Mechanistic Studies on Iron Phosphine Complexes. Part 2.[1] Protonation and Substitution Reactions of Dinitrogen Complexes

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The mechanisms of the reactions of acid (HCl or HBr) or the nucleophiles CO, MeCN, or PhCN with *trans*-$[FeH(N_2)(depe)_2]^+$ and *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ (depe = $Et_2PCH_2CH_2PEt_2$) have been investigated in tetrahydrofuran (I = 0.1 mol dm^{-3}, $[NBu^n_4][BF_4]$; 25.0 °C). In the reactions with acid, rapid phosphine chelate ring opening, from each iron complex, permits protonation of the pendant phosphorus atom, and ultimate loss of the phosphine ligand. In contrast, the mechanisms of the reactions of the nucleophiles L = CO, MeCN, or PhCN depend on the iron complex. Substitution of the bridged-dinitrogen ligand in *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ occurs, in general, by two parallel pathways. After initial phosphine chelate ring opening the vacant site thus generated can be attacked either by a molecule of solvent or the nucleophile. Subsequent loss of dinitrogen and phosphine chelate ring closure (and for the solvent route, displacement of the co-ordinated solvent by a molecule of the nucleophile) yields the product *trans*-$[FeCl(L)(depe)_2]^+$. Despite the rapid phosphine chelate ring-opening reaction associated with *trans*-$[FeH(N_2)(depe)_2]^+$, substitution of the dinitrogen ligand by nucleophiles proceeds by a much slower pathway involving initial rate-limiting dissociation of dinitrogen. The reasons for the change in substitution mechanism between the mononuclear and binuclear complexes are discussed.

In the previous paper[1] the mechanisms of the substitution and protonation reactions of *trans*-$[FeH(X)(diphosphine)_2]$ [X = Cl or Br, diphosphine = $Ph_2PCH_2CH_2PPh_2$ (dppe) or $Et_2PCH_2CH_2PEt_2$ (depe)] were discussed. One theme of that paper on which I wish to elaborate herein is the role played by phosphine chelate ring-opened species in the substitution reactions. It has been shown[1] that for *trans*-$[FeH(X)(diphosphine)_2]$ and *trans*-$[FeCl_2(depe)_2]$ the rapid ring-opening process does not generate an intermediate which is susceptible to attack from 'external' nucleophiles. Rather, nucleophilic substitution of the halide has to await the slow dissociation of that group. In the present paper the protonation and substitution reactions of the mononuclear, *trans*-$[FeH(N_2)(depe)_2]^+$, and the binuclear, *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$, have been compared in tetrahydrofuran (thf), and the factors which affect the relative reactivities of the two species are presented.

Experimental

All manipulations in both the preparative and kinetic aspects of this work were performed routinely under an atmosphere of dinitrogen using standard Schlenk-tube or syringe techniques. All solvents were freshly distilled from an appropriate drying agent immediately prior to use. The complexes *trans*-$[FeH(N_2)(depe)_2]BPh_4$,[2] *trans*-$[FeH(N_2)(dppe)_2]BPh_4$,[3] and *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)][BPh_4]_2$[4] were prepared by the literature methods, and gave microanalytical results in good agreement with their formulation.

The product of the protonation of either *trans*-$[FeH(N_2)(depe)_2]BPh_4$ or *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)][BPh_4]_2$ with HCl in thf is $[FeCl_2(depe)]$.[1]

The products of the substitution reactions of *trans*-$[FeH(N_2)(depe)_2]BPh_4$ with CO, MeCN, or PhCN were established using their characteristic visible absorption spectra, which were identical with those of authentic samples prepared by the literature methods: *trans*-$[FeH(CO)(depe)_2]BPh_4$[2] ($\lambda_{max.}$ = 450 nm, $\varepsilon_{max.}$ = 400.0 dm^3 mol^{-1} cm^{-1}); *trans*-$[FeH(NCMe)(depe)_2]BPh_4$[2] ($\lambda_{max.}$ = 445 nm, $\varepsilon_{max.}$ = 840.0 dm^3 mol^{-1} cm^{-1}); *trans*-$[FeH(NCPh)(depe)_2]BPh_4$[2] ($\lambda_{max.}$ = 410 nm, $\varepsilon_{max.}$ = 6.0 × 10^3 dm^3 mol^{-1} cm^{-1}).

