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Kinetics and mechanism of substitution reactions in *cis*-[RuCl(L)(dppe)$_2$]$^+$ complexes (L = RCN, dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$)†

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The five-co-ordinated [RuCl(dppe)$_2$]$^+$ complex reacted rapidly with nitriles to form the corresponding octahedral *cis*-[RuCl(L)(dppe)$_2$]$^+$ compounds [L = MeCN, PhCN, or 2,6-(MeO)$_2$C$_6$H$_3$CN]. The kinetics of these reactions has been studied in acetone and CH$_2$Cl$_2$ solutions by monitoring the absorbance changes at 425 nm with a stopped-flow instrument. All reactions are first order with respect to the concentration of both the starting complex and the incoming ligand, and the second order rate constants at 25 °C for the reactions with the three nitriles are similar to each other. The poor discriminating ability of [RuCl(dppe)$_2$]$^+$ towards the different incoming ligands used and its selectivity for *cis* addition can be explained by considering the Y-distorted trigonal bipyramidal structure of the complex. The values derived for the activation parameters are in all cases compatible with associative activation, with small effects due to the solvent and the incoming ligand. Octahedral *cis*-[RuCl(L)(dppe)$_2$]$^+$ compounds partially dissociate L in solution to give an equilibrium mixture of the starting complex and [RuCl(dppe)$_2$]$^+$ and so the kinetics of substitution of L by L′ in the octahedral complexes has been studied using an excess of both the leaving ligand and the nucleophile. The kinetic data for these reactions indicate a dissociative mechanism with formation of [RuCl(dppe)$_2$]$^+$ as intermediate. When taken together, the activation parameters for these substitution reactions and those for ligand addition to [RuCl(dppe)$_2$]$^+$ lead to complete activation profiles for the substitution reactions in the octahedral complexes and to the thermodynamic parameters for addition of one ligand to the five-co-ordinated complex. These parameters indicate that the energy required to dissociate L from *cis*-[RuCl(L)(dppe)$_2$]$^+$ is higher than the binding energy of L to [RuCl(dppe)$_2$]$^+$, which has been interpreted in terms of a structural reorganisation of the intermediate.

Introduction

Chelating diphosphines such as 1,2-bis(diphenylphosphino)ethane (dppe) are often used as coligands in a great variety of metal complexes, including some relevant to the activation of small molecules as N$_2$ and H$_2$.[1] The role of the co-ordinated diphosphine in these complexes is frequently assumed to be that of a simple spectator ligand that blocks co-ordination sites and forces reactions to occur at the metal centre or at monodentate ligands. Nevertheless, there have been some reports pointing towards a more direct participation of the diphosphine in the reactivity pattern of the complexes. Thus, Henderson[2] proposed years ago that reaction of *trans*-[FeH(Cl)(dppe)$_2$] with HCl occurs through the initial opening of a dppe chelate ring and protonation of the unco-ordinated PPh$_2$ group. For that case, protonation at phosphorus is favoured against protonation at the metal centre or at one co-ordinated hydride and, actually, the dihydrogen complex *trans*-[FeCl(H$_2$)(dppe)$_2$]$^+$ is so acidic that it does not exist.[3] More recently, chelate ring opening has been invoked to explain the catalytic properties and the reactivity of related complexes.[3,4]

In a recent paper[5] we have shown that substitution reactions of *trans*-[FeH(H$_2$)(dppe)$_2$]$^+$ do not occur through a simple mechanism involving H$_2$ dissociation, despite the inherent weakness of the M–H$_2$ bonds.[1c] We considered then that the existence of a fluxional process[6] gives to all the H atoms a certain hydridic character that hinders H$_2$ dissociation and forces reactions to go through an alternative mechanism, probably one that involves the opening of a chelate ring. However, we found later[7] similar kinetic features for substitution reactions of *trans*-[FeH(MeCN)(dppe)$_2$]$^+$, which lacks fluxional processes that stabilise the interaction of the leaving ligand with the metal centre. Thus, it seems possible that the operation of unexpected mechanisms involving chelate ring opening can be quite common in substitution reactions of this kind of complexes, which contrasts with independent evidence on the existence of [FeH(dppe)$_2$]$^+$ that is the presumed intermediate in simple dissociative mechanisms.[8] At this point it seems important to determine the factors that make reactions to go through the chelate ring-opening pathway or the alternative one involving dissociative loss of the leaving ligand. So, we looked for well characterised complexes that should undergo substitution reactions through a simple dissociatively activated mechanism, and considered that the co-ordinatively unsaturated [RuCl(dppe)$_2$]$^+$ complex described by Morris and co-workers[3] would be a good candidate. This compound adds reversibly MeCN to give *cis*-[RuCl(MeCN)(dppe)$_2$]$^+$ whose substitutions are expected to go through a limiting D mechanism with formation of [RuCl(dppe)$_2$]$^+$ as intermediate.

