Mechanisms of Reactions of Dihydrogen Complexes: Formation of *trans*-$[RuH(H_2)(dppe)_2]^+$ and Substitution of Coordinated Dihydrogen

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The reactions between *cis*-$[RuH_2(DPPE)_2]$ and a number of acids in THF solution (DPPE = $Ph_2PCH_2CH_2PPh_2$) show biphasic kinetics, with initial formation of *trans*-$[RuH(H_2)(DPPE)_2]^+$ followed by slower substitution of coordinated dihydrogen by the anion of the acid. The formation of the dihydrogen complex is a second-order process that occurs with an inverse kinetic isotope effect and rate constants k_{HX} strongly dependent on the nature of the acid. There is a linear correlation between the values of log k_{HX} for *cis*-$[RuH_2(DPPE)_2]$ and the related *cis*-$[FeH_2(PP_3)]$ [$PP_3 = P(CH_2CH_2PPh_2)_3$] that leads to two parameters, *S* and *R*, that can be used as a measure of the selectivity and intrinsic reactivity of the dihydride toward acids. The possible contributions to the values of these parameters are discussed, especially the role of the isomerization of the starting complex and the basicity of the reacting species. The substitution of coordinated dihydrogen in *trans*-$[RuH(H_2)(DPPE)_2]^+$ occurs through a simple dissociative mechanism instead of the more complicated one previously proposed for substitutions in the analogous Fe complex; the mechanistic change is associated with the relative strength of the M−H_2 and M−P(chelate) bonds.

Introduction

Dihydrogen complexes have been the subjects of extensive work during the past years, and their chemistry has been reviewed with special emphasis on the synthetic and structural aspects as well as on their role in catalytic processes and their differences with classical dihydrides.[1,2] Despite the large amount of information available, the mechanistic aspects of reactions of dihydrogen complexes are far from being well understood, and discussions are often based on qualitative observations, theoretical considerations, and the conclusions of a limited number of kinetic works. Thus, the weakness of the metal−dihydrogen bond[3−6] and the existence of related coordinatively unsaturated complexes[7−9] indicate a dissociative behavior in substitution reactions, but there are few reports on the kinetic details of these reactions.[1,10−17] We have started recently a systematic kinetic study of reactions involving dihydrogen complexes, and the first results showed that the reaction mechanisms are not always in agreement with the behavior anticipated from simple considerations.[18−20] For example, kinetic data for protonation of $[FeH_2(PP_3)]$ [$PP_3 = P(CH_2CH_2PPh_2)_3$] with several acids to form $[FeH(H_2)(PP_3)]^+$ are consistent with a mechanism in which the dihydrogen complex is formed through a series of dihydrogen-bonded structures resulting from attack of the coordinated hydride by the acid molecule HX.[18] Despite the need of a cis−trans isomerization to give *trans*-$[FeH(H_2)(DPPE)_2]^+$ (DPPE = $Ph_2PCH_2CH_2PPh_2$), the protonation of *cis*-$[FeH_2(DPPE)_2]$ is faster, which was considered as evidence of the initial attack by the acid to the *cis*-dihydride followed by rapid isomerization.[19] On the other hand, substitution of coordinated H_2 in *trans*-$[FeH(H_2)(DPPE)_2]^+$ also shows interesting kinetic features which suggest that these reactions do not occur through a simple mechanism involving exclusively the coordination site occupied by the leaving ligand.[20] On the contrary, substitutions in *cis*-$[RuCl(nitrile)(DPPE)_2]^+$ complexes occur through a simple dissociative mechanism with formation of $[RuCl(DPPE)_2]^+$ as intermediate.[21] In the present paper we report a kinetic study of reactions involving the well-

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characterized[22−28] *trans*-$[RuH(H_2)(DPPE)_2]^+$ complex, whose results provide new information about the mechanism of both the formation of dihydrogen complexes and the substitution of coordinated H_2.

