Unexpected Mechanism for Substitution of Coordinated Dihydrogen in *trans*-$[FeH(H_2)(DPPE)_2]^+$

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Received April 29, 1997

Substitution reactions of the type *trans*-$[FeH(H_2)(DPPE)_2]^+ + L \rightarrow$ *trans*-$[FeHL(DPPE)_2]^+ + H_2$ (L = MeCN, PhCN, DMSO) occur in a single measurable kinetic step. Although the observed rate constants, k_{obs}, in THF solution show a saturation behavior in [L] with a curvature that is sensitive to the steric requirements of L, the limiting rate constant is almost independent of L (ca. 7×10^{-3} s^{-1} at 30 °C) and agrees with the values obtained under solvolytic conditions. The rate law in acetone solutions is simpler, with k_{obs} being independent of [L] and very close to the limiting value in THF. The thermal and pressure activation parameters for the limiting rate constants of the reaction with MeCN have been determined in THF, acetone and neat acetonitrile. The values of $\Delta H^‡$ are close to 80 kJ/mol for the three solvents while $\Delta S^‡$ is slightly negative in all cases. The activation volumes are very negative and solvent dependent: -23 ± 1 cm^3/mol (THF), -18 ± 1 cm^3/mol (acetone), and -35 ± 2 cm^3/mol (acetonitrile). As a whole, the kinetic and activation parameters do not agree with a mechanism in which a direct substitution of H_2 for the incoming ligand takes place; instead a mechanism is proposed in which the initial opening of a DPPE chelate ring leads to an intermediate containing a monodentate DPPE and a weakly bound solvent molecule. Thus, the rate-determining step is an associative attack of L to this intermediate to form a species containing both coordinated L and H_2. The final substitution product is formed in a rapid intramolecular attack of the dangling PPh_2 arm followed by a cis/trans isomerization.

Introduction

Following the initial efforts that were concentrated in the synthesis and characterization of dihydrogen complexes, interest has been focused more recently in the chemical properties and reactivity of these complexes and their relevance to catalytic processes.[1−6] Consequently, a great amount of information is available but little is known about the mechanisms of the reactions involved.

Substitution of coordinated H_2 is one of the simplest reactions of dihydrogen complexes and it plays surely an important role in some catalytic cycles.[1,3,5,7] Given the fact that both experimental determinations[1,8−10] and theoretical calculations[11,12] show that $M-H_2$ bonds are not very strong (ca. 28−80 kJ/mol), a limiting dissociative mechanism involving the existence of a coordinatively unsaturated intermediate has been proposed frequently for these reactions.[13−18] This assignment has been reinforced by the existence of several 16-electron complexes resulting from H_2 dissociation or able to add H_2 to form stable 18-electron dihydrogen complexes.[19−21] However, some of these presumed intermediates can only be obtained using drastic conditions or do not add H_2 under the mild conditions in which substitution reactions occur.[2,19,22] Alternative pathways are, in fact, found more effective in cases as $[FeH(H_2)(PP_3)]^+$ (PP_3= tris(2-diphenylphosphinoethyl)phosphine), where a mechanism involving the opening of a chelate ring adjacent to coordinated

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S0020-1669(97)00493-X CCC: $15.00

H_2 has been invoked[3] to explain the catalytic properties of the complex, despite the known existence of the unsaturated compound $[FeH(PP_3)]^+$.[23] Moreover, thermodynamic and kinetic studies of H_2 dissociation from iridium complexes have been carried out and the data suggest that the mechanism is not so simple; strong evidence for concerted formation of an agostic bond, or an L → M π-bond, in the resulting unsaturated complexes have been found.[8,9,24,25]

Although it seems clear that H_2 dissociation from these complexes is not necessarily the first step in the substitution processes of coordinated H_2,[1] it is evident that more kinetic work is required to elucidate the mechanisms that operate in these reactions. Following our interest in the tuning of the electronic and steric characteristics that influence the substitution processes of metal phosphine and other type of complexes,[26,27] we have carried out a systematic kinetic study on the substitution of H_2 in one of the best known dihydrogen complexes, *trans*-$[FeH(H_2)(DPPE)_2]^+$ (DPPE = 1,2-bis(diphenylphosphino)ethane).[2,28] The results presented in this paper include the effect of the solvent and the incoming ligand on the kinetics of substitution as well as the determination of thermal and pressure activation parameters; in this case $\Delta V^{\ddagger}$ has been a decisive tool to elucidate the mechanism, as in other substitution[29] and oxidative addition reactions.[30] The data obtained as a whole clearly shows that substitution of H_2 in this complex does not occur in a simple dissociative process and an alternative mechanism is required to explain the kinetic results.