Results and discussion

Kinetics of reaction of [RuCl(dppe)$_2$]$^+$ with MeCN and other nitriles

Despite its co-ordinatively unsaturated nature, the five-co-ordinated [RuCl(dppe)$_2$]$^+$ complex does not react with N$_2$ or O$_2$ and is air-stable both in solid state and solution, although addition of MeCN leads to octahedral *cis*-[RuCl(MeCN)(dppe)$_2$]$^+$.[3] We carried out ^{31}P-{^{1}H} NMR experiments in [^{2}H$_6$]acetone and observed that conversion into the octahedral

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† *Supplementary data available*: observed rate constants. For direct electronic access see http://www.rsc.org/suppdata/dt/1998/3227/, otherwise available from BLDSC (No. SUP 57427, 7 pp.) or the RSC Library. See Instructions for Authors, 1998, Issue 1 (http://www.rsc.org/dalton).

Table 1 Second order rate constants and activation parameters for the reaction of $[RuCl(dppe)_2]^+$ with several incoming ligands L*

L	Solvent	$10^{-4}\ k_L$/mol dm^{-3} s^{-1}	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
MeCN	CH_2Cl_2	14.6(2)	4.7(4)	−19(2)
MeCN	Acetone	9.44(5)	6.9(4)	−12(1)
PhCN	Acetone	9.92(2)	7.2(7)	−12(2)
2,6-$(MeO)_2C_6H_3CN$	Acetone	3.18(2)	10.7(4)	−2(3)

* The numbers in parentheses represent the standard deviation in the last significant digit.

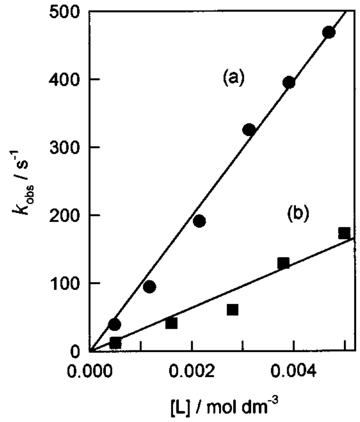

Fig. 1 Plots of k_{obs} *vs.* the concentration of incoming ligand for the reaction of $[RuCl(dppe)_2]^+$ with MeCN (a) and 2,6-$(MeO)_2C_6H_3CN$ (b) in acetone solution at 25 °C.

complex is complete at 25 °C in the time required to carry out the addition of an excess of MeCN and record the phosphorus spectrum (less than 5 min). The absence of spectral changes in the next 24 h indicates that conversion into the *trans* isomer or formation of more substituted reaction product is negligible. Similar observations were made when PhCN or 2,6-$(MeO)_2C_6H_3CN$ replaces acetonitrile as incoming ligand; the NMR spectra show in all cases exclusive formation of the *cis* isomer without any evidence of subsequent reactions.

Preliminary stopped-flow experiments under pseudo-first order conditions (ligand excess) using a diode-array detector showed in all cases the disappearance of the band at 425 nm corresponding to the unsaturated complex without evidence of the formation of any reaction intermediate, eqn. (1) [L =

$$[RuCl(dppe)_2]^+ + L \longrightarrow \textit{cis}\text{-}[RuCl(L)(dppe)_2]^+ \quad (1)$$

MeCN, PhCN or 2,6-$(MeO)_2C_6H_3CN$]. The spectra of all the three octahedral products show a weak shoulder at 300–350 nm. The spectral changes during reaction with MeCN in excess are very similar in acetone and CH_2Cl_2 solutions, and kinetic traces at 425 nm show in all cases well defined absorbance decreases that can be well fitted by a single exponential to obtain the values of k_{obs} (SUP 57427). As shown in Fig. 1, the dependence of k_{obs} with the concentration of L is linear with a zero intercept [eqn. (2)], which indicates that reactions are first

$$k_{obs} = k_L\,[L] \quad (2)$$

order with respect to the concentration of the incoming ligand. Thermal activation parameters were determined from the temperature dependence of the second order rate constant k_L, and are collected in Table 1 together with the values of k_L at 298 K.