Results

The dihydrogen complex *trans*-$[RuH(H_2)(DPPE)_2]^+$ can be prepared by addition of 1 equiv of $HBF_4 \cdot Et_2O$ to *cis*-$[RuH_2(DPPE)_2]$ in ether under H_2 atmosphere (eq 1).[23] We carried

$$cis\text{-}[RuH_2(DPPE)_2] + HBF_4 \rightarrow trans\text{-}[RuH(H_2)(DPPE)_2]^+ + BF_4^- \quad (1)$$

out NMR experiments at −60 °C in acetone-d_6 solutions and confirmed that reaction with a large excess of HBF_4 leads to complete conversion to *trans*-$[RuH(H_2)(DPPE)_2]^+$ without evidence of any reaction intermediate or side product. However, if the reaction is carried out at 25 °C, the product consists of a mixture of the dihydrogen complex and another species characterized by a singlet at 57.8 ppm and a quintet at −3.72 ppm ($^2J_{H,P} = 21$ Hz) in the phosphorus and proton NMR spectra, respectively. These signals disappear when the NMR samples are cooled below −40 °C, and the mixture of both complexes converts quantitatively to *trans*-$[RuH(MeCN)(DPPE)_2]^+$ upon addition of an excess of acetonitrile.

Despite $[RuH_2(DPPE)_2]$ being known to exist as a mixture of the cis and trans isomers, with the cis form being the major species,[23,29] there is no formation of detectable amounts of *trans*-$[RuH_2(DPPE)_2]$ during the conversion of the *cis*-dihydride to the *trans*-hydride−dihydrogen complex. From published NMR data, the equilibrium constant for eq 2 is close to 0.05 in both

$$cis\text{-}[RuH_2(DPPE)_2] \rightleftarrows trans\text{-}[RuH_2(DPPE)_2] \qquad K_i \quad (2)$$

C_6D_6 and THF solutions,[23,29] but the absence of the trans isomer during our experiments indicates a lower value in acetone solution, in agreement with previous observations by Morris and co-workers,[23] who were also unable to detect the trans isomer in acetone-d_6 at room temperature. We derived K_i values from the intensity of the phosphorus NMR signals and found that they are strongly dependent on the nature of the solvent, ranging from 0.05 (C_6D_6) to 0.01(CD_2Cl_2) and even lower (nonmeasurable by NMR) in THF and acetone solutions.

The formation of *trans*-$[RuH(H_2)(DPPE)_2]^+$ as the initial product of reaction between *cis*-$[RuH_2(DPPE)_2]$ and an excess of other acids (HCl, HBr, or CF_3COOH) was also confirmed using low-temperature NMR, although in those cases the process is followed by substitution of H_2 by the anion of the acid. At room temperature, the sequence of reactions in eqs 3 and 4 is completed within the time required to obtain the first spectrum

$$cis\text{-}[RuH_2(DPPE)_2] + HX \rightarrow trans\text{-}[RuH(H_2)(DPPE)_2]^+ + X^- \quad (3)$$

(ca. 5 min), but experiments at lower temperatures demonstrate that substitution is substantially slower than protonation. The product of reaction with trifluoroacetic acid has not been reported previously, but it can be reasonably identified as *trans*-$[RuH(CF_3COO)(DPPE)_2]^+$ from the observation of a singlet (65.2 ppm) and a quintet (−15.8 ppm, $^2J_{H,P} = 19$ Hz) in the phosphorus and proton spectra, respectively. It was not isolated because it is formed in equilibrium with the same intermediate described above for the reaction with HBF_4, which in a few minutes converts partially to an uncharacterized cis compound, probably *cis*-$[Ru(\eta^2\text{-}CF_3COO)(DPPE)_2]^+$, with two triplets in the ^{31}P spectrum (60.0 and 58.6 ppm, $^2J_{P,P} = 18$ Hz). Fortunately, the time scale for this conversion is slower than that corresponding to eqs 3 and 4, and it does not interfere with the kinetic study discussed below.