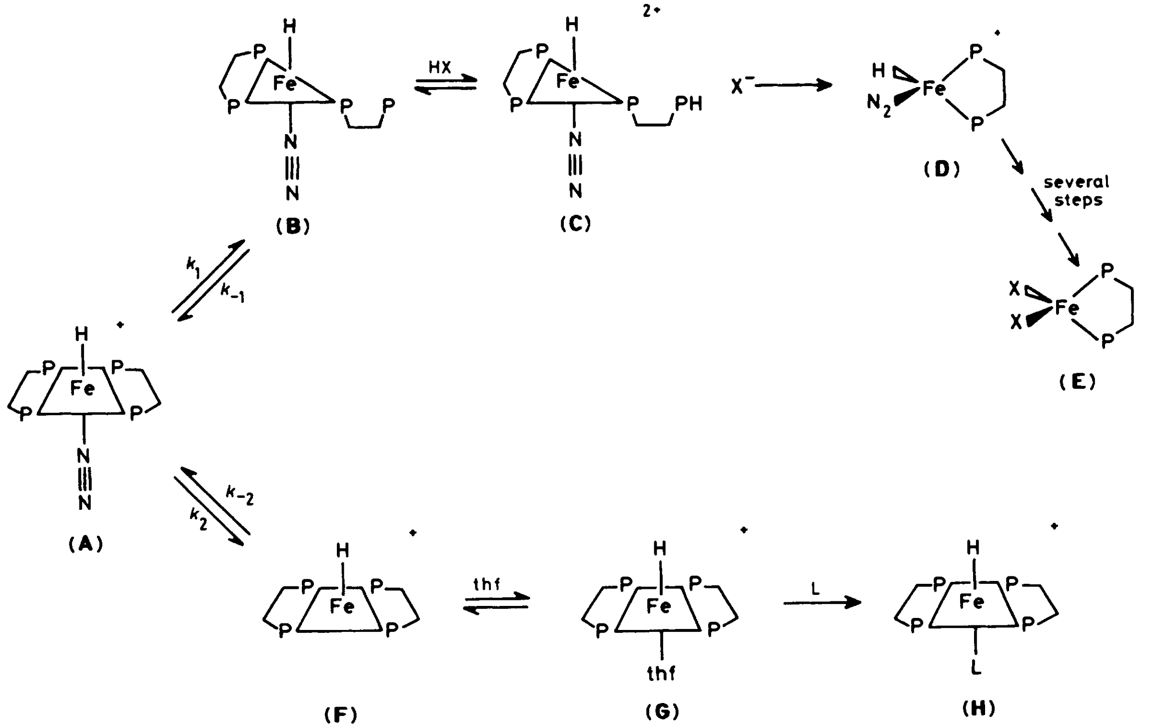
The products of the substitution reactions of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)][BPh_4]_2$ with CO or PhCN were also established by visible absorption spectroscopy: *trans*-$[FeCl(CO)(depe)_2]BPh_4$[4] ($\lambda_{max.}$ = 390 nm, $\varepsilon_{max.}$ = 1.42 × 10^3 dm^3 mol^{-1} cm^{-1}); *trans*-$[FeCl(NCPh)(depe)_2]BPh_4$[5] ($\lambda_{max.}$ = 415 nm, $\varepsilon_{max.}$ = 4.81 × 10^3 dm^3 mol^{-1} cm^{-1}). It is not easy to establish the immediate product of the reaction between the bridged complex and MeCN because of the facile substitution of *trans*-$[FeCl(NCMe)(depe)_2]^+$ in an excess of MeCN[5] to yield *trans*-$[Fe(NCMe)_2(depe)_2]^{2+}$. The kinetics of the reaction between *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ and MeCN were established from the initial phase (absorbance increase) of the reaction and this most probably corresponds to the formation of *trans*-$[FeCl(NCMe)(depe)_2]^+$.

Kinetic Studies.—All kinetic studies were performed in thf in the presence of 0.1 mol dm^{-3} $[NBu^n_4][BF_4]$ and at 25.0 °C. All reactions with *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ and the reaction of *trans*-$[FeH(N_2)(depe)_2]^+$ with HCl were studied using stopped-flow spectrophotometry, as described previously.[1] The substitution of the dinitrogen ligand in *trans*-$[FeH(N_2)(depe)_2]^+$ by CO, MeCN, or PhCN was studied on a Pye-Unicam SP1800 spectrophotometer as described previously.[1] Kinetic data were analysed as described before.[1] No intermediates were observed in any of the reactions discussed. In all cases the initial absorbance was that corresponding to the dinitrogen complex.

Anhydrous HCl and HBr solutions in thf were prepared, analysed, and used as described previously.[6] Various concentrations of CO were prepared by diluting a saturated solution ([CO] = 5.2 mmol dm^{-3})[7] with dinitrogen-saturated thf.