The rate constant and activation parameters for the reactions with MeCN and PhCN in acetone solution are very similar and almost equivalent within experimental error. The values of all the kinetic parameters are reasonable for associative attack of L on the co-ordinatively unsaturated ruthenium complex. Reaction with 2,6-$(MeO)_2C_6H_3CN$ is somewhat slower and occurs with a higher activation barrier and less negative $\Delta S^{\ddagger}$, which suggests that steric crowding caused by the substituents in the phenyl ring inhibits associative attack at the metal centre. In any case, the similar kinetic data for the reactions with the three nitriles show that $[RuCl(dppe)_2]^+$ discriminates little against the incoming ligands used in this work, surely because of its severely distorted trigonal bipyramidal structure.[3] The equatorial plane containing the chloride and one phosphorus of each dppe ligand is Y-distorted with Cl–Ru–P angles significantly larger than 120°, which makes this the preferred orientation for attack by the incoming ligand; this occurs without important steric constraints and leads to the facile and exclusive formation of the *cis* isomer.

The reaction with MeCN is slightly faster when the solvent is changed from acetone to CH_2Cl_2; the value of $\Delta H^{\ddagger}$ decreases to 4.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ becomes more negative, which is consistent with solvation changes during the activation process. Solvent co-ordination, a possibility suggested by Morris and co-workers[3] for acetone and thf solutions, would surely cause more important changes in the kinetic parameters with the solvent nature. Moreover, the similarity of the NMR spectra in CH_2Cl_2 and acetone solutions and their compatibility with the solid state structure seems to indicate that the five-co-ordinated environment about ruthenium is maintained in solution. Thus, although the possibility of a rapidly exchanging and weakly co-ordinated solvent molecule cannot be completely ruled out, the kinetic data can be easily interpreted without invoking that possibility.

Substitution in octahedral *cis*-$[RuCl(L)(dppe)_2]^+$ complexes

The complex *cis*-$[RuCl(MeCN)(dppe)_2]^+$ can be prepared by reaction of $[RuCl(dppe)_2]^+$ with an excess of acetonitrile.[3] Although it can be isolated as the PF_6^- salt, CH_2Cl_2 solutions made from solid samples show NMR spectra that include the signals of both the *cis*-chloroacetonitrile and the five-co-ordinated chloro complex,[3] thus indicating that equilibrium (3)

$$\textit{cis}\text{-}[RuCl(MeCN)(dppe)_2]^+ \rightleftharpoons [RuCl(dppe)_2]^+ + MeCN \quad (3)$$

is established in solution. By using a diode-array detector, we found that stopped-flow scans for the reaction of *cis*-$[RuCl(MeCN)(dppe)_2]^+$ with PhCN reflect essentially the spectral changes observed during the reaction of $[RuCl(dppe)_2]^+$ with benzonitrile, although kinetic traces at fixed wavelength are not well defined and the reaction is slower than for the case of $[RuCl(dppe)_2]^+$ solutions. Thus, the NMR and stopped-flow observations are consistent with substitution of co-ordinated MeCN by PhCN [eqn. (4)] taking place through a limiting

$$\textit{cis}\text{-}[RuCl(MeCN)(dppe)_2]^+ + PhCN \rightleftharpoons \textit{cis}\text{-}[RuCl(PhCN)(dppe)_2]^+ + MeCN \quad (4)$$

$$\textit{cis}\text{-}[RuCl(MeCN)(dppe)_2]^+ + 2,6\text{-}(MeO)_2C_6H_3CN \rightleftharpoons \textit{cis}\text{-}[RuCl\{2,6\text{-}(MeO)_2C_6H_3CN\}(dppe)_2]^+ + MeCN \quad (5)$$

dissociative mechanism involving the formation of $[RuCl(dppe)_2]^+$ as intermediate. The stock solutions of acetonitrile complex used in stopped-flow also contain the five-co-ordinated complex, which reacts with PhCN to give the benzonitrile complex. The net process is conversion of the mixture