It has been previously shown[30] that protonation of *trans*-$[RuH(Cl)(DPPE)_2]$ leads to a chlorodihydrogen complex, and our NMR experiments with HCl excess confirmed the sequence of reactions 5−7, the slowest one being formation of *trans*-

$$trans\text{-}[RuH(H_2)(DPPE)_2]^+ + X^- \rightarrow trans\text{-}[RuHX(DPPE)_2] + H_2 \quad (4)$$

$[RuCl(H_2)(DPPE)_2]^+$. This complex does not undergo further reaction with HCl, and instead of the expected substitution of H_2, it forms *trans*-$[RuH(MeCN)(DPPE)_2]^+$ upon addition of MeCN excess, in a way similar to that previously observed for the reaction with CO.[30]

$$cis\text{-}[RuH_2(DPPE)_2] + HCl \rightarrow trans\text{-}[RuH(H_2)(DPPE)_2]^+ + Cl^- \quad (5)$$

$$trans\text{-}[RuH(H_2)(DPPE)_2]^+ + Cl^- \rightarrow trans\text{-}[RuH(Cl)(DPPE)_2] + H_2 \quad (6)$$

$$trans\text{-}[RuH(Cl)(DPPE)_2] + HCl \rightarrow trans\text{-}[RuCl(H_2)(DPPE)_2]^+ + Cl^- \quad (7)$$

Kinetics of Reaction of *cis*-[$RuH_2(DPPE)_2$] with Acids. We initially tried to study the kinetics of protonation of *cis*-$[RuH_2(DPPE)_2]$ using the electrochemical procedure previously described,[18] but the reaction is too fast and occurs at 25 °C within the time required to mix the reagents (ca. 1 s). Preliminary stopped-flow experiments using a diode-array detector showed that the reactions with HCl and CF_3COOH occur with biphasic kinetics under pseudo-first-order conditions (acid excess, THF solution, 25.0 °C). The time scale of the first step is on the order of a few milliseconds, whereas the second step lasts for almost 1 s. Accurate values of the first rate constant were obtained from kinetic traces at 300 nm, which show a rapid absorbance increase that can be fitted by a single exponential. The values of the second rate constant were then obtained from the fit of traces at 330 nm by two consecutive exponentials, keeping fixed the value of the first one. Detailed listings of both rate constants are given in Table S1 (Supporting Information). Although for reactions showing biphasic kinetics there is always

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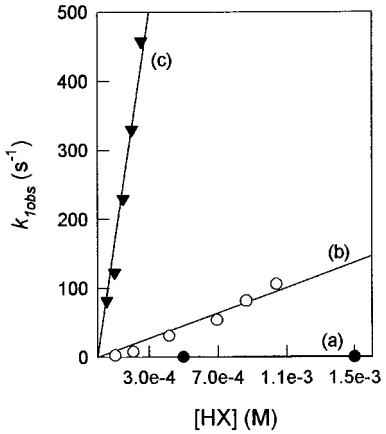

Figure 1. Plots of k_{1obs} versus acid concentration for the reaction of *cis*-[RuH_2(DPPE)$_2$] with HBF_4·Et_2O (a), CF_3COOH (b), and HCl (c). Some points at higher concentrations of HBF_4·Et_2O have been omitted for clarity.