Results and Discussion

trans-$[FeH(N_2)(depe)_2]^+$.—The kinetics of the reaction between *trans*-$[FeH(N_2)(depe)_2]^+$ and anhydrous acid (HCl or HBr) in thf (I = 0.1 mol dm^{-3}, $[NBu^n_4][BF_4]$; 25.0 °C) to yield $[FeCl_2(depe)]$ are simple, exhibiting a first-order dependence



Scheme 1. The mechanisms of the reactions of *trans*-$[FeH(N_2)(depe)_2]^+$ with acid (top line) or nucleophiles (bottom line) in thf at 25.0 °C

on the concentration of the complex, but independent of the concentration of the acid and whether HCl or HBr was used, $k_{obs.} = k_1 = 23.8 \pm 0.4$ s^{-1} ($k_{obs.}$ is the observed rate constant measured under pseudo-first-order conditions). Identical kinetics has been observed in the phosphine chelate ring-opening reaction of *trans*-$[FeCl_2(depe)_2]$ and one of the pathways for *trans*-$[FeH(X)(depe)_2]$ (X = Cl or Br).[1] This rate equation is consistent with the mechanism shown in the top line of Scheme 1. Rate-limiting phosphine chelate ring opening of *trans*-$[FeH(N_2)(depe)_2]^+$ (**A**) generates the sixteen-electron species (**B**), and rapid protonation of the pendant phosphorus atom yields (**C**). The remainder of the mechanism involves loss of the phosphine ligand, dinitrogen, and further interaction with more acid, ultimately resulting in the production of $[FeCl_2(depe)]$(**E**). The simple kinetics observed with this system does not allow establishment of the order of the elementary reactions after species (**B**).

The substitution of the dinitrogen ligand in *trans*-$[FeH(N_2)(depe)_2]^+$ by the nucleophiles L = CO, MeCN, or PhCN under identical conditions to those employed in the protonation studies exhibits similar kinetics to that described for that study: a reaction rate that is first order in the concentration of complex but independent of both the concentration and nature of the nucleophile, $k_{obs.} = k_2 = (1.01 \pm 0.1) \times 10^{-3}$ s^{-1}. Although the same simple rate equation is observed in the reactions with acids or nucleophiles, the factor of 10^4 difference in the rate constants associated with the two reactions means that they do not operate by a common pathway.

The mechanism of the nucleophilic substitution reaction is that shown on the bottom line of Scheme 1. Rate-limiting dissociation of dinitrogen from *trans*-$[FeH(N_2)(dppe)_2]^+$ (**A**) yields the second type of co-ordinatively unsaturated intermediate derived from (**A**), $[FeH(depe)_2]^+$ (**F**). Subsequent nucleophilic attack at the vacant site, probably *via* the weakly co-ordinated solvento-species (**G**), yields the product *trans*-$[FeH(L)(depe)_2]^+$ (**H**).

The reactivity pattern of *trans*-$[FeH(N_2)(depe)_2]^+$ towards protic and nucleophilic attack is identical to that established for *trans*-$[FeH(Cl)(diphosphine)_2]$ and *trans*-$[FeCl_2(depe)_2]$.[1] Thus despite the rapid formation of the co-ordinatively unsaturated species (**B**) through phosphine chelate ring opening, this species is not susceptible to attack by 'external' nucleophiles, rather nucleophilic substitution has to await the slow loss of dinitrogen.

Perhaps a surprising conclusion from this study is that in thf at 25.0 °C the iron–phosphorus bond dissociates faster than the iron–dinitrogen bond. This may purely be a consequence of greater relief of steric strain on dissociation of the phosphine ligand. However both dinitrogen and phosphines bond to a metal by ligand-to-metal σ donation and metal-to-ligand π donation. Earlier Mössbauer studies[8] demonstrated that in *trans*-$[FeH(N_2)(depe)_2]^+$ the dinitrogen ligand is a stronger π acceptor, but poorer σ donor, than the depe ligand, and it may be that in these kinetic studies we are monitoring how these effects are translated into the relative labilities.