Results and Discussion

Coordinated dihydrogen in *trans*-$[FeH(H_2)(DPPE)_2]BF_4$ is substituted easily by MeCN, PhCN, DMSO, and other monodentate ligands. The reactions are clean and take place without any side product formation. Thus, Figure 1 shows the changes observed in the phosphorus NMR spectra for the reaction with acetonitrile in acetone-d_6. No intermediates are detected, and the intensities of both signals can be fitted to single exponentials; the rate constants thus obtained agree within experimental error. Similar conclusions are obtained when the incoming ligand is PhCN or DMSO instead of MeCN. The time required for the reactions to go to completion is adequate for a kinetic study using conventional spectrophotometry; accordingly, the monitoring wavelength was selected in every case from preliminary spectral scanning experiments, details are given in the Experimental Section. When L is present in an excess, the *absorbance versus time* traces in THF solution for the substitution reactions,

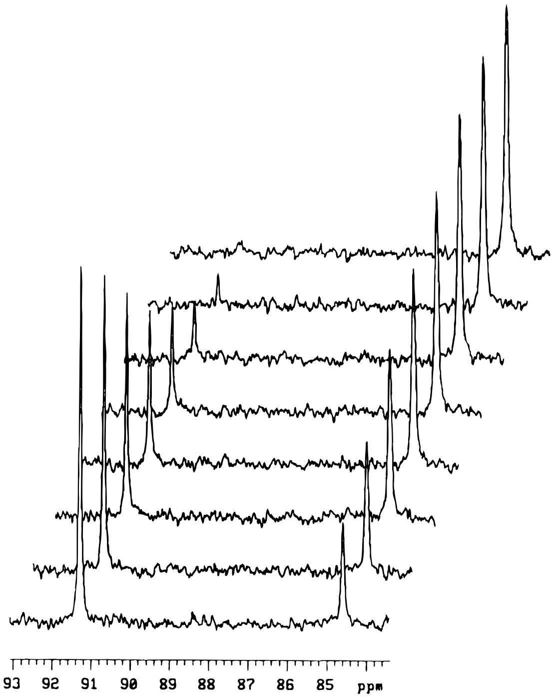

Figure 1. $^{31}P\{^1H\}$ NMR spectra recorded during the reaction of *trans*-$[FeH(H_2)(DPPE)_2]^+$ with MeCN excess showing the conversion to *trans*-$[FeH(MeCN)(DPPE)_2]^+$. Spectra were recorded at 128 s intervals, but some of them have been omitted for clarity. The experiment was carried out in acetone-d_6 at 10 °C under an argon atmosphere. The concentrations of iron complex and MeCN were close to 1×10^{-3} M and 1.2 M, respectively.

$$trans\text{-}[FeH(H_2)(DPPE)_2]^+ + L \rightarrow trans\text{-}[FeHL(DPPE)_2]^+ + H_2$$
$$(L = MeCN, PhCN, DMSO)$$

behave as single exponentials, producing observed rate constants k_{obs} which are independent of the concentration of the iron complex but show saturation kinetics on [L] as indicated in eq 1, Figure 2, and Tables S1 and S2 (Supporting Information).

$$k_{obs} = \frac{ab[L]}{1 + b[L]} \qquad (1)$$

In acetone solution, though, the values of k_{obs} for the same reactions are independent of [L], that is $k_{obs} = a$. The values for the parameters a and b for all the reactions are collected in Table 1, which also includes the data for the corresponding solvolysis reaction (i.e. in neat coordinating solvent). These values correspond within reasonable error to the limiting value of k_{obs} for the saturation kinetics (i.e. a). The values found for a are always close to 7×10^{-3} s^{-1} at 30 °C, and they are little

