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Solvent and incoming ligand effects on the mechanism of substitution reactions of *trans*-[FeH(L)(DPPE)$_2$]$^+$ (L = MeCN), and comparison with the dihydrogen analogue (L = H$_2$) †

Manuel G. Basallote,[a] Joaquín Durán,[a] María J. Fernández-Trujillo,[a] Gabriel González,[b] M. Angeles Máñez[a] and Manuel Martínez[b]

[a] *Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Universidad de Cádiz, Apartado 40, E-11510 Puerto Real, Cádiz, Spain*
[b] *Departament de Química Inorgànica, Universitat de Barcelona, Martí i Franquès 1–11, E-08028 Barcelona, Spain*

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Reaction of *trans*-[FeH(MeCN)(DPPE)$_2$]$^+$ with PhCN to form *trans*-[FeH(PhCN)(DPPE)$_2$]$^+$ occurred with a single measurable kinetic step in THF, acetone or MeOH solutions (DPPE = $Ph_2PCH_2CH_2PPh_2$). The observed rate constants are independent of the concentration of the nucleophile and do not change very much with the solvent nature. However, the activation parameters are strongly solvent-dependent, especially $\Delta V^{\ddagger}$ that changes from 20 cm^3 mol^{-1} in THF to 35 cm^3 mol^{-1} in neat benzonitrile. Kinetic results for the reactions of *trans*-[FeH(MeCN)(DPPE)$_2$]$^+$ with substituted benzonitriles indicate that kinetic parameters for the substitution of co-ordinated MeCN also change with the nature of the entering ligand. The reactions of *trans*-[FeH(L)(DPPE)$_2$]$^+$ complexes (L = MeCN or H$_2$) with the bidentate ligands $C_6H_4(CN)_2$ (1,2-dicyanobenzene) and $Me_2PCH_2CH_2PMe_2$ (DMPE) have been also monitored by NMR at variable temperature. While for the acetonitrile complex and dicyanobenzene, *trans*-[FeH{$C_6H_4(CN)_2$}(DPPE)$_2$]$^+$ is the only product detected with no evidence of the formation of reaction intermediates or side-products, small amounts of free DPPE are detected for the same reaction with the dihydrogen complex to form the same monosubstituted complex. Moreover, whereas the acetonitrile complex does not react with DMPE, free DPPE is the only DPPE-containing product after reaction of *trans*-[FeH(H$_2$)(DPPE)$_2$]$^+$ with DMPE excess. The whole of the kinetic data and NMR observations are, on the one hand, consistent with a chelate ring-opening mechanism for the reactions of the dihydrogen complex and, on the other hand with a simple dissociative mechanism for the reactions of the acetonitrile complex. In all cases, the absolute values of $\Delta V^{\ddagger}$ for these reactions are larger than usual and also show an unusual dependence on the nature of the solvent and the entering ligand.

Introduction

Substitution reactions of 18-electron metal complexes in non-aqueous solvents are frequently assumed to occur through dissociatively activated mechanisms.[1] Although kinetic data often allow alternative interpretations, the existence of 16-electron species able to act as intermediates favours a limiting D mechanism.[2] Substitutions in the low-spin *trans*-[FeH(L)(DPPE)$_2$]$^+$ complexes can be considered a typical example of these reactions (DPPE = $Ph_2PCH_2CH_2PPh_2$); the species *trans*-[FeH(DPPE)$_2$]$^+$ has been isolated,[3,4] and substitution of Cl$^-$ in *trans*-[FeH(Cl)(DPPE)$_2$]$^+$ occurs at a rate that is independent of both the identity and the concentration of the incoming ligand,[5] which suggests a limiting D mechanism. Kinetic results for substitutions in other *trans*-[FeH(L)(diphosphine)$_2$]$^+$ complexes behave in a similar way,[6] consequently the generalisation of the conclusion that these reactions always occur through dissociatively activated mechanisms, as frequently found for substitutions in other low-spin iron(II) complexes,[7] is very tempting.