Table 1. Second-Order Rate Constants and Kinetic Isotope Effects for the Reaction of *cis*-[RuH_2((DPPE)$_2$] with Acids in THF Solution at 25.0 °C

HX	$k_{HX}/(M^{-1}\ s^{-1})$	$k_{DX}/(M^{-1}\ s^{-1})$	k_{HX}/k_{DX}	$(k_{HX}/k_{DX})_{theor}$[a]
HBF_4·Et_2O	$(1.12 \pm 0.08) \times 10^3$			
CF_3COOH	$(9.2 \pm 0.6) \times 10^4$	$(11.5 \pm 0.4) \times 10^4$	0.80 ± 0.06	0.87
HCl	$(1.7 \pm 0.2) \times 10^6$	$(4.5 \pm 0.7) \times 10^6$	0.38 ± 0.07	0.47

[a] Theoretical values calculated by the procedure given in ref 18.

a problem for determining the order of occurrence of both steps, the fit of the diode-array data only gives reasonable spectra for the reaction intermediate assuming that the rapid step occurs first, in agreement with the NMR observation described above. Thus, the values of k_{1obs} in Table S1 correspond to the formation of *trans*-[$RuH(H_2)$(DPPE)$_2$]$^+$, whereas k_{2obs} corresponds to the slower substitution of coordinated H_2. Data in Table S1 show that k_{2obs} remains unaffected when the nature or the concentration of acid is changed, whereas the values of k_{1obs} are significantly different for every acid and show a linear dependence with the acid concentration (eq 8, Figure 1). The values of the second-order rate constant k_{HX} are given in Table 1.

$$k_{1obs} = k_{HX}[HX] \tag{8}$$

The protonation of *cis*-[RuH_2(DPPE)$_2$] with HBr is so rapid that it occurs within the mixing time of the stopped-flow instrument and kinetic traces only show the substitution step (Table S1). On the contrary, protonation with HBF_4·Et_2O is very slow, and a single exponential can fit the traces at 300 and 330 nm, yielding similar values for the observed rate constant. The values so derived are also given in Table S1, and they are assigned to k_{1obs} because substitution is now faster than protonation and the whole process becomes controlled by the formation of the dihydrogen complex. This conclusion was confirmed by additional experiments of protonation with HBF_4·Et_2O and added MeCN; the protonation step is accelerated, and the curves reveal the slower substitution of H_2 by MeCN with a rate constant similar to k_{2obs} for the reaction with other acids (Table S2, Supporting Information). The values of k_{1obs} increase with the concentration of added acetonitrile, surely because the increased dielectric constant favors dissociation of the acid and leads to faster protonation of *cis*-[RuH_2(DPPE)$_2$] through direct proton attack.

Table 2. Effect of the Incoming Ligand and the Solvent on the Activation Parameters for the Substitution of Coordinated H_2 in *trans*-[$RuH(H_2)$(dppe)$_2$]$^+$

incoming ligand	solvent	$\Delta H^{\ddagger}$/(kJ mol^{-1})	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1})
MeCN	THF	89 ± 1	73 ± 4
	acetone	92 ± 1	88 ± 4
	MeCN	85 ± 4	65 ± 13
CF_3COO^-	THF	92 ± 5	85 ± 18
Cl^-	THF	91 ± 3	80 ± 12
Br^-	THF	91 ± 5	78 ± 17

The activation parameters for H_2 substitution were determined using several entering ligands and solvents (Tables 2 and S3). The values in THF for the reaction with MeCN, Cl^-, Br^-, and CF_3COO^- agree within error, showing that the rate-limiting step is the same in all cases, which suggests a limiting dissociative mechanism. The changes of the activation parameters with the solvent nature are also consistent with a D mechanism, the lower activation barrier in acetonitrile solution being a consequence of the preferential solvation of the coordinatively unsaturated transition state.

The results of kinetic studies with DCl and CF_3COOD are included in Tables S1 and 1; in both cases the protonation is faster than for the undeuterated acids and there is an inverse kinetic isotope effect (kie; see values in Table 1). On the contrary, there is a very small positive kie of ca. 1.1 associated with the substitution step (k_2). Although the observation of a positive kie is in agreement with those previously reported for substitution of coordinated dihydrogen in other complexes,[15−17] the value of 1.1 is not a measure of the isotope effect associated with substitution of H_2 in *trans*-[$RuH(H_2)$(DPPE)$_2$]$^+$ because protonation with DX leads to a fluxional complex in which only one of the three hydrogens is deuterated.

