cl_2 showed a broad hydride signal ($\omega_{1/2} = 27$ Hz) at δ −8.20 ppm integrating to two hydrogens. A minimum T_1 value of 21 ms (400 MHz) was obtained for the broad signal at −8.20 ppm, assignable to the $Ru(H_2)$ at 240 K. Acidification of $RuH(HB(pz)_3)(PPh_3)_2$ with 1 equiv of DBF_4 gave the η^2-HD isotopomer, $[Ru(HB(pz)_3)(PPh_3)_2(HD)]BF_4$, which showed a 1:1:1 triplet (^1J(HD) = 32.0 Hz) of a 1:2:1 triplet (^2J(HP) = 6.5 Hz) centered at δ −8.25 ppm in the ^1H NMR spectrum, after nulling the η^2-H_2 peak at δ −8.20 ppm by using the inversion-recovery method with a delay time of 20 ms (see Figure 1). The secondary isotope shift of 50 ppb agrees well with data reported for other η^2-HD complexes,[2,14,21] and the ^1J(HD) (32 Hz) lies at the upper end of the range commonly found for molecular hydrogen complexes. Resolution of further coupling to phosphorus (^2J(HP) = 6.5 Hz) is rather unusual,[2,22] and only a few examples of η^2-HD complexes with resolved H−P couplings (^2J(HP)) have been reported.[4c,21b,23]

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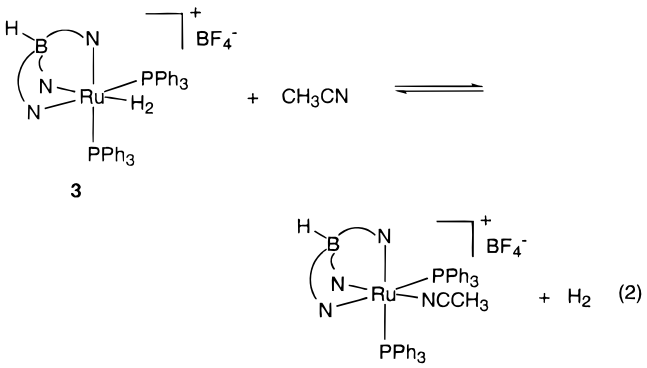
Chemical Properties of $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$. The dihydrogen ligand in complex **3** is labile and can be replaced easily by ligands such as CH_3CN, N_2, and H_2O. Thus when $RuH(HB(pz)_3)(PPh_3)_2$ was protonated in dichloromethane in the presence of excess CH_3CN under a dinitrogen atmosphere, the acetonitrile complex $[Ru(HB(pz)_3)(PPh_3)_2(CH_3CN)]BF_4$, **4**, was isolated, presumably through the intermediate $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$, **3**. Protonation of a metal hydride complex with loss of H_2 is a common method to open up a coordination site; for example, $IrH_5(PCy_3)_2$ reacted with HBF_4 in CH_3CN to give $[IrH_2(CH_3CN)_2(PCy_3)_2]^+$.[24] It could be demonstrated that the CH_3CN ligand in $[Ru(HB(pz)_3)(PPh_3)_2(CH_3CN)]BF_4$ can be at least partially replaced by H_2 to regenerate **3** (eq 2). Thus when a

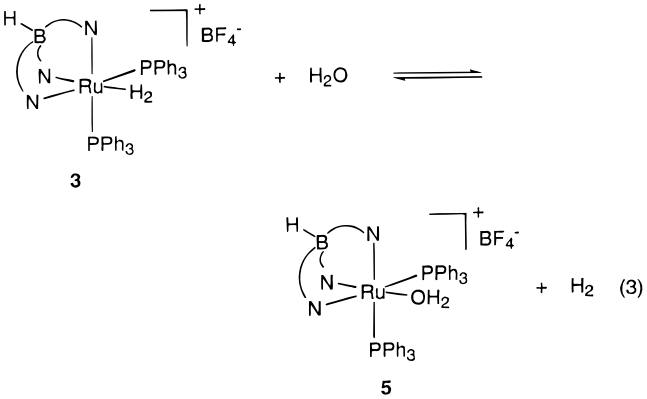


(2)

dichloromethane-d_2 solution of **4** in a Wilmad pressure-valved NMR tube was pressurized with 20 atm of H_2 and the solution was left at 90 °C for 4 h, a small broad peak at δ −8.20 ppm assignable to the dihydrogen compound **3** was observed.

Reaction of the dihydrogen complex **3** with pressurized (20 atm) N_2 in CH_2Cl_2 gave the corresponding dinitrogen complex $[Ru(HB(pz)_3)(PPh_3)_2(N_2)]BF_4$, which exhibits $\nu(N{\equiv}N)$ at 2177 cm^{-1} in the IR spectrum. This $\nu(N{\equiv}N)$ lies at the upper end of the range of $\nu(N{\equiv}N)$ found for the N_2 analogs of stable molecular hydrogen complexes.[25]

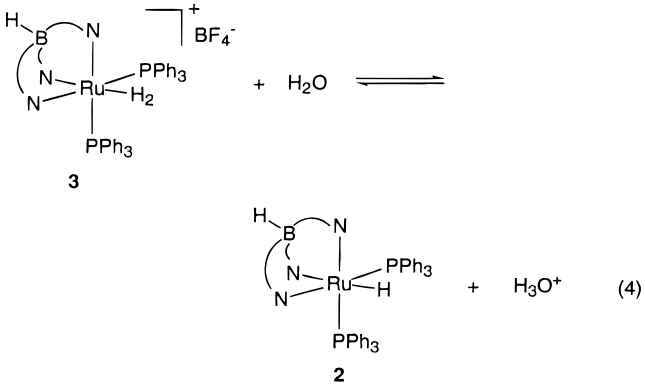
The dihydrogen complex **3** shows very interesting reactivities toward water. In acid medium without hydrogen pressure, the dihydrogen ligand was displaced by H_2O to give $[Ru(HB(pz)_3)(PPh_3)_2(H_2O)]BF_4$, **5** (eq 3).



(3)

In fact the aqua complex **5** was isolated from the protonation reaction of the monohydride complex **2** in the presence of excess H_2O under a dinitrogen atmosphere. The exchange of the H_2 ligand for H_2O is reversible, and the dihydrogen complex **3** was regenerated when a CD_2Cl_2 solution of **5** was subjected to 20 atm of H_2 in a pressure-valved NMR tube, as evidenced by the appearance of the broad hydride peak at δ −8.20 ppm in the ^1H NMR spectrum, assignable to **3**.

Under hydrogen pressure, the substitution reaction of H_2 with H_2O is suppressed and the dihydrogen ligand is deprotonated by water to give the monohydride complex **2** (eq 4), as illustrated in Figure 2. Figure 2a



(4)

is the ^1H NMR spectrum of the aqua complex, $[Ru(HB(pz)_3)(PPh_3)_2(H_2O)]BF_4$, in CD_2Cl_2. Figure 2b is that of $[Ru(HB(pz)_3)(PPh_3)_2(H_2O)]BF_4$ exposed to 10 atm of H_2. It clearly shows the signal at δ −8.20 ppm in the hydride region, owing to the dihydrogen complex **3,** and two sets of $HB(pz)_3^-$ signals in the low-field region, owing to $[Ru(HB(pz)_3)(PPh_3)_2(H_2O)]BF_4$, **5**, and $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$, **3**. The set of $HB(pz)_3^-$ resonances due to **3** are higher in intensity than those of **5**, indicating that, under 10 atm of H_2, most of $[Ru(HB(pz)_3)(PPh_3)_2(H_2O)]BF_4$ was converted to **3**. Figure 2c shows the ^1H NMR spectrum of the same system subjected to 10 atm of H_2 after addition of 0.5 mL of H_2O. It can be seen in the upfield region that the δ −8.20 ppm peak due to the η^2-H_2 signal of **3** diminishes while a triplet ($^2J(HP)$ = 26.4 Hz) due to $RuH(HB(pz)_3)(PPh_3)_2$ appears at δ −13.99 ppm. This NMR study clearly demonstrates that, in the presence of excess H_2O and under hydrogen pressure, the substitution reaction of H_2 with H_2O is suppressed and deprotonation of **3** by water occurs.