Table 2 Rate constants at 25 °C for substitution of L by L′ in *cis*-$[RuCl(L)(dppe)_2]^+$ complexes. The constants k_{-L}, $k_{L'}$ and the quotient $k_{L'}/k_L$ were obtained by fitting the experimental data by use of eqn. (9) in the text[a]

Solvent	L	L′	k_{-L}/s^{-1}	$k_{-L'}/s^{-1}$	$k_{L'}/k_L$	$k_{L'}/k_L$[b]
CH_2Cl_2	MeCN	PhCN	8.25(4)	3.2(1)	0.99(6)	
Acetone	MeCN	PhCN	3.40(1)	2.03(3)	1.5(1)	1.05
	MeCN	2,6-$(MeO)_2C_6H_3CN$	3.6(1)	0.2(2)	0.5(1)	0.34
	PhCN	MeCN	2.38(1)	5.2(4)	1.4(2)	0.95
	2,6-$(MeO)_2C_6H_3CN$	MeCN	0.26(1)	3.8(3)	1.9(3)	2.97

[a] The numbers in parentheses represent the standard deviation in the last significant digit. [b] Calculated from data in Table 1 for reaction of L and L′ with $[RuCl(dppe)_2]^+$.

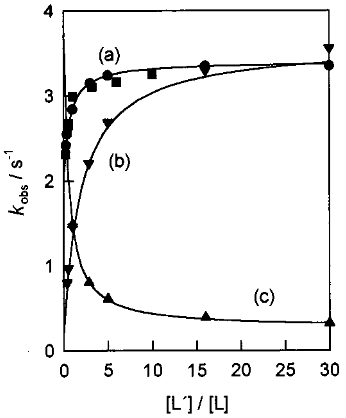

Fig. 2 Plots of observed rate constants for substitution reactions in complexes *cis*-$[RuCl(L)(dppe)_2]^+$ showing the dependence on the concentration of both the incoming and leaving ligands. Curve (a) corresponds to substitution of MeCN by PhCN using [MeCN] = 0.002 mol dm^{-3} (●) and 0.01 mol dm^{-3} (■). Curves (b) and (c) correspond to substitution of MeCN by 2,6-$(MeO)_2C_6H_3CN$ (b), and the same reaction in the reverse direction (c). Some experimental points at higher ratios of concentrations have been omitted for clarity. The lines represent the fit of the experimental data using eqn. (9) in the text.

of both complexes into the final product, and the process is kinetically controlled by conversion of $[RuCl(MeCN)(dppe)_2]^+$ into the five-co-ordinated complex. In order to obtain well defined kinetic traces for reaction (4), it is necessary to carry out the kinetic experiments using a solution of $[RuCl(dppe)_2]^+$ or *cis*-$[RuCl(MeCN)(dppe)_2]^+$ containing an excess of MeCN, which displaces equilibrium (3) to the left. Mixing this solution with an excess of PhCN leads to *cis*-$[RuCl(PhCN)(dppe)_2]^+$ without detectable formation of the five-co-ordinated intermediate. Under pseudo-first order conditions for both the leaving and the incoming ligand, absorbance–time traces at 330 nm are well defined single exponentials. The values derived for the observed rate constant, k_{obs}, depend on the concentration of both the leaving and the incoming ligand (SUP 57427). On the other hand, the equilibrium constants for reactions (4) and (5) can be estimated from the integration of the phosphorus NMR spectra of acetone solutions containing $[RuCl(dppe)_2]^+$ and a mixture of the corresponding nitriles, and the values obtained are $K_4^{NMR} = 2.0$ and $K_5^{NMR} = 5.5$. Despite the errors associated with these determinations, these values indicate a similar stability of the *cis*-octahedral complexes formed with all the three nitriles, which is probably related to the ability of co-ordinated nitriles to adapt their donor–acceptor character to the electronic properties of the binding site.[9]