It has been pointed out above that reaction of *cis*-[RuH_2(DPPE)$_2$] with HCl excess does not end with the formation of *trans*-[RuHCl(DPPE)$_2$]; the complex is further protonated to *trans*-[$RuCl(H_2)$(DPPE)$_2$]$^+$, although in a very slow process that does not affect the determination of the k_{1obs} and k_{2obs} values. It would be very interesting to obtain kinetic data for the formation of the chlorodihydrogen complex and the subsequent elimination of HCl, so we prepared *trans*-[RuHCl(DPPE)$_2$] and attempted kinetic studies. Unfortunately, although low-temperature NMR experiments confirmed that protonation of this complex is slow compared to the reactions of *cis*-[RuH_2(DPPE)$_2$], we have been unable to obtain accurate kinetic data for these reactions.

Discussion

Mechanism of Formation of Dihydrogen Complexes. The major kinetic features for the formation of *trans*-[$RuH(H_2)$(DPPE)$_2$]$^+$ are similar to those previously observed for *trans*-[$FeH(H_2)$(DPPE)$_2$]$^+$ and *cis*-[$FeH(H_2)(PP_3)$]$^+$,[18,19] i.e., second-order kinetics with an inverse kie and large changes in the rate constant with the nature of the acid. The reactivity of *cis*-[RuH_2(DPPE)$_2$] with the different acids increases as HBF_4 < CF_3COOH < HCl < HBr, an ordering that does not parallel the acid strength and was interpreted assuming that (H^+, X^-) ion pairs react slower than HX molecules.[18] We have also shown previously[19] a correlation between the rate constants for the formation of the iron dihydrogen complexes with PP_3 and DPPE that can now be extended to include *trans*-[$RuH(H_2)$(DPPE)$_2$]$^+$. As the Fe−PP_3 complex does not isomerize upon protonation, we chose it as a reference, and the correlation is then represented by eq 9, where *S* and *R* are measures of the selectivity and the intrinsic reactivity of the Ru complex with acids, respectively.

$$\log k_{HX(Ru-DPPE)} = S \log k_{HX(Fe-PP_3)} + R \qquad (9)$$

The values of k_{HX} in Table 1 and ref 18 lead to $S = 1.66$ and $R = 2.87$ (correlation coefficient 0.98; see Figure 2), and extrapolation of the regression line predicts a value of log k_{HBr} higher than 7, in agreement with the experimental observation that reaction of *cis*-[$RuH_2(DPPE)_2$] with HBr is so rapid that k_{HBr} could not be determined.

The use of the *R* and *S* parameters allows an easy ordering of the complexes, which represents an important step for determining the factors that cause the differences in the kinetics of protonation. Thus, the intrinsic reactivity increases as (*R* values in parentheses) *cis*-[$FeH_2(PP_3)$] (0.00) < *cis*-[$FeH_2(DPPE)_2$] (1.75) < *cis*-[$RuH_2(DPPE)_2$] (2.87) i.e., the ruthenium complex is more reactive than the iron analogues, and the reactivity of both DPPE complexes is higher than that of the PP_3 complex despite the need of isomerization to *trans*-[$MH(H_2)(DPPE)_2]^+$. We previously[19] considered this as evidence of the initial protonation of the *cis*-dihydride followed by rapid isomerization to the trans product; in that case, the *R* values of the dihydrides would simply reflect the different electronic environments of coordinated hydrides in the PP_3 and DPPE complexes. However, Morris and co-workers have reported that deprotonation of *trans*-[$RuH(H_2)(DPPE)_2]^+$ with BuLi leads initially to *trans*-[$RuH_2(DPPE)_2$], which converts to the cis isomer in a slower process,[23,29] and microscopic reversibility indicates that isomerization must precede the protonation of the Ru complex in the reverse reaction. Moreover, it has been demonstrated[31] that formation of the closely related DMPE complex occurs preferentially through protonation of the *trans*-dihydride despite the presence of a larger concentration of the cis isomer (DMPE = $Me_2PCH_2CH_2PMe_2$). Thus, although the experimental observations for protonation with HX and deprotonation by BuLi cannot be directly compared, the possibility that both processes occur through the formation of *trans*-[$RuH_2(DPPE)_2$] must be seriously considered. In that case, as the *trans*-dihydride does not accumulate during the formation of the dihydrogen complex, the reaction must occur according to the mechanism in eqs 10 and 11, where the first step is an