The bound H_2 molecule in **3** can also be easily deprotonated by NEt_3, as indicated by the disappearance of the δ −8.20 ppm peak due to the η^2-H_2 signal of $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$ and the concomitant appearance of the metal hydride peak at δ −13.99 ppm due to the monohydride complex $RuH(HB(pz)_3)(PPh_3)_2$ in a ^1H NMR experiment. There are many reported examples of deprotonation reactions of dihydrogen complexes.[21b,23c−f,26−29]

Synthesis and Characterization of $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)(H_2)]BF_4$ and Related Compounds. The preparation and chemical properties of the molec-

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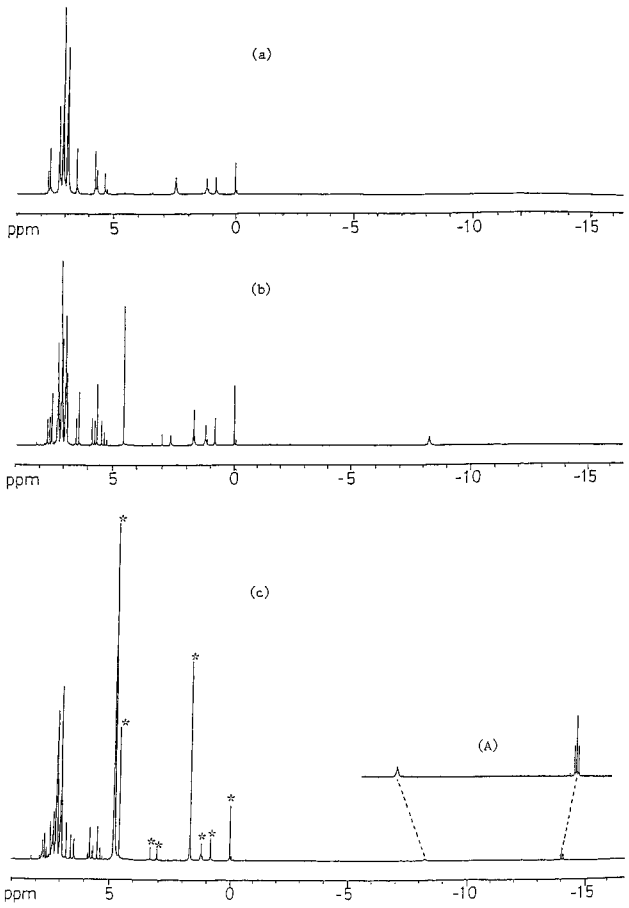
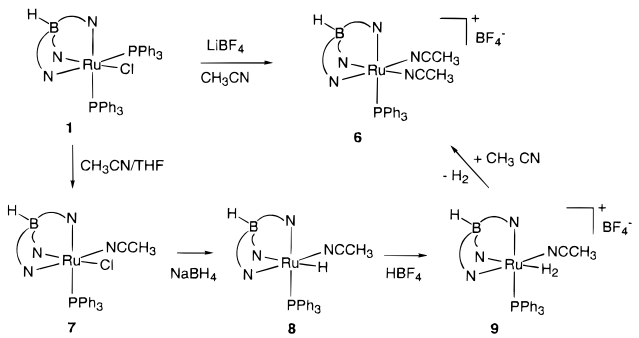


Figure 2. (a) ^{1}H NMR spectrum of [Ru(HB(pz)$_3$)(PPh$_3$)$_2$(H$_2$O)]BF$_4$ under Ar in CD_2Cl_2. (b) ^{1}H NMR spectrum of [Ru(HB(pz)$_3$)(PPh$_3$)$_2$(H$_2$O)]BF$_4$ under 10 atm of H_2 in CD_2Cl_2. (c) ^{1}H NMR spectrum of [Ru(HB(pz)$_3$)(PPh$_3$)$_2$(H$_2$O)]BF$_4$ under 10 atm of H_2 in CD_2Cl_2, after addition of 0.5 mL of H_2O. Peak with asterisks (from right to left) are as follows: grease, residue hexane, residue hexane, H_2O dissolved in CD_2Cl_2, coordinated H_2O, unknown, H_2O suspended in CD_2Cl_2, free H_2. (A) is an expansion of the η^2-H_2 and hydride peaks.

Scheme 1



ular dihydrogen complex [Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)(H$_2$)]BF$_4$, **9**, are summarized in Scheme 1. Treatment of RuCl(HB(pz)$_3$)(PPh$_3$)$_2$[19] with LiBF$_4$ in acetonitrile produced the bis-solvento complex [Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)$_2$]BF$_4$, **6**. Heating a THF/CH$_3$CN (9/1) solution of RuCl(HB(pz)$_3$)(PPh$_3$)$_2$ at 60 °C led to the displacement

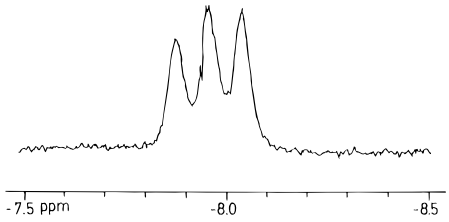


Figure 3. ^{1}H NMR spectrum of [Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)(HD)]BF$_4$ (400 MHz, CD_2Cl_2) in the high-field region. The spectrum was obtained using an inversion-recovery experiment with a delay (τ) set to 20 ms to null the residual signal of the η^2-H_2 isotopomer.

of one of the triphenylphosphine ligands by CH$_3$CN to form RuCl(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN), **7**. The lability of the triphenylphosphine ligand in RuCl(HB(pz)$_3$)(PPh$_3$)$_2$ is in sharp contrast to the inertness of the PPh$_3$ in the isoelectronic cyclopentadienide complex. Bruce *et al.* reported that reactions of CpRuCl(PPh$_3$)$_2$ with RCN afforded [CpRu(PPh$_3$)$_2$(RCN)]$^+$.[30,31] The ready displacement of PPh$_3$ from RuCl(HB(pz)$_3$)(PPh$_3$)$_2$ might be due to steric reasons given that the cone angle of HB(pz)$_3^-$ is 184°[32] while that of Cp$^-$ is only 110°.[33] Steric congestion in RuCl(HB(pz)$_3$)(PPh$_3$)$_2$ might result in labilization of one of the triphenylphosphine ligands. Reaction of RuCl(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN) with NaBH$_4$ in THF produced the yellow monohydride complex RuH(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN), **8**.

Acidification of a dichloromethane-d_2 solution of RuH(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN) with HBF$_4$·Et$_2$O yielded [Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)(H$_2$)]BF$_4$, **9**. Its ^{1}H NMR spectrum showed a broad hydride signal ($\omega_{1/2}$ = 37.2 Hz) at δ −7.86 ppm. T_1(min) for the broad hydride signal was determined to be 16 ms at 231 K (400 MHz). A small sharp peak of free H_2 at δ 4.61 was also observable in the spectrum. The free H_2 peak was not detected in the formation of **3** by protonation of RuH(HB(pz)$_3$)(PPh$_3$)$_2$. The deuterium isotopomer, [Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)(HD)]BF$_4$, was prepared by acidification of RuH(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN) with DBF$_4$. In its ^{1}H NMR spectrum at −60 °C, the deuterium isotopomer showed a broad 1:1:1 triplet (^{1}J(HD) = 33 Hz) centered at δ −7.95 ppm, after nulling the η^2-H_2 peak using the inversion-recovery method (see Figure 3). Unlike the η^2-HD isotopomer of **3**, H−P coupling was not resolved in this case, probably due to the shorter T_2 relaxation. In comparison to **3**, **9** is thermally less stable. Dissociation of H_2 from **9** generated unidentified species. The fact that complex **3** is more stable than **9** toward H_2 dissociation is understandable. Since triphenylphosphine is a stronger σ-donor than CH$_3$CN, the bis(triphenylphosphine) complex is more electron rich than the acetonitrile complex. Therefore, stronger M → σ*(H_2) back-bonding in **3** compared to that in **9** will render the former thermally more stable.