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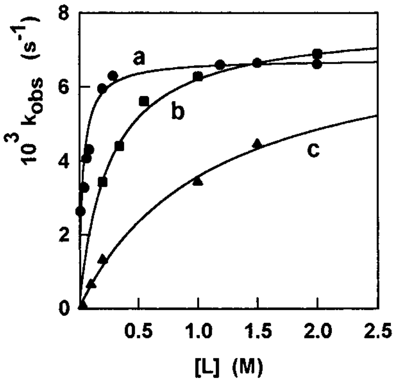

Figure 2. Plots of k_{obs} versus ligand concentration for the reaction of *trans*-[FeH(H$_2$)(DPPE)$_2$]$^+$ with MeCN (a), PhCN (b), and DMSO (c) (THF solvent, 30 °C, argon atmosphere).

Table 1. Kinetic Parameters at 30 °C for the Dihydrogen Substitution Reactions Studied According to Eq 1 (Values in Brackets Indicate the Values of k_{obs} Determined in Neat L)

solvent	L	$10^3 a$/s^{-1}	b/M^{-1}
THF	MeCN	6.7 ± 0.2 (6.7 ± 0.1)	32 ± 3
	PhCN	7.8 ± 0.2 (7.3 ± 0.1)	4.0 ± 0.3
	DMSO	7.6 ± 0.9 (6.4 ± 0.1)	0.9 ± 0.2
acetone	MeCN	8.7 ± 0.3 (6.7 ± 0.1)	
	PhCN	7.2 ± 0.3 (7.3 ± 0.1)	

Table 2. Activation Parameters for the Dihydrogen Susbtitution Reaction of *trans*-[FeH(H$_2$)(Dppe)$_2$]$^+$ with MeCN

solvent	$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1}mol^{-1}	$\Delta V^\ddagger$/cm^{3}mol^{-1}
MeCN	78 ± 3	−29 ± 8	−35 ± 2
THF	80 ± 4	−25 ± 13	−23 ± 1
acetone	86 ± 7	−4 ± 21	−18 ± 1

influenced by the nature of the entering ligand or solvent used. In contrast, it is evident that the values for *b* are highly sensitive to the steric characteristics of the ligand L (increasing from 0.9 to 32 M^{-1} for DMSO and MeCN, respectively) as well as to the electronic characteristics of the solvent (a lower limit of 10^3 M^{-1} can be estimated from the absence of curvature in the plots in acetone, a better coordinating solvent). The temperature and pressure activation parameters for the limiting rate constant, *a*, in the reaction with MeCN have been determined and results are collected in Table 2. Runs carried out at elevated pressure and different concentrations of MeCN in THF indicate the absence of any measurable pressure effect on the curvature of k_{obs} vs[MeCN] plots at the high concentration used for the determination of activation volumes. From data in Table 2, it is clear that the values for the activation enthalpy are the same within error for all the solvents, and the values for the activation entropy are slightly negative but very close to zero in all cases. Nevertheless the activation volumes are significantly negative, and the value found in neat MeCN is clearly more negative.

All the kinetic information clearly indicates that substitution of coordinated dihydrogen in *trans*-[FeH(H$_2$)(DPPE)$_2$]$^+$ does not occur through the limiting D mechanism proposed both for reactions of polyhydride and dihydrogen complexes,[13−18] and the related low-spin Fe(II)−phosphine complexes.[31] In that case, the limiting rate constant *a* would correspond to H$_2$ dissociation and the value of $\Delta V^\ddagger$ should be positive and close to +20 cm^3/mol, as observed for the reductive elimination of H$_2$.[32] Furthermore, if that were the case the values of *b* should correspond to the discriminating ability of the pentacoordinated intermediate between L and H$_2$; since the concentration of dihydrogen is in all cases lower than 1 × 10^{-4} M, our results would suggest that the attack of H$_2$ to the intermediate is several orders of magnitude faster, in clear disagreement with known data.[33] Even so, in that case the concentration of H$_2$ in solution would increase during the reaction and the kinetic traces would not be well-behaved.