Although we found that substitution reactions of *trans*-[Fe(MeCN)$_2$(DPPE)$_2$]$^{2+}$ with anionic monodentate ligands occur with second order kinetics, the rate constants are independent of the nature of the incoming ligand, and the kinetic results could easily be explained by taking into account the formation of outer sphere complexes.[8] However, we have also shown that substitution of co-ordinated H$_2$ in *trans*-[FeH(H$_2$)(DPPE)$_2$]$^+$ occurs with very negative activation volumes that indicate a definite associative character for the rate-determining step,[9] which contrasts with the independent evidence on the existence of the 16-electron complex [FeH(DPPE)$_2$]$^+$.[3,4] For the hydride–dihydrogen complex the fluxional process[4] that makes equivalent the hydrogens of the ligands H$^-$ and H$_2$ and gives a certain hydridic character to all the hydrogen atoms was considered responsible for a stronger Fe–H$_2$ interaction, so hindering H$_2$ dissociation and forcing substitution reactions to occur through an alternative mechanism that involves the opening of a chelate ring.[9] However, we have shown more recently that substitutions in the *trans*-[RuH(H$_2$)(DPPE)$_2$]$^+$ analogue occur through a limiting D mechanism,[10] and the same mechanism has also been proposed for the substitution of H$_2$ in related iron(II) complexes containing other diphosphines.[11] Thus, the operation of a chelate-ring opening mechanism cannot exclusively be associated with a singular behaviour of the H$_2$ ligand; there is now mounting evidence that the mechanism of H$_2$ substitution in these complexes is strongly conditioned by the nature of the metal centre and the ancillary co-ligands.

In view of the fact that for most of the related [MX(H$_2$)(diphosphine)$_2$]$^+$ complexes, the substitution mechanism remains dissociative when the leaving ligand is changed from H$_2$ to another monodentate ligand,[5,6,10–12] we decided to explore more comprehensively the kinetics of the substitution reactions of *trans*-[FeH(MeCN)(DPPE)$_2$]$^+$, including the determination of thermal and pressure activation parameters, which are so informative for substitution of co-ordinated dihydrogen. The study has been extended to reactions with substituted benzo-

† *Supplementary data available*: primary kinetic data. For direct electronic access see http://www.rsc.org/suppdata/dt/1999/3379/, otherwise available from BLDSC (No. SUP 57626, 6 pp.) or the RSC Library. See Instructions for Authors, 1999, Issue 1 (http://www/rsc.org/dalton).

Table 1 Kinetic data for the reaction of *trans*-[FeH(MeCN)(DPPE)$_2$]$^+$ with PhCN and substituted benzonitriles in different solvents (values in parentheses indicate the standard deviation in the last significant digit)

Ligand	Solvent	$10^4\ k_{298}$/s^{-1}	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	$\Delta V^‡$/cm^3 mol^{-1}
PhCN	THF	0.94	91(4)	−16(12)	20(1)
	Acetone	1.69	102(4)	27(12)	28(1)
	MeOH	2.21	106(1)	42(4)	34(1)
	PhCN	0.72	110(2)	44(7)	35(3)[a]
2-MeOC$_6$H$_4$CN	Acetone	1.68	84(6)	−34(20)	25(2)[a]
2,6-(MeO)$_2$C$_6$H$_3$CN	THF	1.06	84(3)	−40(11)	28(1)[a]
	Acetone	3.52	81(2)	−40(7)	40(3)[a]

[a] The results obtained at a different temperature and using a different sample of the starting complex were 35(1) cm^3 mol^{-1} for the reaction with PhCN in neat PhCN, 28(1) cm^3 mol^{-1} for the reaction with 2-MeOC$_6$H$_4$CN in acetone, 28(1) cm^3 mol^{-1} for the reaction with 2,6-(MeO)$_2$C$_6$H$_3$CN in THF, and 38(2) cm^3 mol^{-1} for the reaction with 2,6-(MeO)$_2$C$_6$H$_3$CN in acetone. Thus, the values derived for $\Delta V^‡$ in duplicate experiments agree within experimental error in all cases. Detailed listings of rate constants and conditions are provided in SUP 57626.

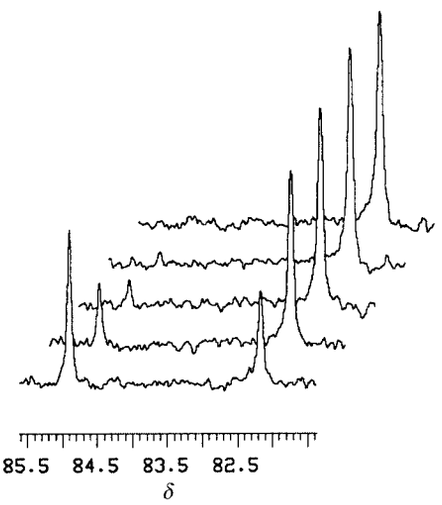

Fig. 1 The ^{31}P-{^{1}H} NMR spectra recorded during the reaction of *trans*-[FeH(MeCN)(DPPE)$_2$]$^+$ with 2,6-(MeO)$_2$C$_6$H$_3$CN excess in [D$_6$]-acetone solution at 35 °C. The spectra were recorded at 922 s intervals and show the complete conversion into *trans*-[FeH(2,6-(MeO)$_2$-C$_6$H$_3$CN)(DPPE)$_2$]$^+$. The concentrations of iron complex and incoming ligand were close to 1×10^{-3} and 0.05 mol dm^{-3}, respectively.

nitriles in order to examine possible steric and electronic effects of the incoming ligand. Given the fact that the activation parameters suggested a drastic mechanistic change for the substitution reactions of *trans*-[FeH(L)(DPPE)$_2$]$^+$ complexes when L is changed from H_2 to MeCN and, in an attempt to obtain some information about the structures of the reaction intermediates, the reactions of both complexes with bidentate ligands were monitored by NMR.