For reactions (6), the absorbance increments and the values

$$cis\text{-}[RuCl(L)(dppe)_2]^+ + L' \rightleftharpoons cis\text{-}[RuCl(L')(dppe)_2]^+ + L \quad (6)$$

of k_{obs} change with the concentration of L and L′ as expected for a reversible reaction occurring through a limiting dissociative mechanism [eqns. (7) and (8)]. Assuming that the five-co-

$$cis\text{-}[RuCl(L)(dppe)_2]^+ \underset{k_L}{\overset{k_{-L}}{\rightleftharpoons}} [RuCl(dppe)_2]^+ + L \quad (7)$$

$$[RuCl(dppe)_2]^+ + L' \underset{k_{-L'}}{\overset{k_{L'}}{\rightleftharpoons}} cis\text{-}[RuCl(L')(dppe)_2]^+ \quad (8)$$

ordinated intermediate is formed under steady-state conditions, the rate law for this mechanism is given by eqn. (9),[10] which

$$k_{obs} = \frac{k_{-L'} + k_{-L}(k_{L'}[L']/k_L[L])}{1 + (k_{L'}[L']/k_L[L])} \quad (9)$$

shows that k_{obs} depends on the ratio of concentrations of the incoming and leaving ligands. Some typical plots showing the dependence of k_{obs} on the value of [L]/[L′] are included in Fig. 2. For the substitution of MeCN by PhCN, the values of k_{obs} for a given concentration of PhCN change with [MeCN] but all the data obey eqn. (9) [curve (*a*) in Fig. 2]. The limiting rate constant for high values of the quotient of ligand concentrations corresponds to k_{-L} (dissociation of L) and, consequently, it must be independent of the nature of the incoming ligand used [curves (a) and (b)]. On the other hand, the zero intercept corresponds to reversible dissociation of the incoming ligand in eqn. (6) ($k_{-L'}$) and it must coincide with the value of the limiting rate constant when L′ is used as leaving ligand [curves (b) and (c)]. The fit of the experimental data using eqn. (9) also provides a value of the quotient $k_{L'}/k_L$, which represents the relative rate of attack on the reaction intermediate by both ligands. The values of the quotient in Table 2 are always close to 1, showing again that $[RuCl(dppe)_2]^+$ discriminates little against the different nitriles. Moreover, the quotient values derived from the curves in Fig. 2 agree well with those calculated from the second order rate constants in Table 1, which constitutes new evidence in favour of the limiting D mechanism for substitution in octahedral *cis*-$[RuCl(L)(dppe)_2]^+$ complexes.

The equilibrium constant for reactions of type (6) can be now calculated from the available kinetic data. If the mechanism in eqns. (7) and (8) is assumed to be valid, the equilibrium constant is given by eqn. (10) and can be calculated from the values

$$K^{kin} = k_{-L}k_{L'}/k_L k_{-L'} \quad (10)$$

of k_{-L}, $k_{-L'}$ and the quotient $k_L/k_{L'}$ derived from curves in Fig. 2. The values obtained in this way are $K_4^{kin} = 1.5$ and $K_5^{kin} = 4.5$, in excellent agreement with those calculated from NMR experiments (2.0 and 5.5, respectively; see above).

The activation parameters for ligand dissociation in *cis*-$[RuCl(L)(dppe)_2]^+$ complexes (Table 3) were determined from the temperature dependence of the limiting rate constant in substitution reactions (SUP 57427). All the $\Delta H_{-L}^{\ddagger}$ values are close to 20 kcal mol^{-1}, independently of the nature of the solvent and the ligand. The values of $\Delta S^{\ddagger}$ are always positive, as expected for dissociative activation, and close to each other. The small change in the activation parameters for MeCN dissociation in acetone and CH_2Cl_2 solutions can also be easily rationalised in terms of solvation effects, which now become more important as the transition state is formed.

Conclusion

Kinetic data in the previous section strongly suggest that substitution reactions in *cis*-$[\mathrm{RuCl(L)(dppe)_2}]^+$ complexes occur through a limiting D mechanism, and the activation profile in Fig. 3 can be particularised for every reaction from data in Tables 1 and 3. From these plots, it is evident that $\Delta H_{\mathrm{L}}^{\ddagger} - \Delta H_{-\mathrm{L}}^{\ddagger}$ corresponds to ΔH° for reaction (11), and the values obtained for ΔH° are included in Table 4 together with other thermodynamic parameters for equilibrium (11). Further

$$[\mathrm{RuCl(dppe)_2}]^+ + \mathrm{L} \rightleftharpoons cis\text{-}[\mathrm{RuCl(L)(dppe)_2}]^+ \quad (11)$$