Attempts to study the protonation and nucleophilic substitution reactions of *trans*-$[FeH(N_2)(dppe)_2]^+$ were not successful. Upon dissolution of the complex in thf the colour changes rapidly from bright yellow to orange-red, which is believed to correspond to the loss of dinitrogen. This would indicate that the lability of the dinitrogen ligand is very sensitive to the nature of the phosphine coligands, the less electron-releasing phosphines being associated with the more labile dinitrogen ligand in *trans*-$[FeH(N_2)(diphosphine)_2]^+$. Similar influences have been observed in *trans*-$[M(N_2)_2(diphosphine)_2]$ (M = Mo or W).[9] In contrast, the labilities of the chloro-group in *trans*-$[FeH(Cl)(diphosphine)_2]$ are not particularly sensitive to the nature of the phosphine;[1] diphosphine = dppe, $k_{obs.} = (8.62 \pm 0.4) \times 10^{-5}$ s^{-1}; diphosphine = depe, $k_{obs.} = (8.27 \pm 0.4) \times 10^{-5}$ s^{-1}. In the substitution reactions of *trans*-$[FeH(N_2)(diphosphine)_2]^+$ charge separation in the transition state is not a problem, as it is in the dissociation of chloride from

Table 1. Kinetic data for the reactions of *trans*-$[FeH(N_2)(depe)_2]^+$ with acids (L = HCl or HBr) or nucleophiles (L = CO, MeCN, or PhCN) in thf at 25.0 °C (I = 0.1 mol dm^{-3}, $[NBu^n_4][BF_4]$)

	$k_{obs.}{}^{a}$/s^{-1}				
[L]/mmol dm^{-3}	L = HBr^{b}	HCl^{b}	CO^{b}	MeCN^{c}	PhCN^{d}
2.60			1.11×10^{-3}		
5.00	23.7	24.0			
10.00	23.5	24.0		1.04×10^{-3}	1.00×10^{-3}
20.00	23.5	23.5		1.02×10^{-3}	0.96×10^{-3}
30.00	24.0	23.7			
40.00	23.5	23.9			
50.00	23.8	24.2		1.00×10^{-3}	0.95×10^{-3}
100.00				1.04×10^{-3}	1.00×10^{-3}

^{a} Kinetic data shown are those for [Fe] = 2.0×10^{-4} mol dm^{-3}. Observed rate constants are independent of complex concentration in the range [Fe] = $(0.5\text{—}4.0) \times 10^{-4}$ mol dm^{-3}. ^{b} λ = 380 nm. ^{c} λ = 370 nm. ^{d} λ = 410 nm.

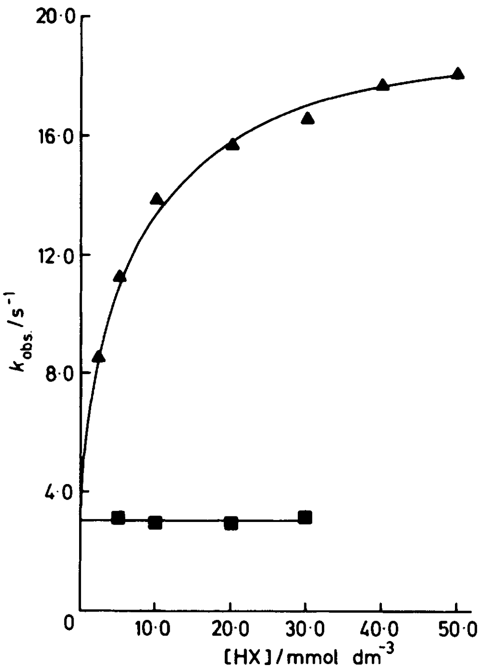


Figure 1. Dependence of $k_{obs.}$ on the concentrations of HCl (▲) or HBr (■) in the reactions of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ with acid in thf at 25.0 °C

trans-$[FeH(Cl)(diphosphine)_2]$. In a poorly ionising solvent, such as thf, it may be that charge-separation factors dominate the reactivity. The kinetic data for both the protonation and substitution reactions of *trans*-$[FeH(N_2)(depe)_2]^+$ are collected in Table 1.

The general reactivity pattern described above for the mononuclear iron phosphine complexes is not maintained with the analogous binuclear complex, rather this latter species reacts with nucleophiles by an unexpectedly facile pathway.

trans-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$.—In contrast to the reactions of mononuclear iron phosphine complexes, where the reactions with acids are several orders of magnitude faster than the rate of nucleophilic substitution, the studies with *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ demonstrate that these reactions can occur at comparable (or even identical) rates at a binuclear site.