Chart 1

$$\begin{array}{ll} \text{Type I} & \text{Type II} \\ A + L \rightleftarrows B \quad (\boldsymbol{K}_1) & A \rightleftarrows B \quad (\boldsymbol{k}_1, \boldsymbol{k}_{-1}) \\ B \longrightarrow P \quad (\boldsymbol{k}_2) & B + L \longrightarrow P \quad (\boldsymbol{k}_2) \end{array}$$

Although the pentacoordinated [FeH(DPPE)$_2$]$^+$ species exists,[2,34] and several coordinatively unsaturated [MX(diphosphine)$_2$]$^+$ (M = Fe, Ru, Os) species react with H$_2$ to form stable H$_2$ complexes,[19−21] this existence does not imply necessarily that it is formed in the H$_2$ substitution processes. In fact, the formation of [FeH(DPPE)$_2$]$^+$ from *trans*-[FeH(H$_2$)(DPPE)$_2$]$^+$ has not been observed, and, although the related [FeH(DTFE)$_2$]$^+$ complex (DTFE = 1,2-bis[bis(*p*-trifluoromethylphenyl)phosphino]ethane) reacts readily with H$_2$, the reverse process can only be achieved under vacuum at 170 °C.[19]

Another possible explanation is the existence of an associatively activated interchange mechanism:

$$trans\text{-}[\mathrm{FeH(H_2)(DPPE)_2}]^+ + \mathrm{L} \overset{K_{os}}{\rightleftarrows} \{trans\text{-}[\mathrm{FeH(H_2)(DPPE)_2}]^+, \mathrm{L}\} \xrightarrow{k} trans\text{-}[\mathrm{FeHL(DPPE)_2}]^+ + \mathrm{H_2}$$

where $a = k$ and $b = K_{os}$; the very negative values found for the activation volume associated with *k* suggest a definite associative character for these substitution reactions. Nevertheless, the values for K_{os} are expected to be larger for solvents with lower dielectric constants, contrarily to the experimental facts. Furthermore, although 20 electron species have been claimed as reasonable transition states for substitution reactions in organometallic complexes, all of them seem to operate for large metal centers.[35] In our case, the small low-spin Fe(II) metal center and the bulky phenyl substituents on the bidentate ligand are difficult to associate with an increased coordination sphere for the transition state.

A point that merits some comment is the fluxional behavior of the *trans*-[FeH(H$_2$)(DPPE)$_2$]$^+$ complex that makes all H atoms homotopic;[2] as a consequence, all hydrogens acquire a certain hydridic character that stabilizes the interaction with the iron center and makes much more difficult their dissociation as H$_2$. In all, it seems clear that direct substitution (associatively or dissociatively activated) is rather inadequate due both to the bulky ligands on a small metal center and the strength of the bond with the leaving ligand in the starting complex.

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The experimental rate law (eq 1) can be interpreted according to one of the reaction sequences shown in Chart 1. For a mechanism of Type I, the limiting rate constant would be k_2 and intermediate B accumulates in the presence of a large excess of L. As both the NMR and UV−vis spectra recorded immediately after mixing do not differ significantly from those obtained in the absence of L, this kind of mechanism requires, unreasonably, that B have NMR and electronic spectral properties very similar to those of the starting complex (to be, for example, an outer-sphere complex). The very negative activation volumes found for step k_2 requires the previous conversion of B to some kind of coordinatively unsaturated intermediate bound to have different spectral characteristics, thus precluding this mechanism.