$$cis\text{-}[RuH_2(DPPE)_2] \rightleftarrows trans\text{-}[RuH_2(DPPE)] \qquad K_i \quad (10)$$

$$trans\text{-}[RuH_2(DPPE)_2] + HX \rightarrow trans\text{-}[RuH(H_2)(DPPE)_2]^+ + X^- \qquad k_{HX(trans)} \quad (11)$$

unfavorable equilibrium ($K_i \ll 1$) and $k_{HX(trans)}$ is the rate constant for HX attack to the *trans*-dihydride. The rate law for this mechanism is similar to the experimental one with $k_{HX} = K_i k_{HX(trans)}$; i.e., the values of k_{HX} include the equilibrium constant for cis−trans isomerization of the starting dihydride. As K_i is independent of the acid used, the effect of isomerization is included in the *R* parameter and consists of increasing it by a constant value of log K_i. The value of K_i is very small for *cis*-[$RuH_2(DPPE)_2$] (less than 0.01), so the contribution of isomerization to *R* is −2.0 or even more negative, which leads to a value of *R* larger than ca. 5 for *trans*-[$RuH_2(DPPE)_2$]. This represents a reactivity higher than that of both its cis isomer and *cis*-[$FeH_2(PP_3)$], which does not undergo isomerization. If the mechanism is similar for the case of *cis*-[$FeH_2(DPPE)_2$], it would indicate again an increased reactivity of the *trans*-dihydride, probably because of a higher electron density on the coordinated hydrides; for the case of *cis*-[$MH_2(dppe)_2$] there are two axial H−M−P groups, and the strong σ-donation from the hydrides can be more easily delocalized through back-donation from the metal to the phosphine through the common d orbital. This remarkable difference of reactivity between isomeric pairs of Ru complexes has been previously recognized for substitution reactions.[32−34] The higher basicity of *trans*-dihydrides is also supported by the observation that the pK_a values of *trans*-[$RuX(H_2)(diphosphine)_2]^+$ complexes are strongly dependent on the nature of X, covering a range of 18 units with a minimum acidity for X = H.[35]

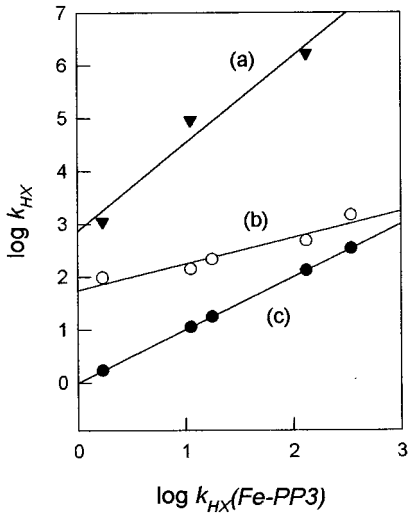

Figure 2. Correlation between the log k_{HX} values for *cis*-[$FeH_2(PP_3)$] and the complexes *cis*-[$RuH_2(DPPE)_2$] (a) and *cis*-[$FeH_2(DPPE)_2$] (b). Also included is the line for the reference compound *cis*-[$FeH_2(PP_3)$] (c).