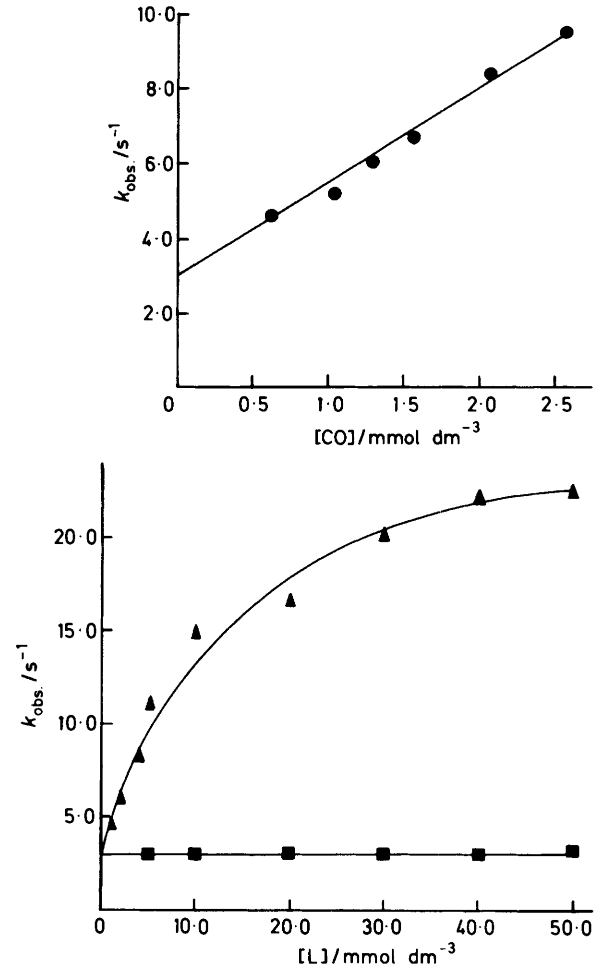
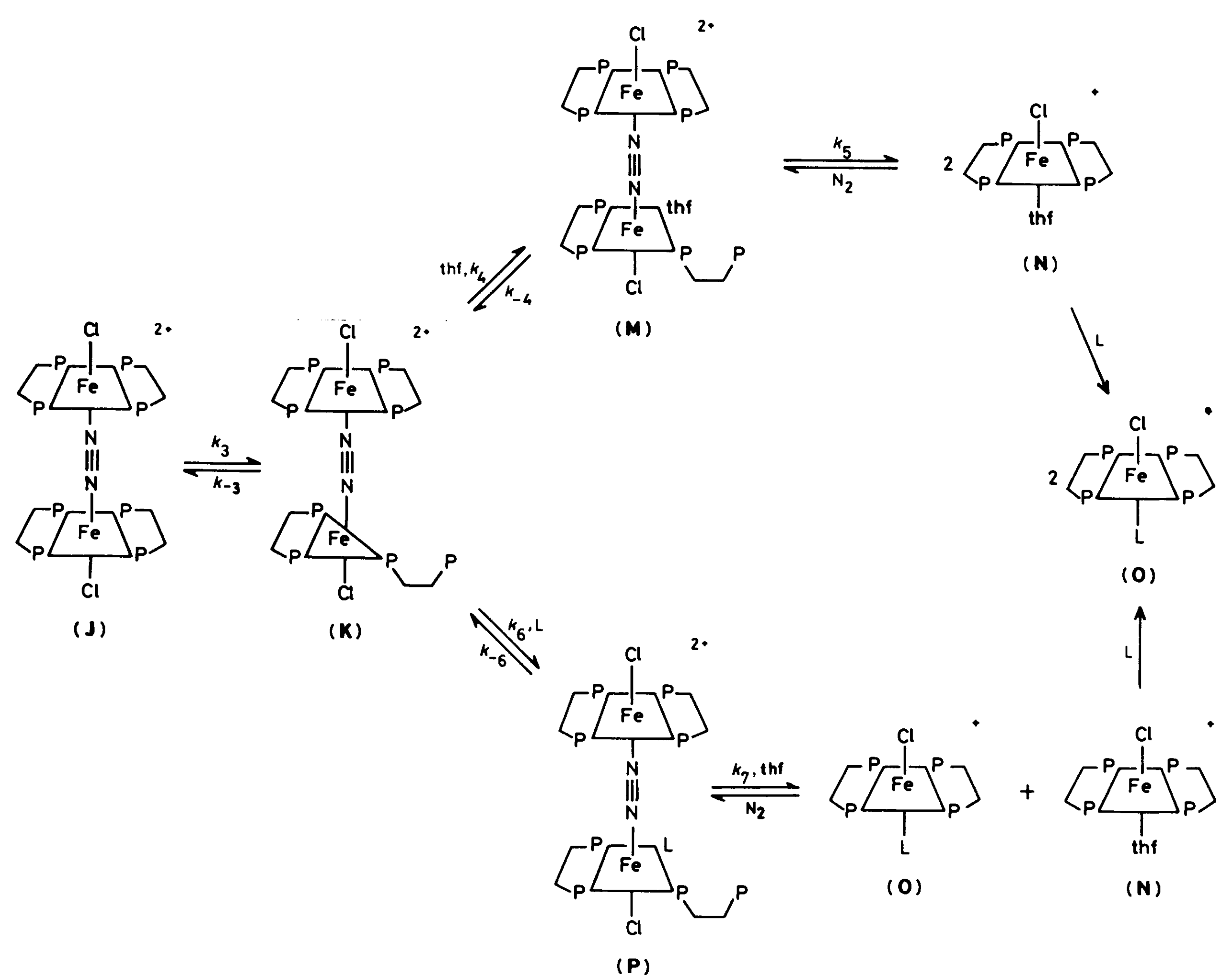