For a mechanism of Type II, the limiting rate constant should correspond to k_1 and no buildup of intermediate will be expected. It is difficult, though, to imagine an intramolecular process involving a very large volume decrease unless there is a previous conversion of *trans*-$[FeH(H_2)(DPPE)_2]^+$ to an unsaturated intermediate. Thus, to accommodate all the experimental observations, both mechanisms require a further additional step to convert the starting compound to a reaction intermediate in very low concentration capable of undergoing an associative substitution. Given the fact that no structural information is available for this intermediate, the experimental data are consistent with any intramolecular transformation of the starting complex (or with participation of the solvent or the counterion). Once the simplest interpretations (H_2 dissociation and direct associative attack of L) can be ruled out by the reasons quoted above other possibilities have to be explored. Although an isomerization process is possible, it is not expected to involve a volume decrease as that determined experimentally; hydrogen bonding of *trans*-$[FeH(H_2)(DPPE)_2]^+$ to BF_4^- is possible, but the anion concentration is very small relative to both L and solvent; furthermore, its effect would be that of stabilizing the starting complex; proton dissociation is also possible, but it would lead to *cis*-$[FeH_2(DPPE)_2]$, which does not react with MeCN. An attractive possibility is that the limiting rate constant corresponds to an associative process that takes place once the opening of one of the chelate rings to form an intermediate species containing a monodentate DPPE has occurred. In fact, the dissociation of a spectator ligand has been suggested to explain both the catalytic properties[3] of *trans*-$[FeH(H_2)(PP_3)]^+$ and the conversion of $[Ru(H_2)(\eta^5\text{-}C_5H_5)(PPh_3)(CNBu^t)]^+$ to its HD isotopomer,[7] as well as for the initial step in H_2-D_2 equilibration catalyzed by Pt−Au clusters.[36] Moreover, the opening of a chelate ring has been also proposed to explain the kinetics of protonation of *trans*-$[FeHX(\text{diphosphine})_2]$ (diphosphine = DPPE, DEPE; X = Cl, Br)[31] and the substitution reactions of *trans*-$[\{FeCl(DPPE)_2\}_2N_2]$.[37] If the unsaturated intermediate is assumed to be formed in a chelate ring-opening process, substitution reactions of *trans*-$[FeH(H_2)(DPPE)_2]^+$ could occur through any of the following mechanisms:

A

$$trans\text{-}[FeH(H_2)(\eta^2\text{-DPPE})_2]^+ + L \rightleftarrows \{trans\text{-}[FeH(H_2)(\eta^2\text{-DPPE})_2]^+, L\} \qquad K_{os}, \text{fast} \quad (2)$$

$$\{trans\text{-}[FeH(H_2)(\eta^2\text{-DPPE})_2]^+, L\} \rightleftarrows \{[FeH(H_2)(\eta^2\text{- DPPE})(\eta^1\text{-DPPE})]^+, L\} \qquad K_1, \text{fast} \quad (3)$$

$$\{[FeH(H_2)(\eta^2\text{- DPPE})(\eta^1\text{-DPPE})]^+, L\} \rightleftarrows [FeH(H_2)L(\eta^2\text{- DPPE})(\eta^1\text{-DPPE})]^+ \qquad k_2 \quad (4)$$

$$[FeH(H_2)L(\eta^2\text{-DPPE})(\eta^1\text{-DPPE})]^+ \rightleftarrows trans\text{-}[FeHL(\eta^2\text{-DPPE})_2]^+ + H_2 \qquad \text{fast} \quad (5)$$

B (similar to **A** with eqs 2 and 3 replaced by eq 6)

$$trans\text{-}[FeH(H_2)(\eta^2\text{-DPPE})_2]^+ + L \rightleftarrows \{[FeH(H_2)(\eta^2\text{- DPPE})(\eta^1\text{-DPPE})]^+, L\} \qquad k_1, k_{-1} \quad (6)$$

For reaction sequence **A**, the rate law would be given by eq 1 with $a = K_1k_2$ and $b = K_{os}$, assuming that the equilibrium constant K_1 for the opening of the chelate ring is small. The major initial product in the presence of a large L excess would be $\{trans\text{-}[FeH(H_2)(DPPE)_2]^+, L\}$, with spectral properties similar to the starting complex. The value of k_2, corresponding to L attack to a little discriminating unsaturated intermediate, has to be little affected by the nature of both the solvent and the incoming ligand. The experimental activation volumes would then correspond to $\Delta V_1° + \Delta V_2^‡$. The value of $\Delta V_1°$ is expected to be small because the partial volume increase caused by the existence of a free PPh_2 group is compensated by the volume decrease due to a reduced coordination sphere and probably also by intramolecular hydrogen bonding between uncoordinated phosphorus and the acidic H_2 ligand. Therefore, the major contribution to the very negative activation volumes is due to $\Delta V_2^‡$, which corresponds to an associative attack of L to the unsaturated intermediate. Nevertheless, the strong solvent dependence of $\Delta V^‡$ suggests some kind of solvent interaction with the $[FeH(H_2)(\eta^2\text{-DPPE})(\eta^1\text{-DPPE})]^+$ species; thus, if solvent and incoming ligand are the same (solvolysis), the volume decrease associated with k_2 would be more negative because of the lack of solvent molecule release. Furthermore, the values of b for a given solvent have to reflect the differences in K_{os} due to steric requirements of the incoming ligand, and the larger b values in acetone show that equilibrium K_{os} does not only involve electrostatic interactions but that there must be also some kind of solvent dependent specific interactions.