Results and discussion

Kinetics of reaction with monodentate ligands

The reactions of *trans*-[FeH(MeCN)(DPPE)$_2$]$^+$ with PhCN and substituted benzonitriles were studied in [D$_6$]acetone by monitoring the changes with time of the ^{31}P NMR spectra in the presence of a large excess of incoming ligand. Fig. 1 shows the spectra corresponding to the reaction with 2,6-(MeO)$_2$C$_6$H$_3$CN, and the results obtained for the other ligands were similar. In all cases the spectra show the full conversion of the starting complex into the substitution product without any evidence of reaction intermediates or side-products. Thus, NMR experiments confirm the nature of the substitution products and indicate that the reactions (1) occur in a single step without

trans-[FeH(MeCN)(DPPE)$_2$]$^+$ + L ⟶ *trans*-[FeH(L)(DPPE)$_2$]$^+$ + MeCN (1)

(L = PhCN, 2-MeOC$_6$H$_4$CN or 2,6-(MeO)$_2$C$_6$H$_3$CN)

accumulation of any reaction intermediate. Monitoring the UV-Vis spectral changes in acetone solution confirms the NMR observations described above. In all cases the band of *trans*-[FeH(MeCN)(DPPE)$_2$]$^+$ at 435 nm disappears with development of a new band at 405 nm corresponding to the substituted product. The positions of the bands do not change significantly when THF or MeOH replaces acetone as solvent, indicating that solvento species are not present in the reaction medium at measurable quantities. As expected, absorbance–time traces at 405 nm show a large absorbance increase that can be fitted by a single exponential to obtain the values of the rate constant, k_{obs} (SUP 57626). The value of k_{obs} at a given temperature is found to be independent of the concentration of the starting complex and only shows minor changes with the nature of the solvent. Although there are also small changes (less than *ca.* 15%) with the concentration of incoming ligand, they occur for very large concentration changes, and the values of k_{obs} decrease with increase of ligand concentration. These changes are better related to a modification in the properties of the reaction medium than to a dependence of k_{obs} on the concentration of the incoming ligand, and the rate law is given by eqn. 2.

$$-\mathrm{d}[\textit{trans}\text{-FeH(MeCN)(DPPE)}_2^+]/\mathrm{d}t = k_{obs}[\textit{trans}\text{-FeH(MeCN)(DPPE)}_2^+] \quad (2)$$

The activation parameters have been determined in several solvents, and their values are collected with the rate constants at 298 K in Table 1. Although the values of k_{obs} only show small changes with the solvent and the incoming ligand, activation parameters are strongly dependent on both factors. All the $\Delta H^‡$ values are in a narrow range (81–110 kJ mol^{-1}); the donor character of the solvent and the incoming ligand seems to affect them in opposite ways. While changing the solvent from THF to PhCN causes an increase in the enthalpic barrier, the change of the incoming ligand from PhCN to substituted benzonitriles decreases it. Although the determination of $\Delta S^‡$ is usually affected by large errors, the values in Table 1 cover a very wide range and seem to indicate that the dissociative character of the limiting step decreases with the donor character of the entering ligand and increases with the same character of the solvent. The activation volumes are always positive and indicate a dissociative mode of activation, although dependent on the nature of both the solvent and the entering ligand. While for the reaction with PhCN there is a good correlation between the increasing values of $\Delta V^‡$ and $\Delta S^‡$ and the donor character of the solvent, the trend is not maintained for the substituted benzonitriles.

Mechanisms for the substitution reactions in *trans*-[FeH(L)(DPPE)$_2$]$^+$ complexes (L = MeCN or H_2)

The whole of the data in Table 1 for substitution of coordinated MeCN in the starting complex, and especially the

large positive values of the activation volumes, clearly indicate dissociative activation, as frequently found for substitution in other low spin d^6 metal complexes.[7,13] The simplest interpretation of kinetic data would be a limiting D mechanism involving dissociation of the leaving ligand and formation of the five-co-ordinate intermediate $[FeH(DPPE)_2]^+$ eqns. (3) and (4).

$$trans\text{-}[FeH(MeCN)(DPPE)_2]^+ \rightleftharpoons [FeH(DPPE)_2]^+ + MeCN;\ k_1, k_{-1} \quad (3)$$

$$[FeH(DPPE)_2]^+ + L \longrightarrow trans\text{-}[FeH(L)(DPPE)_2]^+;\ k_2 \quad (4)$$