The weaker bonding of the H_2 ligand in the acetonitrile complex was further demonstrated by the fact that the complex [Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)(H$_2$)]BF$_4$, **9**,

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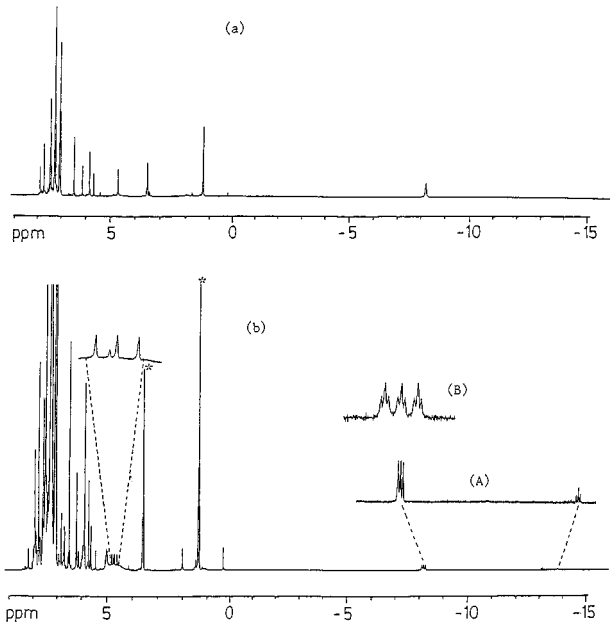


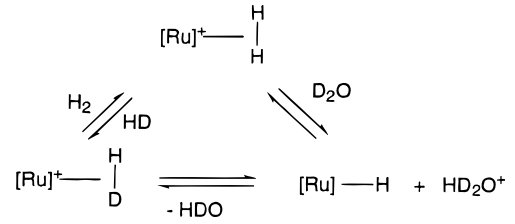
Figure 4. (a) ^{1}H NMR spectrum of $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$ prepared by acidification of $RuH(HB(pz)_3)(PPh_3)_2$ with $HBF_4 \cdot Et_2O$ in CD_2Cl_2. (b) ^{1}H NMR spectrum of the solution in (a) after addition of 0.2 mL of D_2O and then pressurization with 10 atm of H_2. Peaks marked with asterisks are due to Et_2O. (A) is an expansion of the η^2-H_2 and the hydride peaks, and (B) is a further expansion of the η^2-H_2 peak.

was not detected by ^{1}H NMR when a solution of $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)_2]BF_4$ was subjected to 20 atm of H_2. It is possible that dihydrogen complex **9** was formed under this condition, but the amount was too small to be detectable. Unfortunately, NMR studies at higher pressures were not feasible due to pressure limitation of the Wilmad pressure NMR tube.

H/D Exchange Reaction between H_2 and D_2O Catalyzed by $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$. The dihydrogen complex **3** catalyzes the H/D exchange reaction between H_2 and D_2O, as illustrated in Figure 4. Figure 4a shows the ^{1}H NMR spectrum of a CD_2Cl_2 solution of **3** prepared by acidification of $RuH(HB(pz)_3)(PPh_3)_2$ with $HBF_4 \cdot Et_2O$ in a Wilmad pressure-valved NMR tube. Figure 4b shows the ^{1}H NMR spectrum of the solution after adding excess D_2O (0.2 mL) and pressurizing the tube with 10 atm of H_2. The complexity of the $HB(pz)_3^-$ peaks in the low-field region indicates that the solution is a mixture of $[Ru(HB(pz)_3)(PPh_3)_2(L)]BF_4$ (L = H_2, HD, D_2), $RuX(HB(pz)_3)(PPh_3)_2$ (X = H, D), and a minute quantity of $[Ru(HB(pz)_3)(PPh_3)_2(H_xD_{2-x}O)]BF_4$. The presence of these species was confirmed by $^{31}P\{^1H\}$ NMR. An expansion in the upfield region of the ^{1}H NMR spectrum clearly reveals a triplet of a triplet signal at −8.20 ppm due to η^2-HD of $[Ru(HB(pz)_3)(PPh_3)_2(HD)]BF_4$ and a triplet at −13.99 ppm due to the metal hydride of $RuH(HB(pz)_3)(PPh_3)_2$. A small triplet due to free H−D (^1J(HD) = 42.6 Hz) can also be detected at δ 4.57 ppm, along with the peak of free H_2 at δ 4.61 ppm. Water peaks (H_2O and/or HDO resulting from H/D exchange between H_2 and D_2O) are also detectable. The H/D exchange reaction between H_2 and D_2O catalyzed by **3** can be explained by the mechanism depicted in Scheme 2.

Similar mechanisms have been proposed previously, for example, for the isotope exchange between H_2O and

Scheme 2. Proposed Mechanism for H/D Exchange between H_2 and D_2O Catalyzed by $[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$, Where [Ru] = $[Ru(HB(pz)_3)(PPh_3)_2]$



D_2 in a solution of $[W(CO)_3(P\text{-}i\text{-}Pr_3)_2(D_2)]$[8] and for intramolecular proton exchange reactions in [RhH(CO)-($^{bu}S_4$)] ($^{bu}S_4$ = 1,2-bis((2-mercapto-3,5-di-*tert*-butylphenyl)thio)ethanato(2−))[27a] and $[IrH_2(HS(CH_2)_3SH)(PCy_3)_2]^+$.[10] There are several other reported cases of H/D exchange reactions between deuterated solvents and H_2 involving dihydrogen complexes.[6,7,9]

Catalytic Hydrogenation of Olefins with $[Ru(HB(pz)_3)(PPh_3)_2(CH_3CN)]BF_4$ (4) and $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)_2]BF_4$ (6). In this study, catalytic hydrogenation of olefins was carried out with **4** and **6** in THF solution (anhydrous or with addition of H_2O) at 110 °C and under 40 atm H_2. Tables 1 and 2 show the results of hydrogenation of olefins catalyzed by **4** and **6**, respectively. For both **4** and **6,** enhancement of catalytic activity was observed in the presence of water or NEt_3, but addition of aqueous HBF_4 led to catalytic activities (see entries 2 and 7 in Table 1; entries 2 and 7 in Table 2) comparable to those in anhydrous THF for both **4** and **6**. This phenomenon will be discussed later. Addition of 4 equiv of PPh_3 or 1 mL of CH_3CN to the reaction with **4** resulted in decrease of activity. These observations indicate that the CH_3CN molecule and one of the phosphine ligands in **4** must dissociate to provide two sites for the substrate and H_2. In the case of **6**, addition of 2 equiv of PPh_3 did not have any significant effect on the catalytic activity, while, in the presence of 1 mL of CH_3CN, the conversion of styrene to ethyl benzene decreased significantly. Thus it is likely that, in catalytic hydrogenation with **6**, only two CH_3CN ligands must be dissociated. The olefinic function in benzylideneacetone was preferentially reduced over the carbonyl group in both systems. The homogeneity of the systems was established by addition of 1 drop of Hg to each, with no observed pernicious effect on the catalytic activity.[34]

The enhancement effect of water on the catalytic activities of **4** and **6** in the hydrogenation reactions lead to the belief that H_2O is an active participant in the catalytic reactions. We therefore studied the catalytic hydrogenation of styrene with **4** and **6** in the presence of D_2O, in the hope that analysis of the distribution of deuterium in the hydrogenation products would shed some light on the role of water in the catalysis. When D_2O, instead of H_2O, was added to the system, incorporation of deuterium into the products of styrene hydrogenation was observed. Analysis of the products in entry 3 of Table 1 by a combination of ^{1}H, ^{2}H, and $^{13}C\{^1H\}$ NMR spectroscopy and EI-MS gave the following results: Ph−CH_2CH_3 (55%), Ph−CHD−CH_3 (3%), Ph−CH_2−CH_2D (31%), Ph−CHD−CH_2D (11%). Deu-

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Table 1. Catalytic Hydrogenation of Olefins with $[Ru(HB(pz)_3)(PPh_3)_2(CH_3CN)]BF_4$[a]

entry	substrate	additive (amt)	product (% conversion)[b]
1	styrene	none	ethylbenzene (34)
2	styrene	H_2O (1 mL)	ethylbenzene (95)
3	styrene[c]	D_2O (2 mL)	deuterated ethylbenzene (35) ethylbenzene (44)
4	styrene	PPh_3 (4 equiv)	ethylbenzene (4)
5	styrene	CH_3CN (1 mL)	ethylbenzene (19)
6	styrene	NEt_3 (1 mL)	ethylbenzene (82)
7	styrene	HBF_4 (aq, 1 mL)	ethylbenzene (35)
8	styrene	Hg (1 drop)	ethylbenzene (34)
9	1-octene	none	n-octane (71), 2-octene (11)
10	1-octene	H_2O	n-octane (91), 2-octene (3)
11	norbornene	none	norbornane (68)
12	norbornene	H_2O (1 mL)	norbornane (97)
13	cyclohexene	H_2O (1 mL)	cyclohexane (30)
14	methyl acrylate[d]	H_2O (1mL)	methyl propionate (93)
15	diethyl maleate	H_2O (1 mL)	diethyl succinate (33)
16	butyl vinyl ether	H_2O (1 mL)	butyl ethyl ether (27)
17	2,3-dimethylbutene	H_2O (1 mL)	2,3 - dimethylbutane (15)
18	benzylideneacetone	H_2O (1 mL)	4-phenylbutan-2-one (8)
19	3-nonanone	H_2O (1 mL)	none

[a] Typical reaction conditions: catalyst = 0.01 mmol, substrate = 0.01 mol, solvent = THF (10 mL), H_2 = 40 atm, reaction time = 4 h, temperature = 110 °C. [b] Based on substrate used. [c] Catalyst = 0.02 mmol, substrate = 0.02 mol, solvent = THF (20 mL), and reaction time = 3 h. [d] Solvent = CH_3OH (20 mL).