Figure 2. Dependence of $k_{obs.}$ on the concentrations of PhCN (▲), MeCN (■), or (insert) CO (●) in the reactions of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ with acid in thf at 25.0 °C

The kinetics for the reactions of both anhydrous acids (HCl or HBr) or the nucleophiles, L = CO, MeCN, or PhCN with *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ in thf exhibits a first-order dependence on the concentration of complex, under all conditions. However the dependence on the concentration of acid, or of nucleophile, demonstrates that in general the reactions proceed by two parallel pathways as defined by equation (1) and illustrated in Figures 1 and 2. In general, the



Scheme 2. The nucleophilic substitution mechanism for the reactions of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ in thf at 25.0 °C. Although not shown, the mechanism for the reactions with acid involves rapid protonation of the pendant phosphorus atoms in (**M**) and (**P**; L = HCl)

Table 2. Kinetic data for the reactions of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ with acids (L = HCl or HBr) or nucleophiles (L = CO, MeCN, or PhCN) in thf at 25.0 °C (I = 0.1 mol dm^{-3}, $[NBu^n{}_4][BF_4]$; λ = 380 nm)*

	$k_{obs.}/s^{-1}$				
[L]/mmol dm^{-3}	L = HBr	HCl	CO	MeCN	PhCN
0.65			4.60		
1.04			5.00		
1.30			6.20		
1.50			6.60		
2.08			8.40		
2.60			9.40		
1.00					4.62
2.00		8.62			5.90
4.00					8.35
5.00	3.20	11.25		3.00	11.22
10.00	3.15	13.92		3.00	14.75
20.00	3.00	15.68		3.20	16.60
30.00	3.20	16.52		3.20	20.05
40.00		17.65		3.20	21.90
50.00		18.00		3.30	22.62

* Kinetic data shown are those for $[Fe_2]$ = 1.0 × 10^{-4} mol dm^{-3}. Observed rate constants are independent of complex concentration in the range $[Fe_2]$ = (0.5—4.0) × 10^{-4} mol dm^{-3}.

kinetic data were fitted by use of equation (1) and a least-squares analysis, with the value of a obtained from the reaction with MeCN as an initial estimate. When L = HBr, a =

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

3.14 ± 0.06 s^{-1}, b = 0; L = HCl, a = 3.00 ± 0.10 s^{-1}, b = (2.86 ± 0.08) × 10^{3} dm^{3} mol^{-1} s^{-1}, c = (1.57 ± 0.10) × 10^{2} dm^{3} mol^{-1}; L = CO, a = 3.10 ± 0.10 s^{-1}, b = (2.42 ± 0.20) × 10^{3} dm^{3} mol^{-1} s^{-1}, $c < 38.5$ dm^{3} mol^{-1}; L = MeCN, a = 3.15 ± 0.15 s^{-1}, b = 0; L = PhCN, a = 3.00 ± 0.10 s^{-1}, b = (1.79 ± 0.11) × 10^{3} dm^{3} mol^{-1} s^{-1}, c = 89.3 ± 0.10 dm^{3} mol^{-1}. The kinetic data for the reactions of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ are presented in Table 2. Those for the reactions with either acid or the nucleophiles can be accommodated by the mechanism shown in Scheme 2. However for simplicity the explicit details of the reactions with acid have not been included, but are analogous to the pathway shown for the mononuclear complex (Scheme 1) involving protonation of the pendant phosphorus atom in species (**M**) and (**P**).