The limiting value of the rate constant for this mechanism (k_1) corresponds to the breaking of the MeCN–Fe bond and should be independent of the nature of the incoming ligand. The small differences of the rate constants and thermal activation parameters for the reactions with PhCN and substituted benzonitriles should be then attributed to medium effects. For a limiting dissociative mechanism an increase in the co-ordinating character of the solvent is expected to stabilise the five-co-ordinate intermediate and, consequently, to decrease the activation barrier, and the data in Table 1 show the inverse trend. We have also studied recently substitutions in the closely related *cis*-$[RuCl(nitrile)(DPPE)_2]^+$ and *trans*-$[RuH(H_2)(DPPE)_2]^+$ complexes,[10,12] whose reactions occur through a D mechanism, and the changes in the rate constants and thermal activation parameters are smaller than those in Table 1, showing the normal solvent dependence expected from solvation differences in a simple dissociative process. Although the absence of a detectable intermediate and the small changes in the values of k, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the reactions of *trans*-$[FeH(MeCN)(DPPE)_2]^+$ suggest a D mechanism, the large differences in the values of $\Delta V^{\ddagger}$ and the comparison with previously reported data[9] for substitution of H_2 in the related *trans*-$[FeH(H_2)(DPPE)_2]^+$ make also possible alternative interpretations.

For the case of the dihydrogen complex the activation volumes are very negative and indicate a definite associative activation with a strong dependence on the nature of the solvent.[9] On the contrary, substitution of MeCN in *trans*-$[FeH(MeCN)(DPPE)_2]^+$ always occurs with positive activation volumes. It is important to note that the few values of $\Delta V^{\ddagger}$ available for substitution reactions of the type (5) span from

$$trans\text{-}[FeH(L)(DPPE)_2]^+ + L' \longrightarrow trans\text{-}[FeH(L')(DPPE)_2]^+ + L \quad (5)$$

-35 to $+40$ cm^3 mol^{-1}, which is one of the largest ranges found for a series of so closely related reactions. Fig. 2 compares most of these activation volumes and it shows clearly that the absolute value of $\Delta V^{\ddagger}$ increases with the donor ability of the solvent. The general situation is that activation volumes for substitution of L by L′ are always very large, although either positive or negative. The magnitude of the volume changes during the activation process depends on the nature of the incoming ligand and the solvent, with the maximum absolute values being always observed in the solvolysis experiments.

If reactions (5) occur through a simple mechanism involving exclusively the co-ordination site of the leaving ligand, the values of $\Delta V^{\ddagger}$ indicate a change from a strongly dissociative activation for MeCN to strongly associative activation for H_2. This would represent an unusual behaviour of the dihydrogen complex because of the strong tendency of octahedral low spin d^6 complexes to undergo dissociatively activated substitutions. The acidic character of co-ordinated H_2 allows the formation of a dihydrogen bonded structure of the type $Fe(H_2)^+ \cdots L$, similar to those proposed to occur during the protonation of metal hydrides to form dihydrogen complexes.[14] Although this interaction could justify a certain decrease of the activation volume corresponding to the substitution, it does not explain

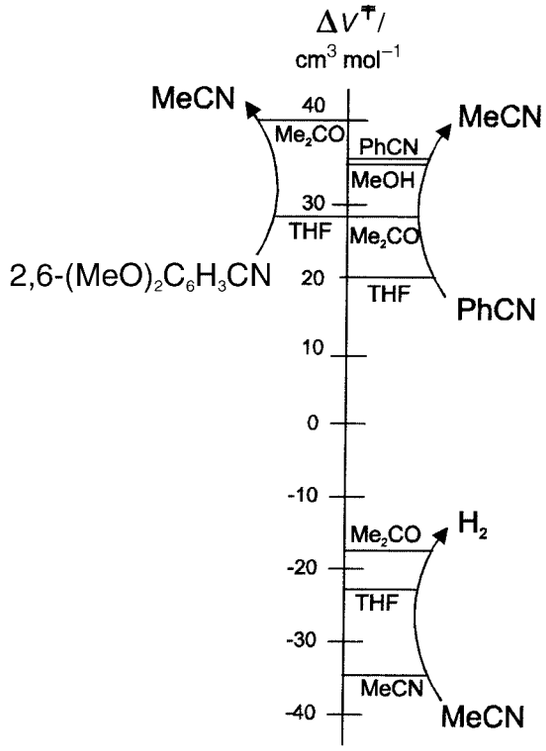

Fig. 2 Graphical presentation of $\Delta V^{\ddagger}$ values for substitution reactions of *trans*-$[FeH(L)(DPPE)_2]^+$ complexes (L = H_2 or MeCN). Horizontal lines connected to a common arrow represent the values obtained for the same reaction in different solvents, and the labels at both ends of the arrows indicate the leaving and incoming ligands.