If reaction sequence **B** is considered, application of the improved steady-state[38] approximation also leads to eq 1, with $a = k_2$ and $b = k_1/(k_{-1} + k_2)$. The activation volumes determined from the limiting rate constants would correspond directly to the associatively activated k_2 step as defined above, and most comments about sequence **A** would also apply, including those relative to the role of the solvent. Furthermore, the value of b would be the result of several contributions and

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the curvature in the plots should reflect, as it does, the steric effects of L and the ability of the solvent to favor formation of the intermediate. In this case, the steady-state approximation applied also accounts for the lack of spectral differences between the starting material and the reaction mixture at very short reaction times.

Thus, although the nature of the reaction intermediate is not defined by experimental data, both reaction sequences, **A** and **B**, satisfactorily explain the kinetic results, and it is clear at this time that the rate-determining step for substitution of coordinated H_2 in *trans*-$[FeH(H_2)(DPPE)_2]^+$ corresponds to a rather unexpected process involving an associatively activated transition state. As pointed out before, the fluxional process can be responsible for a stronger $H-Fe-H_2$ interaction that hinders H_2 dissociation and favors the chelate ring-opening pathway. However, there is also the possibility that the Fe−P(chelate) bond is inherently weaker than the $Fe-H_2$ bond, and so it is dissociated preferentially. Actually, there is evidence[37] of a chelate ring-opening process in the protonation of the related complex *trans*-$[FeHCl(DPPE)_2]$, which lacks the fluxional processes that stabilize the leaving ligand. However, the vacant coordination site created does not seem to be used in the substitution reactions of that complex.[37] Another question that arises from the mechanism proposed for substitution of H_2 in *trans*-$[FeH(H_2)(DPPE)_2]^+$ is the reason that makes substitution of H_2 in the intermediate species $[FeHL(H_2)(\eta^2\text{-DPPE})(\eta^1\text{-DPPE})]^+$ faster than in the starting material. Recent works have revealed a significant labilization of H_2 in complexes containing a π-donor ligand in cis,[10,18,20,25] which would account for the faster substitution in the intermediates formed by all the entering ligands, better π-donors than the PPh_2 group. Nevertheless, important changes in the electronic and steric characteristics of the complexes are also associated to the opening of the DPPE chelate ring and may contribute to labilization of H_2. That is, both the relief of steric constraints on going from an η^2- to an η^1-diphosphine and the decrease in electron density on the metal once phosphorus is dissociated can easily enhance associative substitution.

From the previous discussion, it is evident that the mechanism proposed can only be considered a first approximation to substitution mechanisms in this kind of dihydrogen complexes and more work is in progress to gain insight into the many questions that arise from the results obtained for *trans*-$[FeH(H_2)(DPPE)_2]^+$. In any case, it seems clear at this time that experimental observations cannot be explained with a single mechanism involving direct substitution of H_2 for L. Due to the limited kinetic data available, it is not possible to decide if the mechanism proposed is valid for reactions of other dihydrogen complexes. In fact, the rate law is similar for all the complexes studied to date (the observed rate constants are independent of the concentration of incoming ligand, or they show saturation behavior), and the thermal activation parameters are also similar to those in Table 2 ($\Delta H^‡$ ranging from 28 to 80 kJ/mol, and $\Delta S^‡$ usually close to zero).[8,10,13,14,18,25,40] Although the value of the $M-H_2$ bond dissociation energy has been calculated to be between 40 and 82 kJ/mol for the model compound *trans*-$[FeH(H_2)(PH_3)_4]^+$ [11] and other complexes,[12] covering a range very similar to that of the values found for $\Delta H^‡$, these are also similar to those found in classical associative substitutions. Thus, there is the possibility that substitution of coordinated H_2 in some other complexes occur through a mechanism similar to that proposed for *trans*-$[FeH(H_2)(DPPE)_2]^+$. Consideration of $[M(CO)_3(PCy_3)_2(H_2)]$ complexes requires special attention; elimination of H_2 from the Cr and W complexes leads to a pentacoordinate intermediate with a value of $\Delta H^‡$ several kJ/mol larger than the $M-H_2$ bond energy.[8,9] A mechanism involving concerted dissociation of the leaving ligand and formation of an agostic bond with a cyclohexyl group has been proposed to explain the kinetics of these reactions.[24] Thus, despite the reduced number of kinetic studies, a variety of mechanisms have been proposed for substitution of coordinated dihydrogen. Although reactions may proceed in some cases through simple dissociative mechanisms, it is evident that more work is required to understand the reasons that lead to the operation of alternative mechanisms and their relevance to catalyzed hydrogenations.