evidence in favour of a D mechanism with formation of $[\mathrm{RuCl(dppe)_2}]^+$ as intermediate comes from the good agreement between the data in Table 3 for L = MeCN in acetone solution with the values calculated directly from the initial spectra at different temperatures in the diode-array experiments, that lead to $\Delta H^{\circ} = -10.9$ kcal mol^{-1} and $\Delta S^{\circ} = -22$ cal K^{-1} mol^{-1}. Data in Table 4 show that the formation of *cis*-$[\mathrm{RuCl(L)(dppe)_2}]^+$ complexes is only slightly favoured, with small negative values of ΔG° that arise because ΔH° only exceeds slightly the unfavourable entropy term. Although the values of $\Delta H_{-\mathrm{L}}^{\ddagger}$ are close to those found in other ruthenium–nitrile complexes that undergo substitution reactions through a D mechanism,[11] it is somewhat surprising that ΔH° for addition of nitriles to the unsaturated $[\mathrm{RuCl(dppe)_2}]^+$ complex are significantly smaller. Thus, the values of $\Delta H_{-\mathrm{L}}^{\ddagger}$ are always close to 20 kcal mol^{-1} and represent an activation barrier clearly higher than ΔH° for addition of L to $[\mathrm{RuCl(dppe)_2}]^+$, which indicates that the activation process must involve some other structural changes in addition to ligand co-ordination or dissociation. A similar situation was found for reactions of $[\mathrm{M(CO)_3(PCy_3)(H_2)}]$ complexes (M = Cr or W),[12] and kinetic results were interpreted in terms of formation of an agostic bond between the metal centre and one cyclohexyl group. However, Morris and co-workers[3] did not report any evidence of agostic bond formation in the solid state structure of $[\mathrm{RuCl(dppe)_2}]\mathrm{PF_6}$, although this kind of interaction has been observed in related complexes.[1c,13] Another attractive possibility to explain the kinetic behaviour is the formation of a Ru←Cl π bond in $[\mathrm{RuCl(dppe)_2}]^+$, which should have the same consequences as the agostic bond. The formation of additional bonds with π donors has been observed in related unsaturated complexes,[14,15] and leads to a decrease of the Ru–Cl distance from *ca.* 2.41 Å in octahedral non-π bonded complexes to *ca.* 2.37 Å in complexes with significant Ru←Cl π bonding.[15] The Ru–Cl distance in $[\mathrm{RuCl(dppe)_2}]\mathrm{PF_6}$ is 2.394 Å, which indicates that π bond formation is not too important for this complex[3] and it would only explain partially the stability of the five-co-ordinated complex and the significant activation barrier for ligand addition.

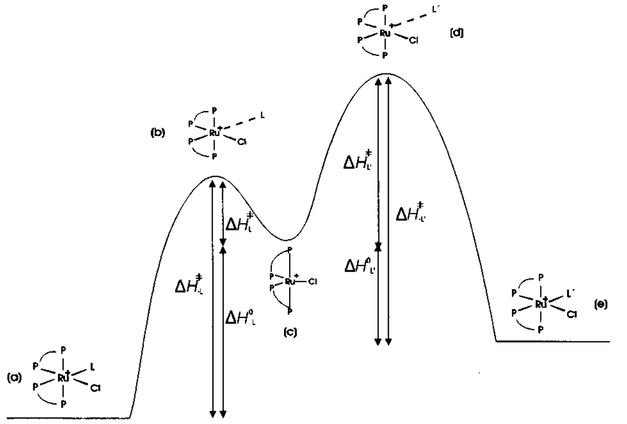

Fig. 3 Typical activation profile for the substitution of L by L′ in octahedral *cis*-$[\mathrm{RuCl(L)(dppe)_2}]^+$ complexes. The figure also contains the structural changes proposed to occur during the course of the reaction.

Table 3 Activation parameters for dissociation of L in *cis*-$[\mathrm{RuCl(L)(dppe)_2}]^+$ complexes *

L	Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/cal K^{-1} mol^{-1}
MeCN	$\mathrm{CH_2Cl_2}$	20.6(6)	15(2)
MeCN	Acetone	19.1(9)	8(4)
PhCN	Acetone	20.8(4)	13(1)
2,6-$\mathrm{(MeO)_2C_6H_3CN}$	Acetone	20.1(2)	6(1)

* The numbers in parentheses represent the standard deviation in the last significant digit.