the large change of more than 70 cm^3 mol^{-1} observed experimentally and so kinetic results for the dihydrogen complex were interpreted on the basis of a mechanism involving the opening of a DPPE chelate ring.[9] The major advantage of the latter mechanism is that it involves exclusively the formation of 16- and 18-electron intermediates that undergo ligand addition or dissociation in purely associative or dissociative steps. The chelate ring opening mechanism can easily be accommodated to explain the change in the activation mode between the dihydrogen and the acetonitrile complexes. Following the initial opening of the ring, the vacant co-ordination site can be occupied by the solvent or the entering ligand, and the rate determining step for the acetonitrile complex would be dissociation of the leaving ligand with highly positive activation volumes. For the case of the dihydrogen complex the fluxional behaviour stabilises the intermediate with the opened DPPE ring and causes attack by the solvent or the entering ligand to become the rate-determining step with very negative activation volumes.

An obvious alternative to the latter interpretation is that substitutions in *trans*-$[FeH(MeCN)(DPPE)_2]^+$ occur through a simple D mechanism similar to that found for many related complexes and that the ring opening mechanism operates exclusively for the reactions of the dihydrogen complex because of the accumulation of a series of favourable circumstances. In an attempt to discriminate between those possibilities we decided to study the reactions of the MeCN and the H_2 complexes with some bidentate ligands.

The reaction of *trans*-$[FeH(L)(DPPE)_2]^+$ complexes (L = MeCN or H_2) with bidentate ligands

Since any possible intermediate in the substitution reactions of *trans*-$[FeH(L)(DPPE)_2]^+$ complexes with monodentate ligands is formed under steady-state conditions, it is very difficult to discriminate between the dissociative and the ring opening mechanisms (see above). However, under favourable circumstances, there is the possibility to obtain some information

about the structure of the reaction intermediate if the reactions are carried out using bidentate ligands as nucleophiles. Thus, if the substitution of L occurs through a D mechanism the intermediate $[FeH(DPPE)_2]^+$ will be formed and, in the presence of an excess of a bidentate ligand Y ~ Y, the monosubstituted *trans*-$[FeH(Y \sim Y)(DPPE)_2]^+$ complex will be the only initial reaction product. On the contrary, if the reaction goes through the opening of a chelate ring there will be at some point along the reaction coordinate an intermediate containing two bidentate ligands co-ordinated in a monodentate way. Following dissociation of the leaving ligand the reaction could proceed through closure of the DPPE or the Y ~ Y ring. The latter case should lead to products containing monodentate DPPE; if any of these products were sufficiently long-lived to be detected by NMR it would constitute very strong evidence on the operation of a ring opening mechanism.

NMR experiments at variable temperature in which the reactions of both *trans*-$[FeH(L)(DPPE)_2]^+$ complexes (L = H_2 or MeCN) with the bidentate ligands 1,2-dicyanobenzene and DMPE have been carried out. Dicyanobenzene reacts with *trans*-$[FeH(MeCN)(DPPE)_2]^+$ as monodentate nitriles do, yielding *trans*-$[FeH\{C_6H_4(CN)_2\}(DPPE)_2]^+$, in which only one of the cyano groups is co-ordinated. The reaction takes place slowly and there is no NMR evidence of any intermediate or subsequent reaction product when the reaction is carried out at temperatures ranging from −40 to +40 °C. Nevertheless, although the reaction product of *trans*-$[FeH(H_2)(DPPE)_2]^+$ with $C_6H_4(CN)_2$ is the same monosubstituted complex, significant amounts of free DPPE are detected when the reaction is carried out at temperatures lower than 0 °C. That is, at −30 °C the release of DPPE is observed before the formation of *trans*-$[FeH\{C_6H_4(CN)_2\}(DPPE)_2]^+$, whereas at +30 °C the substituted complex is formed exclusively and no free DPPE is detected in the reaction medium. Although we have been unable to detect any intermediate species, the release of free DPPE in the reaction of the dihydrogen complex has to take place through the opening of a chelate ring, in agreement with our previous mechanistic proposal.[9] In order to accommodate our results, it seems clear that the steady-state intermediate resulting from ring-opening can undergo two parallel processes, one of them leading to complete dissociation of DPPE and the other to a substitution product similar to that formed with monodentate ligands. Furthermore, the process leading to free DPPE surely involves also the formation of a tetrahedral iron(II) complex containing one bidentate DPPE; these tetrahedral species are paramagnetic and non-observable by NMR.[15] By contrast, the absence of DPPE during the reaction of the MeCN complex suggests a D mechanism, although formation of an intermediate with an opened chelate ring that converts exclusively into the substitution product cannot be ruled out.