The correlation in eq 9 indicates[19] that k_{HX} values follow a Bronsted-type relationship similar to that found in classical proton-transfer reactions[36] and proton transfers from metal hydrides to bases.[37−39] In those cases there is a linear correlation between log *k* and the difference between the pK_a values for both acid−base pairs. By analogy, the values of k_{HX} for reaction with a common acid are expected to increase with the basicity of the metal hydrides, which can be measured by the pK_a of the dihydrogen complex. As the pK_a values for *trans*-[$FeH(H_2)(DPPE)_2]^+$ and *trans*-[$RuH(H_2)(DPPE)_2]^+$ in the scale defined by Morris are 12 and 14.1, respectively,[1,29] this would explain the higher intrinsic reactivity of the Ru complex. However, although the pK_a of *cis*-[$FeH(H_2)(PP_3)]^+$ is not available, it must be[40] higher than 12, and the intrinsic reactivity of the corresponding dihydride should be higher than that found experimentally, placing [$FeH_2(PP_3)$] higher in the *R* scale. The cause of this apparent inversion of the ordering of *R* values is probably a different meaning of the reported pK_a values; whereas for the PP_3 complex it would have the usual meaning, the pK_a of the

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DPPE complexes also includes the isomerization to the *cis*-dihydride. The experimental values (pK_a) and the values in the absence of isomerization (pK_a') are related[29] by eq 12, and pK_a'

$$pK_a = pK_a' + \log K_i \quad (12)$$

is higher than pK_a by 1−2 units in the Ru complex and by an unknown amount in the Fe complex. If the formation of the dihydrogen complexes occurs through reaction of *trans*-[MH_2-$(DPPE)_2$] (eqs 10 and 11), the basicity of the reacting species is determined by the values of pK_a', so the intrinsic reactivity of these complexes is higher than that of *cis*-[$FeH_2(PP_3)$].

Whereas the value of *R* for protonation of the dihydride complexes appears to be reasonably explained by considering both the isomerization to a more reactive species and the basicity of the species attacked by the acid, the factors leading to a different selectivity toward acids are not so clear. The selectivity follows the order (*S* values in parentheses)

cis-[$FeH_2(DPPE)_2$] (0.50) < *cis*-[$FeH_2(PP_3)$] (1.00) < *cis*-[$RuH_2(DPPE)_2$] (1.66)

and steric factors cannot be invoked because the Ru−DPPE complex is 3 times more selective than its Fe analogue despite the lower steric requirements. More work is in progress to determine the factors that lead to a different selectivity.

Mechanism of Substitution of Coordinated Dihydrogen. The kinetic data for substitution of dihydrogen in *trans*-[$RuH(H_2)(DPPE)_2$]$^+$ strongly suggest a simple D mechanism. Actually, the NMR experiments demonstrate that, in the absence of suitable entering ligands, the complex dissociates H_2 and exists in equilibrium with another species, probably in a way similar to that observed for the DMPE analogue.[31] The signal at 57.8 ppm in the phosphorus spectra had been previously observed after argon was bubbled through a THF solution of the dihydrogen complex and was tentatively assigned to the coordinatively unsaturated species [$RuH(DPPE)_2$]$^+$.[30] However, related five-coordinate ruthenium(II) hydrides usually give rise to resonances close to −22 ppm,[31,41] and the observation of the hydride signal at −3.72 ppm in our experiments suggests some interaction with the solvent, especially in the NMR experiments (acetone solution). The tendency of [$RuH(DPPE)_2$]$^+$ to form *trans*-[$RuH(solvent)(DPPE)_2$]$^+$ has been previously recognized.[23,25,30]