An interesting observation in the crystal structure of $[\mathrm{RuCl(dppe)_2}]\mathrm{PF_6}$ is that the Ru–P bonds with equatorial $\mathrm{PPh_2}$ groups are exceptionally shorter than the corresponding distances with the axial groups (2.24 and 2.37 Å, respectively).[3] Thus, it seems that electron deficiency in $[\mathrm{RuCl(dppe)_2}]^+$ is compensated with an increased σ donation from two of the co-ordinated phosphine groups. The phosphorus NMR spectrum suggests that the strengthening of the Ru–P$_{\mathrm{eq}}$ bonds is maintained in solution. Thus, while the position of the signal for P$_{\mathrm{ax}}$ is similar to that found for octahedral complexes (δ 54.5), the signal for P$_{\mathrm{eq}}$ is clearly downfield (δ 82.4) and indicates that these atoms are significantly less shielded. When $[\mathrm{RuCl(dppe)_2}]^+$ adds one ligand to form octahedral *cis*-$[\mathrm{RuCl(L)(dppe)_2}]^+$, the Ru–P$_{\mathrm{eq}}$ distances must change along the reaction coordinate to reach values similar to Ru–P$_{\mathrm{ax}}$, and Fig. 3 shows the structural changes that should occur during the dissociative substitution of L by L′. Conversion of the starting complex (a) into the five-co-ordinated intermediate (c) would occur through an activated complex (b) in which the leaving ligand L separates from the metal centre. The energy required for this process is close to 20 kcal mol^{-1} and it would correspond approximately to the energy of the Ru–L bond in the absence of increased σ donation from the $\mathrm{PPh_2}$ groups. As L is moving far enough from Ru, both P atoms in the equatorial plane approach the metal centre to compensate the electron deficiency, and intermediate (c) is formed. The addition of L′ to (c) requires not only the approach of the incoming ligand but also desolvation and, more importantly, the reorganisation of the co-ordination sphere to regenerate the electron deficiency and to allow σ donation from L′. The final conversion of the activated complex (d) into the reaction product (e) would simply require complete co-ordination of L′, in a process favoured now by *ca.* 20 kcal mol^{-1}. The possibility of a square pyramidal form of the intermediate cannot be completely ruled out, although its formation would probably lead to a faster attack by the nucleo-

Table 4 Thermodynamic parameters for the reaction of $[\mathrm{RuCl(dppe)_2}]^+$ with several incoming ligands L to form *cis*-$[\mathrm{RuCl(L)(dppe)_2}]^+$ [a]

L	Solvent	$10^{-4}K_{\mathrm{L}}$ [b]/mol dm^{-3}	ΔH°/kcal mol^{-1}	ΔS°/cal K^{-1} mol^{-1}	ΔG°_{298} [c]/kcal mol^{-1}
MeCN	$\mathrm{CH_2Cl_2}$	1.79	−15.9	−34	−5.8
MeCN	Acetone	2.80	−12.2	−20	−6.2
PhCN	Acetone	4.12	−13.6	−25	−6.2
2,6-$\mathrm{(MeO)_2C_6H_3CN}$	Acetone	12.72	−9.4	−8	−7.0

[a] Values derived from kinetic data in Tables 1 and 3. [b] Calculated at 25 °C as $k_{\mathrm{L}}/k_{-\mathrm{L}}$. [c] Values calculated from ΔH° and ΔS°, which agree well with those calculated from K_{L}.

phile and would also be unable to account for the consistency of experimental data corresponding to the five-co-ordinated and the octahedral complexes.