The different behaviour of these complexes is much more evident when their reactions with DMPE are considered. On one hand the product expected from simple monosubstitution, *trans*-$[FeH\{\eta^1\text{-DMPE}\}(DPPE)_2]^+$, is not observed either as intermediate or as final substituted product in the reactions of both *trans*-$[FeH(H_2)(DPPE)_2]^+$ and *trans*-$[FeH(MeCN)(DPPE)_2]^+$. This is a clear indication that co-ordination of a Me_2P group of DMPE at the $FeH(DPPE)_2^+$ site is not favoured thermodynamically, probably because of the steric constraints imposed by the bulky Ph_2P groups of the DPPE ligands. This behaviour is very different from that of *trans*-$[FeH(H_2)(DMPE)_2]^+$, which initially forms *trans*-$[FeH(\eta^1\text{-DMPE})(DMPE)_2]^+$ presumably through a dissociative mechanism.[16] On the other hand, whereas there is no reaction between *trans*-$[FeH(MeCN)(DPPE)_2]^+$ and an excess of DMPE after two days at 30 °C, the analogous dihydrogen complex reacts at an appreciable rate even at −40 °C. In the latter case the reaction mixture shows very complex NMR spectra that indicate the formation of small amounts of several species with multiple couplings; anyhow, the appearance of free DPPE is detected from the beginning of the reaction. Actually, although the details of this reaction are very complex and are currently under study, the NMR experiments show that the only DPPE-containing species detectable by NMR after two days of reaction at 30 °C is DPPE itself, which indicates that the dihydrogen complex has a reaction pathway unavailable for the acetonitrile complex. Kinetic data for the reaction of *trans*-$[FeH(H_2)(DPPE)_2]^+$ with monodentate ligands and the release of free DPPE during the reaction with bidentate ligands strongly support our previously proposed mechanism involving the opening of a chelate ring. On the contrary, the kinetic data and NMR observations for the reactions of *trans*-$[FeH(MeCN)(DPPE)_2]^+$ are much more consistent with a limiting D mechanism; if a chelate ring-opening pathway were also available for this complex there is no reason to understand the lack of reaction with DMPE.

Although the reduced number of detailed kinetic studies does not allow us to obtain general conclusions about the actual requirements for substitution reactions in *trans*-$[FeH(L)(DPPE)_2]^+$ complexes to go through the simple D mechanism or the more complex one involving the opening of a chelate ring, the experimental evidence on the operation of the latter mechanism in the reactions of the H_2 complex is now even more solid. There are also previous reports invoking the opening of phosphine chelate rings to explain experimental observations relative to the protonation,[5,6,17] substitution reactions,[4] and catalytic[18] and acidic[19] properties of metal complexes containing polydentate phosphines. The operation of this kind of mechanism requires that the activation barrier for the opening of the ring is lower than that corresponding to direct substitution of the leaving ligand. A chelate ring-opening mechanism involves the breaking of a Fe^{II}–P (chelate) bond, but the energy required for this process is probably not very high because of both the greater relief of steric strain on dissociation of a bulky PPh_2 group[6] and the relatively low affinity of Fe^{II} for phosphine ligands.[15] In fact, Fe^{II} is not considered a good Lewis acid for phosphines, presumably due to the small size of iron and the weakness of the Fe–P bond and there is evidence that the chemistry of these complexes is sometimes dominated by the ready loss of a DPPE molecule.[15] Thus, the activation barriers for dissociation of a monodentate ligand and a PPh_2 group of DPPE are almost balanced and, consequently, chelate ring opening may be a competitive pathway for the reactions of *trans*-$[FeH(L)(DPPE)_2]^+$ complexes, especially when there is an additional stabilisation of the leaving ligand. The fluxional process, that makes equivalent the H atoms in the H_2 and H^- ligands of *trans*-$[FeH(H_2)(DPPE)_2]^+$ and stabilises the leaving ligand, and/or the acidic character of co-ordinated dihydrogen, that allows the formation of dihydrogen-bonded adducts with the entering ligand or an unco-ordinated PPh_2 group thus making H_2 less susceptible to dissociation, can be considered responsible for the operation of a chelate ring opening mechanism in the reactions of this complex. On the contrary, the acetonitrile ligand of *trans*-$[FeH(MeCN)(DPPE)_2]^+$ is not involved in any fluxional process and there is no evidence of acidic behaviour; under these conditions the only favoured reaction pathway for substitution goes through acetonitrile dissociation.