Table 2. Catalytic Hydrogenation of Olefins with $[Ru(HB(pz)_3)(PPh_3)(CH_3CN)_2]BF_4$[a]

entry	substrate	additive (amt)	product (% conversion)[b]
1	styrene	none	ethylbenzene (29)
2	styrene	H_2O (1 mL)	ethylbenzene (92)
3	styrene[c]	D_2O (2 mL)	deuterated ethylbenzene (34) ethylbenzene (62)
4	styrene	PPh_3 (2 equiv)	ethylbenzene (29)
5	styrene	CH_3CN (1 mL)	ethylbenzene (8)
6	styrene	NEt_3 (1 mL)	ethylbenzene (75)
7	styrene	HBF_4(aq) (1 mL)	ethylbenzene (30)
8	styrene	Hg (1 drop)	ethylbenzene (28)
9	1-octene	none	*n*-octane (84), 2-octene (16)
10	1-octene	H_2O (1 mL)	*n*-octane (95), 2-octene (5)
11	1-octene[d]	H_2O (1 mL)	*n*-octane (20)
12	norbornene	none	norbornane (50)
13	norbornene	H_2O (1 mL)	norbornane (97)
14	cyclohexene[d]	H_2O (1 mL)	cyclohexane (76)
15	methyl acrylate[e]	H_2O (1 mL)	methyl propionate (98)
16	diethyl maleate	H_2O (1 mL)	diethyl succinate (60) diethyl fumarate (20)
17	butyl vinyl ether	H_2O (1 mL)	butyl ethyl ether (43)
18	3,3-dimethylbutene	H_2O (1 mL)	2,2-dimethylbutane (71)
19	benzylideneacetone	H_2O (1 mL)	4-phenylbutan-2-one (48) 1-phenylbut-1-en-ol (2) 4-phenylbutan-2-ol (2)

[a] Typical reaction conditions: catalyst = 0.01 mmol, substrate = 0.01 mol, solvent = THF (10 mL), H_2 = 40 atm, temperature = 110 °C, reaction time = 4 h. [b] Based on substrate. [c] Catalyst = 0.02 mmol, substrate = 0.02 mol, solvent = THF (20 mL), and reaction time = 6 h. [d] Temperature = 90 °C. [e] Solvent = methanol (10 mL).

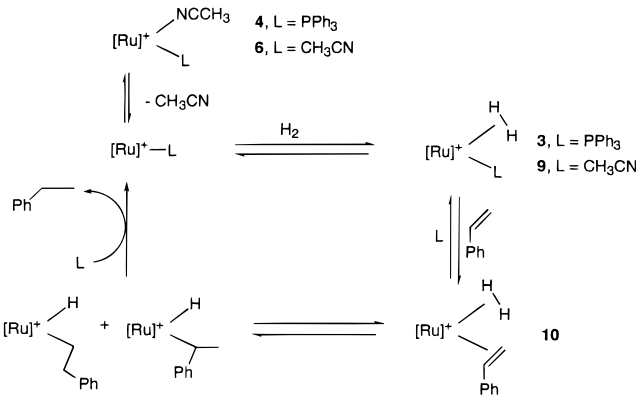
terium distribution in the product of entry 3 of Table 2 is as follows: $Ph-CH_2-CH_3$ (65%), $Ph-CHD-CH_3$ (6%), $Ph-CH_2-CH_2D$ (25%), $Ph-CHD-CH_2D$ (4%).

In order to study the fate of complexes **4** and **6** in the hydrogenation reactions, we have attempted to identify ruthenium-containing species after the hydrogenation reactions. It can be shown that complexes **4** and **6** can be recovered after the hydrogenation reactions. Thus a light yellow solid was obtained by removing the solvents of the reaction mixture of hydrogenation of cyclohexene in hydrous THF using **6** as the catalyst (or catalytic precursor). The ^{31}P NMR of the solid exhibited a major singlet signal due to complex **6** and several small singlet signals due to other unidentified phosphine-containing species which we suspect to be $[Ru(HB(pz)_3)(PPh_3)(S)(S')]^+$ (S = CH_3CN, THF, H_2O; S′ = THF, H_2O). Refluxing a THF/CH_3CN (9/1) solution of the light yellow solid for 8 h resulted in complete conversion of $[Ru(HB(pz)_3)(PPh_3)(S)(S')]^+$ to **6**. Similarly, a yellow solid could be obtained in the cyclohexene hydrogenation reaction in hydrous THF using **4** as the catalyst (or catalytic precursor). The ^{31}P NMR of the solid indicated that it is a mixture of **4** (major), free PPh_3, **6** (minor), and small amounts of other unidentified species which can all be converted to **6** on refluxing in THF/CH_3CN (9/1).

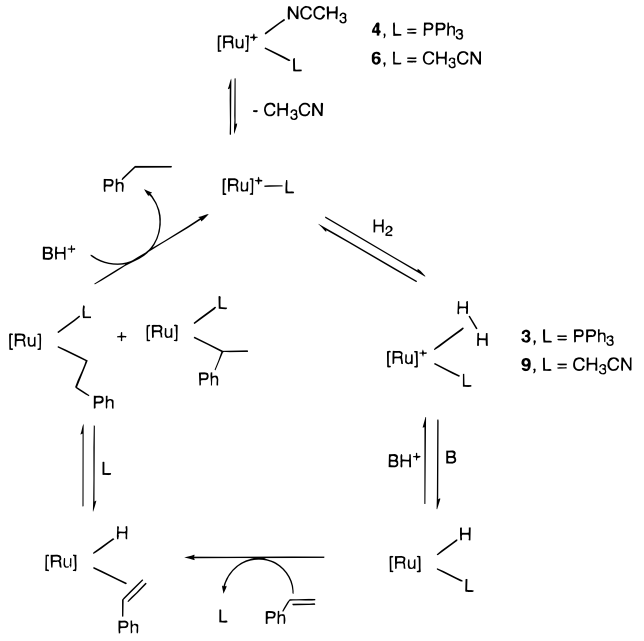
Discussion

Mechanism of Hydrogenation in Anhydrous THF. It is evident from Tables 1 and 2 that in anhydrous THF, **4** and **6** show moderate activities in catalytic hydrogenation of olefins. A mechanism (using styrene as an example) different from the common dihydride mechanism analogous to that involving Wilkin-

Scheme 3. Proposed Mechanism for Hydrogenation of Styrene in Anhydrous THF ([Ru] = [Ru(HB(pz)$_3$)(PPh$_3$)]; L = PPh$_3$, CH$_3$CN)



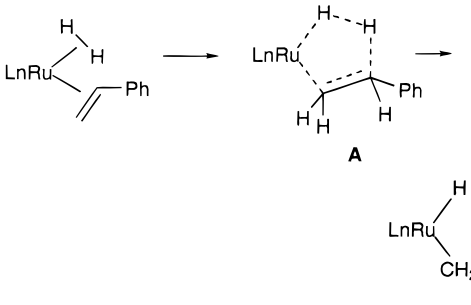
Scheme 4. Alternative Mechanism for the Hydrogenation of Styrene in the Presence of Water and NEt$_3$ ([Ru] = [Ru(HB(pz)$_3$)(PPh$_3$)]; L = PPh$_3$, CH$_3$CN; B = H$_2$O, NEt$_3$)

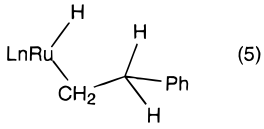


sons' catalyst[35] is suggested for the hydrogenation of olefins catalyzed by **4** or **6** in anhydrous THF (see Scheme 3).