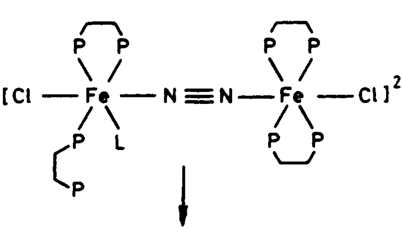
We have seen before[1] how the reactions of iron phosphine complexes with acids allow the determination of the rate of phosphine chelate ring opening. The reaction pathway described by the first term in equation (1) is consistent with a pathway (top line of Scheme 2) involving rate-limiting phosphine chelate ring opening from *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}$

$N_2)]^{2+}$(**J**) to yield (**K**) prior to rapid protonation of the pendant phosphorus in species (**M**). This is analogous to the mechanism described before for protonation of mononuclear complexes. It is unlikely that the pathway described by the second term of equation (1) represents {as it did for *trans*-$[FeH(Cl)(depe)_2]$} protonation of the metal prior to chelate ring opening, for the following reasons. (*i*) This pathway is observed only with the *weaker* acid and, (*ii*) the pathway is not associated with a primary isotope effect. It seems more likely that this pathway involves attack of the chlorine atom of HCl at the binuclear complex (bottom line of Scheme 2). That is, the HCl molecule is sufficiently nucleophilic to attack the co-ordinatively unsaturated species (**K**) prior to protonation of the pendant phosphorus. Whether the protonation of the free phosphorus in (**P**) is intramolecular (from the adjacent, co-ordinated HCl) or from another molecule of HCl is not clear. Certainly the HCl molecule would be rendered more acidic upon co-ordination. This sort of mechanism, in which weak acids co-ordinate or associate with a metal complex prior to protonation, has been observed in aqueous solution.[10,11] Analysis of the rate law, predicted by Scheme 2, for the reactions with acids will be delayed until after discussion of the reactions of nucleophiles with the binuclear complex.

One detail of the mechanism for *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ which is different to that proposed for the mononuclear complexes is the solvation of the chelate ring-opened species (**K**). In previous studies[1] (and those described herein) on mononuclear complexes it has been shown that 'external' nucleophiles cannot bind at the vacant site generated by chelate ring opening [species (**B**), Scheme 1]. For this reason it is unlikely that solvent can co-ordinate at this site. However in the reactions of the binuclear complex where HCl and nucleophiles (see below) can co-ordinate to species (**K**), it seems likely that a molecule of solvent could also bind [to generate species (**M**)].

The kinetics of the substitution reactions of *trans*-$[\{FeCl(dppe)_2\}_2(\mu\text{-}N_2)]^{2+}$ with L = CO, MeCN, or PhCN are similar to those described in the reactions with acids. All three nucleophiles react *via* the pathway involving initial attack of solvent at species (**K**). Indeed this is the only pathway discernible with MeCN. With L = CO or PhCN an additional pathway is observed, which involves direct attack of the nucleophile on species (**K**) (bottom line, Scheme 2). Two features of the kinetics associated with the nucleophile-dependent pathway are particularly pertinent in interpreting the mechanism. First, at high concentrations of PhCN the rate of the reaction is independent of the concentration of the nucleophile (Figure 2), and this limiting rate is identical to the limiting value observed at high concentrations of HCl (Figure 1). Secondly, inspection of Figure 2 shows that the nature of the nucleophile has a profound effect on the rate of the reaction in the order, CO > PhCN ≫ MeCN. These observations can be rationalised by the mechanism shown in Scheme 2. After initial phosphine chelate ring opening from (**J**), attack of a molecule of solvent or nucleophile (including HCl) at the co-ordinatively unsaturated metal centre in (**K**) defines the two pathways. Subsequent elimination of the bridging dinitrogen ligand from the species (**M**) and (**P**), and ring closure of the phosphine chelate, followed by rapid substitution of the solvento-species (**N**) yields the product *trans*-$[FeCl(L)(depe)_2]^+$(**O**).

It seems unlikely that species (**M**) and (**P**) cleave as shown in equation (2), leaving the dinitrogen ligand co-ordinated to one of the iron atoms.



trans-$[FeCl(L)(depe)_2]^+$

+

trans-$[FeCl(N_2)(depe)_2]^+$ (2)

Although it is not possible to investigate the reactivity of *trans*-$[FeCl(N_2)(depe)_2]^+$ in isolation, it seems likely, from the experience with *trans*-$[FeH(N_2)(depe)_2]^+$, that substitution at these mononuclear complexes would be slow, having to await dissociation of the dinitrogen ligand. In the reactions of the binuclear complex, stoicheiometry and kinetic experiments show that 2 mol of the products (**O**) are formed from 1 mol equivalent of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$ within 30 s of mixing the reagents.

Clearly, for the nucleophile-dependent pathway, the electronic influence of the ligand, L, can influence the rate of dinitrogen elimination. Thus when L = CO the strongly electron-withdrawing effect of this ligand has the greatest effect whereas MeCN has no labilising effect greater than that imparted by co-ordinated thf on the solvent pathway.