The effects of the solvent and the incoming ligand on the activation parameters for substitution of co-ordinated acetonitrile are much larger than usual for dissociative substitutions and illustrate the complex dependence of the activation parameters for these reactions on the properties of the reaction medium. Although there is the possibility of an isokinetic correlation between the experimentally determined values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, we have not found such large variations in the dissociative substitutions of the closely related complexes *trans*-$[RuH(H_2)(DPPE)_2]^+$ and *cis*-$[RuCl(nitrile)(DPPE)_2]^+$.[10,12] Thus, the data in Table 1 suggest that, despite the co-ordinatively unsaturated nature of the intermediate $[FeH(DPPE)_2]^+$, there is

a preferential interaction of both the solvent and the entering ligand with the starting acetonitrile complex. As the donor power of the solvent and/or the entering ligand increases there is a stronger interaction with the starting complex that increases the activation barrier and leads to larger volume changes. Although we cannot explain satisfactorily at this time the reduced ability of the 16-electron intermediate to interact with the solvent and the entering ligand, there is the possibility that electron deficiency is compensated through the formation of an agostic bond or through a structural reorganisation of the phosphine ligands of the type proposed for five-co-ordinate $[RuCl(DPPE)_2]^+$;[12] an increased electron donation to the metal centre and extensive structural reorganisation of the intermediate could result in a reduced affinity for the solvent and the entering ligand.

Experimental

All the preparative and kinetic work was carried out under an argon atmosphere using standard Schlenk and syringe techniques. The solvents THF, MeCN, acetone and methanol (SDS) were dried by refluxing them from sodium–benzophenone, P_4O_{10} or $CaSO_4$; alternatively, solvents dried over Linde 4 A molecular sieves led to similar kinetic results. In all cases the solvents were also deoxygenated by bubbling argon through them immediately before use. Benzonitrile, 2-methoxybenzonitrile, 2,6-dimethoxybenzonitrile, 1,2-dicyanobenzene, DMPE and DPPE were obtained from Aldrich and used as received. The NMR spectra were recorded with a Varian Unity 400 spectrometer. Chemical shifts are reported relative to TMS for the proton spectra and to 85% H_3PO_4 for the phosphorus spectra.

The complex *trans*-$[FeH(H_2)(DPPE)_2]BF_4$ was prepared using the literature procedure;[20] *trans*-$[FeH(MeCN)(DPPE)_2]BF_4$ was prepared by dissolving *trans*-$[FeH(H_2)(DPPE)_2]BF_4$ in MeCN and stirring overnight at room temperature; addition of an excess of diethyl ether precipitating the acetonitrile complex. The UV-Vis, ^1H and ^{31}P NMR spectra agree satisfactorily with those published previously.[9,21] The PhCN substituted product was identified as *trans*-$[FeH(PhCN)(DPPE)_2]^+$ on the basis of its UV-vis and NMR spectra.[9,21] The products of reaction with substituted benzonitriles have not been described previously but they were easily characterised as *trans*-$[FeH(2\text{-}MeOC_6H_4CN)(DPPE)_2]^+$ and *trans*-$[FeH(2,6\text{-}(MeO)_2C_6H_3CN)(DPPE)_2]^+$ on the basis of their NMR spectra: δ_P 83.4 (singlet), δ_H −19.0 (quintuplet) and $^2J_{H,P} = 53$ Hz for the 2-$MeOC_6H_4CN$ complex, and δ_P 82.2 (singlet), δ_H −19.4 (quintuplet) and $^2J_{H,P} = 52$ Hz for the 2,6-$(MeO)_2C_6H_3CN$ complex. The singlet in the phosphorus spectra of both complexes converts into a doublet in the proton-coupled spectra. The electronic spectra of the substitution products are similar in all cases with a band centred at 405 nm and $\varepsilon_{max} = 2.83 \times 10^3$ (PhCN complex), 2.98×10^3 (2-$MeOC_6H_4CN$ complex), and 2.89×10^3 dm^3 mol^{-1} cm^{-1} [2,6-$(MeO)_2C_6H_3CN$ complex]. The reaction product between *trans*-$[FeH(H_2)(DPPE)_2]^+$ or *trans*-$[FeH(MeCN)(DPPE)_2]^+$ and 1,2-dicyanobenzene was also characterised as *trans*-$[FeH\{C_6H_4(CN)_2\}(DPPE)_2]^+$ on the basis of the NMR spectra: δ_P 82.5 (singlet), δ_H −17.3 (quintuplet) and $^2J_{H,P} = 48$ Hz.

Kinetic experiments at room pressure were carried out under pseudo-first-order conditions (ligand excess) using the experimental procedure described previously for reactions of *trans*-$[FeH(H_2)(DPPE)_2]^+$.[9] All reactions were monitored at 405 nm by recording absorbance–time traces with a Perkin-Elmer Lambda 3B instrument interfaced to a PC. The curves were analysed by conventional least-squares procedures and thermal activation parameters obtained from kinetic data at different temperatures using standard Eyring plots.