The generation of the dihydrogen complex **3** from **4** under H_2 pressure has been established through the high-pressure ^{1}H NMR study mentioned in previous discussion. Although the formation of **9** from **6** was not unequivocally ascertained under 20 atm of H_2 in the NMR study, it is possible that a catalytic amount of **9** was formed given the fact that the catalytic reactions were carried out under higher H_2 pressure (40 atm) and the fact that **3** and **9** can be produced in a similar manner through acidification of their respective hydride precursors. Formation of the dihydrogen intermediate [Ru(HB(pz)$_3$)(PPh$_3$)(olefin)(H$_2$)]BF$_4$ (**10**) or the dihydride intermediate [RuH$_2$(HB(pz)$_3$)(PPh$_3$)(olefin)]BF$_4$ is consistent with the lower catalytic activity when excess PPh$_3$ or CH$_3$CN was present. However, we believe that involvement of the dihydride complex [RuH$_2$(HB(pz)$_3$)(PPh$_3$)(olefin)]BF$_4$ is unlikely, because oxidative addition of H_2 to the less electron rich fragment [Ru(HB(pz)$_3$)(PPh$_3$)(olefin)]$^+$ is not expected since the more electron rich fragment [Ru(HB(pz)$_3$)(PPh$_3$)$_2$]$^+$ forms the stable dihydrogen complex **3** (note PPh$_3$ is a better electron donor than olefins like PhCH=CH$_2$).

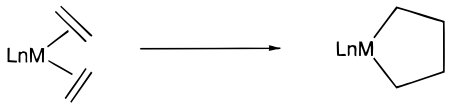
Five-membered ring species like **A** can be proposed as the transition structures for the conversion of [Ru(HB(pz)$_3$)(PPh$_3$)(olefin)(H$_2$)]BF$_4$ to [RuH(alkyl)(HB(pz)$_3$)(PPh$_3$)]BF$_4$ (see eq 5). This step could be formally





(5)

regarded as an oxidative coupling reaction between η^2-H$_2$ and η^2-olefin. Formation of five-membered ring metallocycles via oxidative coupling reactions involving η^2-olefin/η^2-olefin (e.g. eq 6), η^2-olefin/η^2-alkyne, and η^2-



(6)

alkyne/η^2-alkyne are well-established reactions.[36] Species like **A** have recently been studied theoretically.[37] It is noted that four-membered ring transition structures involving the H_2 ligand have been previously proposed for some metathesis reactions.[38]

Mechanism of Hydrogenation in the Presence of H$_2$O and NEt$_3$. While Scheme 3 could account for the catalytic activity of **4** and **6** in anhydrous THF, it fails to explain the enhanced catalytic activity in the presence of water or NEt$_3$. Thus a mechanism other than that in Scheme 3 may also be involved. An additional mechanism for the hydrogenation reactions of olefins (using styrene as an example) catalyzed by **4** or **6** in the presence of H$_2$O or NEt$_3$ is proposed in Scheme 4. In this mechanism, the first step in the catalytic cycle is the generation of the dihydrogen complex **3** or **9**, respectively, when **4** or **6** is subjected to H_2 pressure. This step has been established previously. The establishment of the [Ru]−(η^2-H$_2$) ↔ [Ru]−(H) equilibrium illustrated in eq 4 lends support to the second step of the catalytic cycle. The catalytic cycle is completed by insertion of an olefin into the Ru−H bond followed by protolysis of Ru−alkyls with H$_3$O$^+$ or HNEt$_3^+$. The last two steps are well documented in organometallic chemistry.[39] Thus in this proposed mechanism, olefins are reduced through a stepwise H$^-$/H$^+$ transfer process.

(35) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc.* **1966**, 1711.

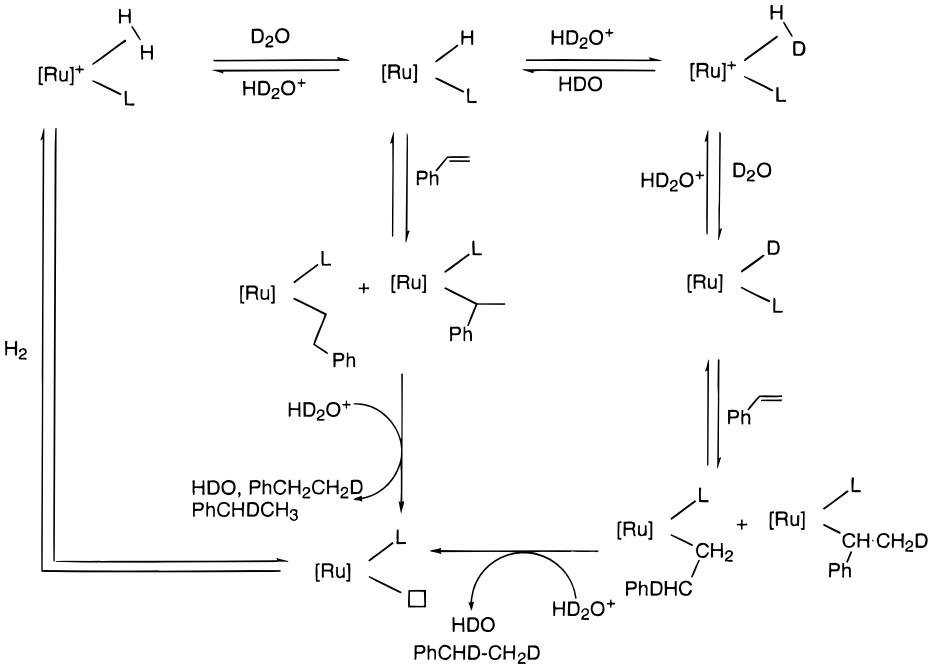
(36) Crabtree, R. H. *The Organometallic Chemistry of the Transitional Metals*, 2nd ed.; Wiley: New York, 1994; Chapter 6.

(37) Holthausen, M. C.; Fiedler, A.; Schwarz, H.; Koch, W. *Angew. Chem., Int. Ed. Engl.* **1995,** *34*, 2282.

(38) Ziegler, T.; Folga, E.; Berces, A. *J. Am. Chem. Soc.* **1993**, *115*, 636 and references therein.

(39) See for example: Collman, J. P.; Hegdus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

Scheme 5. Proposed Mechanism for the Formation of Deuterated Products in the Hydrogenation of Styrene in the Presence of D_2O, Where [Ru] = [Ru(HB(pz)$_3$)(PPh$_3$)] (L = PPh$_3$, CH$_3$CN) and HD_2O^+ Represents Deuterated Species $H_xD_{3-x}O^+$



The effect of acids, water, and NEt_3 on the catalytic activities of complexes **4** and **6** can be explained by assuming that the hydrogenation products were produced by both pathways shown in Schemes 3 and 4. The catalytic activities increased in the presence of water or NEt_3 because reactions involving the mechanism in Scheme 4 are now possible. Both water and NEt_3 can act as a base to deprotonate the η^2-H_2 ligand to generate the active hydride species. It was noted that the enhancement effect of the amine is less pronounced than that of water. The slightly lower enhancement effect of NEt_3 compared to that of H_2O is probably due to NEt_3 being a keen competitor with the substrate molecule in binding to the ruthenium center in the catalytic reaction or to $HNEt_3^+$ being a weaker acid than H_3O^+ so that protonation of the metal alkyl is more difficult. It can be seen in entry 7 of Table 1 and entry 7 of Table 2 that addition of 1 mL of diluted aqueous HBF_4 to either one of the systems resulted in a yield of ethylbenzene nearly identical to that of the reactions performed in anhydrous THF. It can be visualized that the acid quenched the water-promoted reaction pathway of Scheme 4 by pushing the [Ru]−(η^2-H_2) ↔ [Ru]−(H) equilibrium far to the side of the dihydrogen complex and the reactions had to follow the pathway of Scheme 3, and therefore, the catalyses proceeded as if they were performed in anhydrous solutions.

The reaction pathway depicted in Scheme 4 accounts not only for the increase in catalytic activity in the presence of water and NEt_3, but also for the distribution of deuterium in the reaction product (ethylbenzene) in the D_2O-promoted hydrogenation of styrene. Scheme 5 describes the mechanism for deuterium incorporation in the hydrogenation products through the pathway of Scheme 4. According to Scheme 5, deuterium can be incorporated into the hydrogenation products at the last step (protonation of Ru−alkyls with $D_xH_{3-x}O^+$). The higher percentage of deuterium incorporated into the methyl group of ethylbenzene in the D_2O-promoted hydrogenation reactions of styrene is expected from the mechanism as $PhCH_2CH_2D$ was produced from the more stable Ru−CH_2CH_2Ph intermediate (compared to Ru−$CH(CH_3)Ph$).

It is also noted that, in either one of the D_2O-promoted reactions, small amounts of dideuterated ethylbenzene ($PhCHDCH_2D$) were produced. As shown in Scheme 5, $PhCHDCH_2D$ can be produced via ruthenium deuteride complexes as a result of H/D exchange reactions between H_2 and D_2O. It should also be pointed out that deuterated complexes [Ru(HB(pz)$_3$)(L)(HD)]BF_4 and/or [Ru(HB(pz)$_3$)(PPh$_3$)(L)(D_2)]BF_4 resulted from H/D exchange can also enter the minor reaction pathway of Scheme 3 to generate mono- and/or dideuterated ethylbenzene.