The activation enthalpy for dissociative loss of H_2 in *trans*-[$RuH(H_2)(DPPE)_2$]$^+$ is 90 kJ/mol, close to the values found for nitrile substitution in the related *cis*-[$RuCl(nitrile)(DPPE)_2$]$^+$ complexes, which also undergo substitution through a dissociative mechanism.[21] Although it is tempting to use that value as an estimation of the Ru−H_2 binding energy, there can be significant differences because of the possibility of energy changes associated with solvation and/or structural reorganization of the intermediate, as demonstrated for [$RuCl(DPPE)_2$]$^+$.[21] Actually, although the NMR spectra of the five-coordinate hydride do not show any evidence of agostic interactions or structural rearrangement, the complex exchanges the hydride with the hydrogen atom of a CH group in a way similar to that of some analogues with related diphosphines, which form an agostic interaction with a CH bond to compensate electron deficiency.[42]

The limiting D mechanism for substitutions in *trans*-[$RuH(H_2)(DPPE)_2$]$^+$ differs from the behavior of the iron analogue *trans*-[$FeH(H_2)(DPPE)_2$]$^+$, whose kinetic data are not consistent with a simple mechanism involving exclusively the coordination site of the leaving ligand.[20] On the contrary, a simple D mechanism also operates in substitutions of *cis*-[$RuCl(RCN)(DPPE)_2$]$^+$,[21] which suggests that H_2 does not behave as a leaving ligand in a way very different from that of other monodentate ligands; it is the metal center which plays a fundamental role in determining the substitution mechanism, with a D mechanism being operative for the Ru complexes and a chelate ring-opening mechanism for the iron analogue. The reason for this change in the mechanism must be related to the relative energy of the M−P(chelate) and M−H_2 (or M-NCR) bonds. The affinity of Fe(II) for the phosphine ligands is not very high[43] and favors the ring-opening mechanism in the iron complexes, but the energy of the M−H_2 bond decreases[1,23,29] as Fe > Ru and favors the simple D mechanism for the ruthenium complexes. The general behavior is probably more complicated because the strength of both the M−P and M−H_2 bonds also depends on the other ligands in the complex and subtle modifications in the coordination environment can also lead to a change in the substitution mechanism.

Experimental Section

The complex *cis*-[$RuH_2(DPPE)_2$] was prepared by the literature procedure.[23] The reagents $RuCl_3$, CF_3COOH, CF_3COOD, HBF_4·Et_2O, CH_3OD, chorotrimethylsilane, and bromotrimethylsilane were obtained from Aldrich. Tetrahydrofuran, acetonitrile, acetone, acetone-d_6, and methanol were obtained from SDS (Solvants Documentation Syntheses). The acids HCl and HBr were generated in THF solution from methanol and choro- or bromotrimethylsilane, respectively. The deuterated acids were obtained by the same procedure using CH_3OD. All the synthetic, NMR, and kinetic work was carried out under an inert atmosphere of Ar or N_2 with solvents dried by distillation from the appropriate drying agents and deoxygenated by bubbling inert gas immediately before use.

The NMR experiments were carried out with a Varian Unity 400 spectrometer. The samples were prepared under an inert atmosphere, and the acids were added after the samples were cooled at −90 °C inside the NMR probe. The experiments were started by warming the samples to the desired temperature before starting the acquisition of the spectra.

The kinetic experiments were carried out with an Applied Photophysics SX17MV stopped-flow spectrophotometer. The solutions of the metal complex and the acids were prepared using Schlenk techniques and transferred under argon atmosphere to the instrument syringes using Teflon tubes. The concentrations of acid solutions were determined immediately before use by diluting with water (50 mL) an aliquot (1−3 mL) of the THF solution and titrating with KOH using phenolphthalein indicator. The analysis of kinetic traces was carried out using the standard software of the stopped-flow instrument, and the activation parameters were derived from conventional Eyring plots of kinetic data at different temperatures.

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Supporting Information Available: Tables containing observed rate constants for the reaction of *cis*-[$RuH_2(DPPE)_2$] with several acids at 25 °C, for the reaction with HBF_4·Et_2O in the presence of different concentrations of added acetonitrile, and for the substitution of coordinated dihydrogen at different temperatures. This material is available free of charge via the Internet at http://pubs.acs.org.

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