The experimental procedure for kinetic runs at high pressure has also been described recently.[9] The high pressure UV-Vis cell used was a cylindrical polished quartz cell with a mobile Teflon stopper and a volume of *ca*. 1.5 ml. Kinetic traces were obtained in this case using either a Shimadzu UV1230 instrument fitted with fibre optics or a TIDAS instrument, and rate constants were also obtained using conventional fitting procedures. Activation volumes were obtained from standard linear plots of ln *k vs. P*. Since some of the experiments were initially carried out at temperatures higher than room temperature and some of the observed rate constants could be presumably too high for the experimental procedure used, these experiments were repeated at lower temperature. The activation volumes derived in these duplicate experiments always agreed within experimental error.

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References

1 J. D. Atwood, *Inorganic and Organometallic Reaction Mechanisms*, Brooks/Cole, Monterey, CA, 1985, ch. 4; J. P. Collman, L. S. Hegedus, J. R. Norton and R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987, p. 236.

2 A. Mezzetti, A. Del Zotto and P. Rigo, *J. Chem. Soc.*, *Dalton Trans.*, 1990, 2515; A. Mezzetti, A. Del Zotto, P. Rigo and E. Farnetti, *J. Chem. Soc.*, *Dalton Trans.*, 1991, 1525; L. D. Field, T. W. Hambley and B. C. K. Yau, *Inorg. Chem.*, 1994, **33**, 2009; E. Rocchini, A. Mezzetti, H. Rüeger, U. Burckhardt, V. Gramlich, A. Del Zotto, P. Martuzzini and P. Rigo, *Inorg. Chem.*, 1997, **36**, 711.

3 M. Aresta, P. Giannoccaro, M. Rossi and A. Sacco, *Inorg. Chim. Acta*, 1971, **5**, 115.

4 M. T. Bautista, E. P. Cappellani, S. D. Drouin, R. H. Morris, C. T. Schweitzer, A. Sella and J. Zubkowski, *J. Am. Chem. Soc.*, 1991, **113**, 4876.

5 R. A. Henderson, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 509.

6 R. A. Henderson, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 515.

7 R. G. Wilkins, *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd edn., VCH, Weinheim, 1991, p. 394 and refs. therein.

8 M. A. Máñez, M. J. Fernández-Trujillo and M. G. Basallote, *Polyhedron*, 1996, **15**, 2305.

9 M. G. Basallote, J. Durán, M. J. Fernández-Trujillo, G. González, M. A. Máñez and M. Martínez, *Inorg. Chem.*, 1998, **37**, 1623.

10 M. G. Basallote, J. Durán, M. J. Fernández-Trujillo and M. A. Máñez, *Inorg. Chem.*, in the press.

11 C. A. Helleren, R. A. Henderson and G. J. Leigh. *J. Chem. Soc.*, *Dalton Trans.*, 1999, 1213.

12 M. G. Basallote, J. Durán, M. J. Fernández-Trujillo and M. A. Máñez, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 3227.

13 K. B. Reddy and R. van Eldik, *Inorg. Chem.*, 1991, **30**, 596; G. Stochel, J. Chatlas, P. Martínez and R. van Eldik, *Inorg. Chem.*, 1992, **31**, 5480.

14 M. G. Basallote, J. Durán, M. J. Fernández-Trujillo, M. A. Máñez and J. Rodríguez de la Torre, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 745; M. G. Basallote, J. Durán, M. J. Fernández-Trujillo and M. A. Máñez, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 2205.

15 J. E. Barclay, G. J. Leigh, A. Houlton and J. Silver, *J. Chem. Soc.*, *Dalton Trans.*, 1988, 2865.

16 M. V. Baker, L. D. Field and D. J. Young, *J. Chem. Soc.*, *Chem. Commun.*, 1988, 546.

17 S. C. Davies, R. A. Henderson, D. L. Hughes and K. E. Oglieve, *J. Chem. Soc.*, *Dalton Trans.*, 1998, 425.

18 C. Bianchini, A. Meli, M. Peruzzini, P. Frediani, C. Bohanna, M. A. Esteruelas and L. A. Oro, *Organometallics*, 1992, **11**, 138.

19 B. Chin, A. J. Lough, R. H. Morris, C. T. Schweitzer and C. D'Agostino, *Inorg. Chem.*, 1994, **33**, 6278.

20 R. H. Morris, J. F. Sawyer, M. Shiralian and J. D. Zubkowski, *J. Am. Chem. Soc.*, 1985, **107**, 5581.

21 S. D. Ittel, C. A. Tolman, P. J. Krusic, A. D. English and J. P. Jesson, *Inorg. Chem.*, 1978, **17**, 3432.

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