Concluding Remarks. In spite of intensive studies on the synthesis, spectroscopic characterization, theoretical aspects, and stability of dihydrogen complexes in the last decade, the catalytic properties of this class of complexes have received relatively little attention. Among the reported applications of dihydrogen complexes to catalytic hydrogenation of unsaturated organic substrates, the dihydrogen complexes usually have both M(H_2) and M−H functional groups. In these catalytic systems, the H_2 ligand usually serves as a good leaving group to provide a vacant site, for example, in the hydrogenation of 2-butyne[3a] with [Ir(H_2)H_2(PMe$_2$Ph)$_3$]$^+$, hydrogenation of 9-methylanthracene and cyclohexanone[3b] with $RuH_2(H_2)(PPh_3)_3$, and hydrogenation of phenylacetylene[3c] and benzylideneacetone[3d] with Os(H_2)HCl(CO)(PR_3)$_2$ (PR_3 = P-*i*-Pr$_3$, PMe-*t*-Bu$_2$). Catalytic systems involving dihydrogen complexes directly in catalytic cycles are still limited. The selective hydrogenation of 1-alkynes to alkenes by [Fe(H_2)H(pp_3)]$^+$ [pp_3 = P($CH_2CH_2PPh_2$)$_3$] provides a rare example in which the dihydrogen complex is thought to be within the catalytic cycle. In the proposed mechanism, hydrogenation proceeds via migration of the hydride to give a vinyl intermediate with the H_2 and σ-vinyl ligands being

mutually cis-disposed. The catalytic cycle is completed by intramolecular protonation of the adjacent vinyl ligand by an η^2-H_2 ligand to give the alkene.[11] Thus reduction of unsaturated substrates can be achieved via intramolecular acid/base reactions, without going through oxidative addition steps. Similar mechanisms are probably involved in catalytic hydrogenation and hydrosilylation reactions using $Os(H_2)HCl(CO)(PR_3)_2$.[3c,h]

The present study indicates that dihydrogen complexes $[Ru(HB(pz)_3)(PPh_3)(L)(H_2)]BF_4$ (L = PPh_3, CH_3CN) are likely involved in hydrogenation of olefins catalyzed by **4** and **6**. There are reports on hydrogenation reactions catalyzed by ruthenium poly(pyrazolyl)borate complexes. $RuCl(HB(pz)_3)(PhCN)_2$ and $RuCl(Bpz_4)(PhCN)_2$ were reported to be active catalysts for olefin hydrogenation in the presence of triethylamine.[40] Chaudret and co-workers recently showed that the hydride complexes $RuH\{HB(3,5\text{-}Me_2pz)_3\}(COD)$ and $RuH(H_2)\{HB(3,5\text{-}Me_2pz)_3\}$ exhibited good catalytic activities for the reduction of unactivated ketones either by dihydrogen at 3 or 4 atm or by hydrogen transfer from alcohols in basic media.[41] They have shown that, in the hydrogenation reaction with $RuH\{HB(3,5\text{-}Me_2pz)_3\}(COD)$, high pressure of dihydrogen inhibited the catalytic reaction. This unexpected pressure effect was attributed to the stability and lack of reactivity of $RuH(H_2)\{HB(3,5\text{-}Me_2pz)_3\}$, which precipitated out of the solution in these conditions. Contrary to Chaudret's hydride complexes, **4** and **6** show very little activity toward hydrogenation of olefins at low hydrogen pressure (3−5 atm). The requirement of higher hydrogen pressure is consistent with the generation of dihydrogen complexes in the catalytic reactions. In anhydrous THF, it is proposed that an intermediate containing cis-disposed η^2-H_2 and π-bonded olefin is involved, and stepwise hydrogen transfer from the η^2-H_2 ligand to the coordinated olefin yields the products. In the presence of water, H_2O acts as a base to deprotonate the η^2-H_2 to form ruthenium hydride intermediates. Hydride shift to the coordinated olefin gives the metal alkyl, which is then cleaved by H_3O^+ to yield the alkane. Such mechanisms involving dihydrogen complexes could explain the enhanced catalytic activity in the presence of water and incorporation of deuterium in the hydrogenation products in the presence of D_2O. The catalyst recovery experiments demonstrated that **4** and **6** did not undergo decomposition in the catalytic reactions. They functioned as catalyst precursors dissociating the phosphine and/or acetonitrile ligands to provide vacant sites for H_2 and the substrates. In summary, this study provides additional examples of direct involvement of dihydrogen complexes in catalytic hydrogenation of olefins.

Experimental Section

All reactions were performed under an atmosphere of dry nitrogen or argon using standard Schlenk techniques. Solvents were distilled under nitrogen with appropriate drying agents (solvent/drying agent): Methanol/Mg−I_2; ethanol/Mg−I_2; *n*-butanol/Mg−I_2; acetonitrile/P_2O_5; dichloromethane/P_2O_5; tetrahydrofuran/Na−benzophenone; diethyl ether/CaH_2; *n*-hexane/Na.[42] Ruthenium trichloride ($RuCl_3 \cdot 3H_2O$) and lithium tetrafluoroborate were purchased from Aldrich. Pyrazole, sodium borohydride, and tetrafluoroboric acid in ethereal solution ($HBF_4 \cdot Et_2O$, 56%) were obtained from Fluka. These chemicals were used as received. Triphenylphosphine was obtained from Merck and was recrystallized from ethanol before use. Substrates used for hydrogenation studies were obtained from Aldrich, Fluka, or Acros. Their purities were checked by NMR spectroscopy and GC, and when necessary, the reagents were distilled under nitrogen prior to use. Potassium hydrotris(1-pyrazolyl)borate,[43] $RuCl_2(PPh_3)_3$,[44] and $RuCl(HB(pz)_3)(PPh_3)_2$[19] were synthesized according to published procedures. High-purity hydrogen gas was supplied by Hong Kong Oxygen and was used directly.

Infrared spectra were obtained from a Nicolet Magna 750 FT-IR spectrophotometer or a Perkin-Elmer 983 Model IR spectrophotometer. ^1H NMR spectra were taken on a Jeol FX90Q, a Jeol GX-400, or a Bruker DPX-400 spectrometer. Chemical shifts (δ, ppm) are reported relative to tetramethylsilane (TMS). $^{13}C\{^1H\}$ NMR spectra were taken on a Bruker ARX-300 spectrometer or a Jeol GX-400 NMR spectrometer, and the chemical shifts were internally referenced to solvent $CDCl_3$ (δ 77.0). $^{31}P\{^1H\}$ NMR spectra were taken on a Jeol GX-400, a Bruker DPX-400, or a Bruker ARX-300 spectrometer. ^{31}P chemical shifts were externally referenced to 10% $P(OMe)_3$ solution in $CDCl_3$ (δ 140.4). T_1 relaxation measurements were carried out in CD_2Cl_2 at 400 MHz by the inversion-recovery method using standard 180°-τ-90° pulse sequences. High-pressure NMR studies were performed using a Wilmad pressure-valved NMR tube; the maximum pressure used was 20 atm (room temperature). FAB MS was carried out with a Finnigan MAT-90 mass spectrometer using nitrobenzyl alcohol as matrix. Gas chromatography was carried out using a Perkin-Elmer Sigma 3B apparatus equipped with an FID. A 25 m × 0.32 mm OV-1 capillary column or a 50 m × 0.32 mm OV-17 capillary column was used for product analyses. Elemental analyses were performed by Butterworth Laboratories Ltd., London, U.K., and the Institute of Chemistry, Academia Sinica, Beijing, China.