Application of the steady-state treatment to species (**K**), (**M**), and (**P**) in Scheme 2, assuming rate-limiting elimination of dinitrogen, yields the generalised rate equation (3).

$$k_{\text{obs.}} = \frac{k_3k_4k_5(k_{-6} + k_7)[\text{thf}] + k_3k_6k_7(k_{-4} + k_5)[\text{L}]}{k_{-3}(k_{-6} + k_7)(k_{-4} + k_5) + k_4k_5(k_{-6} + k_7)[\text{thf}] + k_6k_7(k_{-4} + k_5)[\text{L}]} \qquad (3)$$

This rather complicated equation has three important limiting forms relevant to the discussion of the kinetic data shown in Figures 1 and 2. At low concentrations of L the intercept in the graphs is given by equation (4). Correcting the value of $k_{\text{obs.}}$ for the

$$k'_{\text{obs.}} = \frac{k_3k_4k_5[\text{thf}]}{k_4k_5[\text{thf}] + k_{-3}(k_{-4} + k_5)} \qquad (4)$$

contribution of the solvent pathway ($k'_{\text{obs.}}$) yields the rate equation (5) for the nucleophile pathway. At high concentrations of L, equation (5) simplifies to the form (6) where the reaction

$$k''_{\text{obs.}} = \frac{k_3k_6k_7[\text{L}]}{k_6k_7[\text{L}] + k_{-3}(k_{-6} + k_7)} \qquad (5)$$

$$k''_{\text{obs.}} = k_3 \qquad (6)$$

rate is independent of both the concentration and nature of L, as observed in the reactions with HCl or PhCN. The kinetic data on the reaction between the binuclear complex and CO are limited by the solubility of the gas in thf. It is confidently predicted that if higher concentrations of CO could be attained, the rate with this nucleophile would also limit at the value of k_3.

The elementary rate constants (or quotients) for the reactions of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$, determined from the kinetic analysis, are summarised in Table 3.

Prior to the study described herein it had been possible to compare only the reactivities of a mononuclear, end-on and a bridged dinitrogen in the aquation reactions of $[Ru(NH_3)_5(N_2)]^{2+}$ ($k_{\text{obs.}} = 2.0 \times 10^{-6}$ s^{-1}) and $[\{Ru(NH_3)_5\}_2(\mu\text{-}N_2)]^{4+}$ [$k_{\text{obs.}} = (2.7$—$4.6) \times 10^{-6}$ s^{-1}].[12] In the ruthenium system the reactivity is dominated by metal–dinitrogen bond dissociation. This pattern stands in stark contrast to that observed for the

Table 3. Summary of the elementary rate constants for the reactions of *trans*-$[\{FeCl(depe)_2\}_2(\mu\text{-}N_2)]^{2+}$

L	$\frac{10^2k_4k_5{}^a}{k_{-3}(k_{-4}+k_5)}$/dm^3 mol^{-1}	$\frac{k_6k_7}{k_{-3}(k_{-6}+k_7)}$/dm^3 mol^{-1}	k_3/s^{-1}
HCl	1.19 ± 0.1	157.0 ± 0.2	18.2 ± 0.5
HBr	1.18 ± 0.1		
PhCN	1.08 ± 0.1	89.3 ± 0.2	20.0 ± 0.5
MeCN	1.18 ± 0.1[b]		
CO	1.17 ± 0.1[b]	121.0 ± 0.2	

[a] Using [thf] = 13.9 mol dm^{-3}. [b] Calculated assuming k_3 = 19.1 s^{-1} the average of the two determined values.

iron–phosphine complexes. The question remains, why are nucleophiles able to compete for the unsaturated metal centre in species (**K**) (Scheme 2), but not in the corresponding mononuclear species (**B**) (Scheme 1)? The attack of 'external' nucleophiles at the sixteen-electron intermediates (**B**) and (**K**) can be successful only if the rate of ring closure (k_{-1} or k_{-3}, respectively) is sufficiently slow. Unfortunately the studies described have not allowed the determination of these values, but clearly for a variety of mononuclear iron–phosphine complexes the value of k_{-1} is sufficiently large to inhibit effective attack of 'external' nucleophiles at the unsaturated metal centre. However in the mechanism of the reaction of the binuclear complex, the relatively small value of k_{-3} which permits attack of 'external' nucleophiles at species (**K**) is most probably a consequence of unfavourable steric interactions, from substituents on the phosphine chelates, across the dinitrogen bridge.

References

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