Experimental Section

Products. All the preparative and kinetic work was carried out under an argon atmosphere using Schlenk and syringe techniques. NMR spectra were obtained with a Varian Unity 400 spectrometer. The complex *trans*-$[FeH(H_2)(DPPE)_2](BF_4)$ was prepared from the corresponding dihydride complex according to literature procedures[2] and its purity was checked by ^1H and ^{31}P NMR. $FeCl_2$, DPPE, and PhCN were obtained from Aldrich. DMSO, acetonitrile, acetone, and tetrahydrofuran were obtained from SDS (Solvants Documentation Syntheses). The solvents were dried by refluxing them from appropriate drying agents and deoxygenated by bubbling argon through them immediately before use. All the products of substitution reactions showed a singlet in the phosphorus spectra at positions typical of *trans*-$[FeHX(DPPE)_2]^+$ complexes:[40] 84.3 ppm (X = MeCN), 83.5 ppm (X = PhCN), and 103.1 ppm (X = DMSO).

Kinetics. Kinetic experiments at room pressure were carried out under pseudo-first-order conditions (ligand excess) by adding weighed amounts of solid *trans*-$[FeH(H_2)(DPPE)_2](BF_4)$ to previously thermostated solutions containing the desired concentration of incoming ligand. The resulting solutions, with a concentration of iron complex of 5×10^{-4} M, were rapidly transferred with a Teflon tube to a thermostated flow cell. The time required to carry out the transfer is not significant with respect to the reaction time. Absorbance versus time traces were obtained with a Perkin-Elmer Lambda 3B spectrophotometer interfaced to a PC computer and were analyzed by conventional least-squares procedures. The monitoring wavelength was selected for every reaction from preliminary spectral scanning experiments: 445 nm (MeCN), 405 nm (PhCN), and 370 nm (DMSO). The first-order dependence of the rate on the concentration of iron complex was confirmed in some preliminary experiments that led to observed rate constants independent of the concentration of *trans*-$[FeH(H_2)(DPPE)_2]^+$. Thermal activation parameters were obtained from kinetic data at different temperatures using the standard Eyring plots.

For runs at elevated pressure, a previously described pressurizing system[41] and cylindrical cell fitted with a plunger were used.[27d] The solutions were made directly in the pressure cell by mixing the necessary amounts of solid product, or nonreacting THF or acetone solution, with the entering MeCN ligand. In these cases the absorbance versus time traces were recorded at a fixed wavelength on a Shimadzu UV1230 instrument fitted with fiber optics; alternatively, a TIDAS instrument measuring the full spectrum has also been used. Rate constants were derived from exponential least-squares fitting by the standard routines at a fixed wavelength or evaluating all the spectral changes.

Acknowledgment. Financial support from the Junta de Andalucía (Universidad de Cádiz) and the DGICYT (PB94-0857) and the Direcció General d'Universitats (Universitat de Barcelona) is gratefully acknowledged.

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Supporting Information Available: Tables of observed rate constants as a function of solvent, entering ligand, temperature, pressure and concentration of entering ligand, and limiting rate constants as a function of solvent, entering ligand, temperature and pressure. Figure including plots of ln *a*, as defined in eq 1, versus *P* for the reaction of *trans*-$[FeH(H_2)(DPPE)_2]^+$ with MeCN in (a) neat MeCN, (b) acetone, and (c) THF (15.1 °C, argon atmosphere) (3 pages). Ordering information is given on any current masthead page.

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