$RuH(HB(pz)_3)(PPh_3)_2$, 2. A sample of $RuCl(HB(pz)_3)(PPh_3)_2$ (0.20 g, 0.23 mmol) and 0.09 g (2.4 mmol) of sodium borohydride were added to a nitrogen-flushed two-necked round bottom flask fitted with a condenser. The setup was evacuated and then filled with nitrogen, and this procedure was repeated three times. Degassed and freshly distilled ethanol (40 mL) was added to the flask through a cannular, and the reaction mixture was refluxed for 3 h. After the mixture was cooled to room temperature, a yellow solid settled out and was filtered out under nitrogen. The solid was washed with a few portions of degassed ethanol and then dried under vacuum for 8 h. Yield: 0.15 g (77%). Anal. Calcd for $C_{45}H_{41}BN_6P_2Ru$: C, 64.37; H, 4.92; N, 10.01. Found: C, 64.62; H, 5.01; N, 10.32. IR (KBr, cm^{-1}): ν(Ru−H) 2008 (w), ν(B−H) 2448 (br, med). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ −14.06 (t, ^2J(HP) = 26.4 Hz, 1H, Ru−*H*), 5.42 [t, 2H, H^4(pz′)], 5,72 [t, 1H, H^4(pz)], 6.35 [d, 1H, H^5(pz)], 6.68 [d, 2H, H^5(pz′)], 6.88−7.09 (m, 30H, PC_6H_5) 7.32 [d, 2H, H^3(pz′)], 7.64 [d, 1H, H^3(pz)] (pz = pyrazolyl group trans to hydride, pz′ = pyrazolyl group trans to PPh_3, all coupling constants for pyrazolyl proton resonance were about 2 Hz). $^{31}P\{^1H\}$ NMR (161.70 MHz, $CDCl_3$, 25 °C): δ 66.2 (s). FAB-MS (nba matrix) (*m*/*z*): 840, $[M]^+$; 576 $[M - H - PPh_3]^+$; 510, $[M - H - PPh_3 - pz]^+$.

$[Ru(HB(pz)_3)(PPh_3)_2(H_2)]BF_4$, 3. Tetrafluoroboric acid in ethereal solution (20 μL, $HBF_4 \cdot Et_2O$, 56%) was added to a dichloromethane solution of $RuH(HB(pz)_3)(PPh_3)_2$ (30 mg, 0.036 mmol in 2 mL of dichloromethane) in a small Schlenk sample tube under nitrogen. After the solution was shaken

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for a while, 10 mL of degassed hexane was layered onto the solution. The mixture was allowed to stand for 1 day. Diffusion of hexane into the dichloromethane solution resulted in formation of yellow crystals. The crystals were collected by filtration, washed with hexane under nitrogen, and dried under vacuum overnight. Yield: 24 mg (80%). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ −8.20 [br, $\omega_{1/2}$ = 27 Hz, 2H, Ru−(H_2)]; 5.75 [t, 1H, H^4(pz); 5.92 [t, 2H, H^4(pz′)]; 6.23 [d, 1H, H^5(pz); 6.54 [d, 2H, H^5(pz′)]; 7.06−7.55 (m, 30H, PC_6H_5); 7.80 [d, 2H, H^3(pz′)]; 7.96 [d, 1H, H^3(pz)] (pz = pyrazolyl group trans to η^2-H_2, pz′ = pyrazolyl group trans to PPh_3; all coupling constants for pyrazolyl proton resonance were about 2 Hz). ^{31}P NMR (161.70 MHz, $CDCl_3$, 25 °C): δ 43.4 (s). Variable-temperature T_1 measurements on the η^2-H_2 signal were carried out by the inversion-recovery method using standard 180°−τ−90° pulse sequences. T_1 (400 MHz, CD_2Cl_2, ms): 32 (297 K), 27 (283 K), 25 (273 K), 23 (263 K), 22 (253 K), 21 (243 K), 21 (233 K), 23 (223 K), 30 (203 K). T_1(min) (21 ms at 240 K and 400 MHz) was obtained from the "V"-shaped ln T_1 vs 1000/T plot.[45]

[Ru(HB(pz)$_3$)(PPh$_3$)$_2$(HD)]BF$_4$, 3-*d*$_1$. The HD isotopomer of **3** was not isolated but was prepared and observed in an NMR tube. Thus a sample of 10 mg of RuH(HB(pz)$_3$)(PPh$_3$)$_2$ was loaded into a 5 mm NMR tube which was then capped with a rubber septum. The tube was evacuated and filled with nitrogen, and this procedure was repeated three times. Dichloromethane-d_2 (0.5 mL) was syringed in to dissolve the sample, followed by addition of 6 μL of DBF_4 solution (prepared by adding 0.1 mL of D_2O into 0.4 mL of 56% HBF_4·Et_2O) through a microsyringe. The ^{1}H NMR spectrum of the resulting solution was then taken. The η^2-HD signal (δ −8,25 (tt), ^1J(HD) = 32.0 Hz, ^2J(HP) = 6.5 Hz) was observed after nulling the η^2-H_2 peak at δ −8.20 using the inversion-recovery method with a delay time of 20 ms.

[Ru(HB(pz)$_3$)(PPh$_3$)$_2$(CH$_3$CN)]BF$_4$, 4. A sample of RuH(HB(pz)$_3$)(PPh$_3$)$_2$ (0.50 g, 0.59 mmol) was added to a two-necked round bottom flask which was evacuated and flushed with nitrogen. Degassed dichloromethane (100 mL) was added to the flask through a cannular, and degassed acetonitrile (0.5 mL) was added using a syringe and needle. The mixture was stirred for 15 min. One equivalent (20 μl) of tetrafluoroboric acid in ethereal solution (HBF_4·Et_2O, 56%) was added through a syringe. The mixture was stirred for 0.5 h. At the end of the reaction, the solution was concentrated to a few milliliters and a creamy-white solid precipitated out. The solid was filtered out and washed with diethyl ether. Finally, it was collected and dried under vacuum at room temperature. Yield: 0.47 g (83%). Anal. Calcd for $C_{47}H_{43}B_2F_4N_7P_2Ru$: C, 58.41; H, 4.48; N, 10.14. Found: C, 58.72; H, 4.35; N, 10.30. IR (KBr, cm^{-1}): ν(C≡N) 2276 (w); ν(B−H) 2487 (br, med). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 2.17 (s, 3H, CH_3CN); 5.49 [t, 1H, H^4(pz)]; 5.76 [t, 2H, H^4(pz′)]; 6.14 [d, 1H, H^5(pz)]; 6.32 [d, 2H, H^5(pz′)]; 6.83−7.26 (m, 30H, PC_6H_5); 7.64 [d, 2H, H^3-(pz′); 7.74 [d, 1H, H^3(pz)] (pz = pyrazolyl group trans to CH_3-CN, pz′ = pyrazolyl group trans to PPh_3; all coupling constants for pyrazolyl proton resonance were about 2 Hz). ^{31}P{^{1}H} NMR (161.1 MHz, $CDCl_3$, 25 °C): δ 40.1 (s).

[Ru(HB(pz)$_3$)(PPh$_3$)$_2$(H$_2$O)]BF$_4$, 5. A sample of 0.50 g (0.59 mmol) of RuH(HB(pz)$_3$)(PPh$_3$)$_2$ was added to a 50 mL two-necked pear-shaped flask under nitrogen. Degassed dichloromethane (2 mL) was syringed into the flask, followed by addition of slightly over 1 equiv of tetrafluoroboric acid in ethereal solution (20 μL, HBF_4·Et_2O, 56%). After the mixture was stirred at room temperature for 5 min, 1 mL of H_2O was added to the mixture, and the resulting solution was stirred for a further 10 min. Addition of degassed hexane (30 mL) led to the precipitation of a yellowish brown solid. This was then filtered out and dried under vacuum. Yield: 0.42 g (75%). Anal. Calcd for $C_{45}H_{42}B_2F_4N_6OP_2Ru$: C, 57.29; H, 4.49; N, 8.91. Found: C, 57.95; H, 4.60; N, 8.82. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.54 (br, s, 2H, H_2O); 5.39 [t, 1H, H^4(pz)]; 5.71 [d, 1H, H^5(pz)]; 5.79 [t, 2H, H^4(pz′)]; 6.54 [d, 2H, H^5(pz′)]; 6.94−7.30 (m, 30H, PC_6H_5); 7.63 [d, 2H, H^3(pz′)]; 7.71 [d, 1H, H^3(pz)] (pz = pyrazolyl group trans to H_2O, pz′ = pyrazolyl group trans to PPh_3; all coupling constants for pyrazolyl proton resonance were about 2 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 40.4 (s).

[Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)$_2$]BF$_4$, 6. Samples of 0.50 g (0.57 mmol) of RuCl(HB(pz)$_3$)(PPh$_3$)$_2$ and 0.054 g (0.57 mmol) of $LiBF_4$ were added to a two-necked round bottom flask fitted with a condenser. The setup was flushed with nitrogen for 15 min. Distilled acetonitrile (50 mL) was added through a cannular under nitrogen. The mixture was refluxed for 4 h, and the resulting pale yellow solution, which was suspended with white fine solids, was filtered through Celite under nitrogen. The pale yellow filtrate solution was concentrated to a few milliliters, and diethyl ether was added to obtain an off-white fine solid, which was filtered out and washed with ether. Finally the solid was vacuum-dried at room temperature for 8 h. Yield: 0.26 g (52%). Anal. Calcd for $C_{31}H_{31}B_2F_4N_8PRu$: C, 49.96; H, 4.19; N, 15.03. Found: C, 49.73; H, 4.00; N, 14.73. IR (KBr, cm^{-1}): ν(B−H) 2488 (br, med), ν(C≡N) 2281 (w), ν(B−F) 1084 (br, vs). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 2.23 (s, 6H, CH_3CN), 5.83 [t, 2H, H^4(pz)], 6.22 [t, 1H, H^4(pz′)], 6.61 [d, 2H, H^5(pz)], 7.04−7.35 (m, 15H, PC_6H_5), 7.58 [d, 1H, H^5(pz′)], 7.64 [d, 2H, H^3(pz)], 8.04 [d, 1H, H^3(pz′)] (pz = pyrazolyl group trans to CH_3CN; pz′ = pyrazolyl group trans to PPh_3; all coupling constants for pyrazolyl proton resonance were about 2 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 45.6 (s).

RuCl(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN), 7. A sample of 0.50 g (0.57 mmol) of RuCl(HB(pz)$_3$)(PPh$_3$)$_2$ was added to a two-necked round bottom flask fitted with a condenser, and the system was evacuated and flushed with nitrogen. A degassed solution mixture of tetrahydrofuran and acetonitrile (30 mL) in 9:1 ratio was added through a syringe. The solution was stirred under nitrogen at 60 °C for 6 h. At the end of the reaction, the solution was concentrated to a few milliliters and a yellow solid precipitated out. The solid was filtered out and washed with diethyl ether and then hexane. Finally, it was collected and dried under vacuum at room temperature. Yield: 0.26 g (67%). Anal. Calcd for $C_{29}H_{28}BClN_7PRu$: C, 53.35; H, 4.32; N, 15.02. Found: C, 53.80; H, 4.65; N, 14.92. IR (KBr, cm^{-1}): ν(C≡N) 2278 (w); ν(B−H) 2474 (br, med). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.10 (s, 3H, CH_3CN), 5.75 (t, 1H), 5.84 (t, 1H), 6.22 (t, 1H), 6.62 (d, 1H), 6.94 (d, 1H), 7.23−7.41 (m, 15H, PC_6H_5), 7.63 (d, 1H + 1H), 7.65 (d, 1H), 8.07 (d, 1H), (all coupling constants for the pyrazolyl proton resonance were about 2 Hz). ^{31}P{^{1}H} NMR (121.49 MHz, $CDCl_3$, 25 °C): δ 51.7 (s). FAB-MS (nba matrix) (m/z): 653, $[M]^+$; 612, $[M - CH_3CN]^+$; 576, $[M - CH_3CN - Cl]^+$; 363, $[RuPPh_3]^+$.

RuH(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN), 8. A 50 mL two-necked pear-shaped flask was loaded with RuCl(HB(pz)$_3$)(PPh$_3$)(CH_3-CN) (0.30 g, 0.46 mmol) and $NaBH_4$ (0.16 g, 4.2 mmol). The flask was degassed and then filled with nitrogen, and this procedure was repeated three times. Freshly distilled anhydrous THF (20 mL) was added to the flask. The reaction mixture was stirred and refluxed under nitrogen for 14 h. At the end of the reaction, the mixture was filtered. The filtrate solvent was removed, and a yellow powder was obtained. Anhydrous diethyl ether (10 mL) was added to dissolve the solid. Any insoluble matter was filtered off. The filtrate solution was then concentrated to ca. 1−2 mL, and dry pentane was added to give an air-sensitive yellow solid. The solid was vacuum dried and stored under nitrogen. Yield: 0.26 g (52%). Anal. Calcd for $C_{29}H_{29}BN_7PRu$: C, 56.32; H, 4.73; N, 15.85. Found: C, 56.70; H, 4.90; N, 15.66. IR (KBr, cm^{-1}): ν(B−H) 2461 (br, med), ν(C≡N) 2258 (w), ν(Ru−H) 1890 (w). ^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ −13.91 (d, 1H, ^2J(HP) = 28.0 Hz, Ru−H), 1.69 (s, 3H, CH_3CN), 5.60 (t, 1H), 5.93 (t, 1H), 6.14 (t, 1H), 6.50 (d, 1H), 7.11 (d, 1H), 7.12−7.28 (m, 15H, PC6H_5), 7.53 (d, 1H), 7.60 (d, 1H), 7.75 (d, 1H); (all coupling

constants for pyrazolyl proton resonance were about 2 Hz). $^{31}P\{^1H\}$ NMR (161.70 MHz, CD_2Cl_2, 25 °C): δ 77.6 (s).

[Ru(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)(H$_2$)]BF$_4$, 9. Due to the thermal instability of this complex, no attempt was made to isolate it. It was prepared and observed in an NMR tube. Thus, a sample of 10 mg of RuH(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN) was loaded into a 5 mm NMR tube which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen, and this procedure was repeated three times. Dichloromethane-d_2 (0.4 mL) was added to the tube to dissolve the hydride, followed by the addition of 5 μL of tetrafluoroboric acid in ethereal solution (HBF_4·Et_2O, 56%). Evolution of gas (H_2) was observable upon addition of the acid. The ^1H NMR spectrum of the resulting solution was taken at room temperature. The triplet due to Ru−*H* (δ −13.91) disappeared, and a broad weak signal ($\omega_{1/2}$ = 37 Hz) was detected at δ −7.86. A sharp singlet at δ 4.61, which was due to free H_2, was also observed. The signals of the pyrazolyl groups and PPh_3 were complex, probably due to the result of partial dissociation of the η^2-H_2 (see Results and Discussion). Variable-temperature T_1 measurements of the δ −7.86 signal were carried out by the inversion-recovery method using standard 180°−τ−90° pulse sequences. T_1 (400 MHz, CD_2Cl_2, ms): 29 (293 K), 22.4 (273 K), 19 (258 K), 19 (258 K), 17 (248 K), 17 (226 K), 18 (219 K), 20 (206 K). The plot of ln T_1 vs 1000/T showed the familiar "V" shape, and T_1(min) was found to be 16 ms at 231 K and 400 MHz.[45]

[Ru(HD)(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN)]BF$_4$, 9-*d*$_1$. This complex was not isolated but was prepared in an NMR tube and detected by NMR spectroscopy. Thus, a sample of 10 mg of RuH(HB(pz)$_3$)(PPh$_3$)(CH$_3$CN) was loaded into a 5 mm NMR tube which was then capped with a rubber septum. The tube was evacuated and then filled with nitrogen, and this procedure was repeated three times. Dichloromethane-d_2 (0.5 mL) was syringed into the tube to dissolve the sample. The solution was cooled to −78 °C, and 6 μL of DBF_4 solution (prepared by adding 0.1 mL of D_2O into 0.4 mL of 56% HBF_4.Et_2O) was added through a microsyringe. The tube was then loaded into an NMR probe precooled to −60 °C, and the ^1H NMR spectrum of the solution was taken. The η^2-HD signal was observed after nulling the η^2-H_2 peak at δ −7.86 by the inversion-recovery method with a delay time of 20 ms.

Catalytic Hydrogenation with 4 or 6. The reactions were carried out in a 250 mL stainless steel autoclave. In a typical run, 0.01 mmol of **4** or **6** in 10 mL of freshly distilled tetrahydrofuran and 0.01 mol of organic substrate were added to the autoclave. Additives, if used, were then added according to the amount specified in Tables 1 and 2. After being flushed with H_2 three times, the system was heated with stirring at 110 °C and under 40 atm of H_2. At the end of the required length of time, the reactor was cooled rapidly and vented carefully. The products were analyzed by gas chromatography.

Catalytic Hydrogenation of Styrene with 4 or 6 in the Presence of D$_2$O. Samples of 0.02 mmol of **4** or **6** and 2.3 mL (0.02 mol) of styrene in 20 mL of freshly distilled THF were added to the autoclave, followed by addition of 2 mL of distilled D_2O. After being flushed with H_2 three times, the system was heated with stirring at 110 °C and under 40 atm of H_2. At the end of the required length of time, the reactor was cooled rapidly and vented carefully. An aliquot of the solution was removed for GC analysis to determine the percent conversion. The solvent and D_2O were carefully distilled off, and the resulting liquid products were analyzed by a combination of ^1H-, ^2H-, and ^{13}C-NMR spectroscopy and electron-impact mass spectrometry.

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