According to comments in the previous paragraph, the increased donation of electron density from two PPh_2 groups would be responsible for the relatively high stability of the 16-electron $[RuCl(dppe)_2]^+$ complex because co-ordination of a sixth ligand requires the prior reorganisation of the co-ordination sphere and this represents an activation barrier of several kcal mol^{-1}. It seems reasonable that a similar situation will occur in reactions of related five-co-ordinated complexes as $[OsX(dppe)_2]^+$ (X = Cl or Br)[16] or $[MCl(dppp)_2]^+$ [M = Ru or Os; dppp = 1,3-bis(diphenylphosphino)propane],[15] although in some of these cases π bonding or agostic interactions may cause the same effect that increased σ donation in $[RuCl(dppe)_2]^+$. In any case, ligand addition to these unsaturated complexes seems to involve a low activation barrier and, actually, these compounds usually reversibly form octahedral complexes under mild conditions. Substitution reactions of these octahedral compounds are reasonably expected to go through simple dissociative mechanisms. On the contrary, formation of other co-ordinatively unsaturated complexes such as $[FeH(dppe)_2]^+$ does not occur so easily,[8] which is difficult to harmonise with a simple dissociative mechanism for substitution reactions in the corresponding octahedral complexes $[FeH(L)(dppe)_2]^+$, and we have found strong evidence for the operation of an alternative mechanism involving the opening of a chelate ring.[5,7] Thus, it seems that the energy of the M–P (chelate) bonds can be in some cases lower than that of bonds with monodentate ligands, and this provides a route to the ring opening mechanism, which can be facilitated by labilising effects from the incoming ligand or other ligands already present in the molecule.[5]

Experimental

The complexes $[RuCl(dppe)_2]PF_6$ and $[RuCl(MeCN)(dppe)_2]PF_6$ were prepared by the published procedure and their nature was confirmed by the similarity of the NMR spectra with those in the literature.[3] The NMR spectra were recorded with a Varian Unity 400 spectrometer using samples prepared in $[^2H_6]$acetone. The preparative work and the initial kinetic runs were carried out under an inert atmosphere, that was eliminated after verifying that kinetic results with samples prepared in air are similar to those obtained under an atmosphere of argon or N_2. The solvents CH_2Cl_2 and acetone were obtained from SDS and were dried immediately before use. All other reagents were from Aldrich and used without further purification.

The nature of products formed upon reaction of $[RuCl(dppe)_2]PF_6$ with MeCN, PhCN and $2,6\text{-}(MeO)_2C_6H_3CN$ was confirmed by their $^{31}P\text{-}\{^1H\}$ NMR spectra in $[^2H_6]$acetone. For *cis*-$[RuCl(MeCN)(dppe)_2]^+$, the agreement with the previously published[3] spectrum in CH_2Cl_2 is good, although the signals are slightly displaced: δ 61.1 and 43.5 in $[^2H_6]$acetone *vs* δ 59.6 and 42.9 in CH_2Cl_2. The spectra of reaction products with PhCN and $2,6\text{-}(MeO)_2C_6H_3CN$ also showed two multiplets typical of *cis*-octahedral compounds centred at δ 59.2 and 43.5 for *cis*-$[RuCl(PhCN)(dppe)_2]^+$, and δ 54.9 and 41.1 for *cis*-$[RuCl\{2,6\text{-}(MeO)_2C_6H_3CN\}(dppe)_2]^+$. Conversion of the starting complex into the reaction products was complete during the time required to carry out the addition of nitriles and recording the NMR spectra (*ca.* 5 min). No other signals were observed in the spectra even at longer reaction times (24 h), which indicates negligible formation of the *trans* isomers or products resulting from further substitution.

Kinetic experiments were carried out using an Applied Photophysics SX17MV stopped-flow spectrophotometer. For reactions of $[RuCl(dppe)_2]^+$ the concentration of the complex was close to 1.0×10^{-4} mol dm^{-3} and an excess of the corresponding ligand was employed (see SUP 57427). The kinetic traces at 425 nm could be well fitted in all cases by a single exponential, and the first-order dependence on the concentration of complex was confirmed in some preliminary experiments by the independence of the observed pseudo-first-order rate constants on the complex concentration. The initial experiments for substitution reactions of *cis*-$[RuCl(L)(dppe)_2]^+$ complexes were carried out using a sample of *cis*-$[RuCl(MeCN)(dppe)_2]PF_6$, which was replaced by solutions containing $[RuCl(dppe)_2]PF_6$ (*ca.* 5.0×10^{-4} mol dm^{-3}) and an excess of the corresponding nitrile for the reasons discussed in the previous section. In all cases, experiments were also carried out under pseudo-first order conditions at 330 nm using an excess of both the leaving and the incoming ligand at the concentrations detailed (SUP 57427). Activation parameters were obtained from kinetic data at different temperatures using the standard Eyring plots, and they are reported including the standard deviation of the fit, although it is well known that these values surely underestimate the errors, especially for the case of $\Delta S^\ddagger$ values.[17]

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