Mechanistic Studies on Iron Phosphine Complexes. Part 1. Protonation and Substitution of *trans*-[FeH(X)(diphosphine)$_2$] (X = Cl or Br, diphosphine = $Et_2PCH_2CH_2PEt_2$ or $Ph_2PCH_2CH_2PPh_2$)

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The mechanisms of protonation and substitution of *trans*-[FeH(X)(diphosphine)$_2$] [X = Cl or Br, diphosphine = $Et_2PCH_2CH_2PEt_2$ (depe) or $Ph_2PCH_2CH_2PPh_2$ (dppe)] have been investigated in tetrahydrofuran at I = 0.1 mol dm^{-3} ([NBu$^n_4$][BF$_4$]) and 25 °C. In the presence of acid, HX, loss of phosphine and formation of [FeX$_2$(diphosphine)] occurs by a variety of pathways dependent upon the nature of the phosphine. When diphosphine = dppe rapid ring opening of the chelate from *trans*-[FeH(X)(diphosphine)$_2$] allows protonation of the pendant phosphorus atom. Subsequent dissociation of the phosphine ligand, and protonation of the metal, with release of dihydrogen, results in the formation of [FeCl$_2$(dppe)]. When diphosphine = depe a further pathway involving initial protonation of the metal is identifiable. In contrast, substitution of *trans*-[FeH(X)(diphosphine)$_2$] by L = CO, MeCN, or PhCN to yield *trans*-[FeH(L)(diphosphine)$_2$]$^+$ has to await the slow dissociation of halide.

This and the succeeding paper will describe kinetic studies on the protonation and substitution reactions of several iron complexes, all based on the Fe(diphosphine)$_2$ site [diphosphine = $Et_2PCH_2CH_2PEt_2$ (depe) or $Ph_2PCH_2CH_2PPh_2$ (dppe)]. The work described herein is concerned with the protonation and substitution reactions of *trans*-[FeH(X)(diphosphine)$_2$] (X = Cl or Br). The following paper will describe analogous studies on both mononuclear and binuclear dinitrogen complexes.

Interest in the *trans*-[FeH(X)(diphosphine)$_2$] system arose from attempts to generate a substrate binding site *via* initial protonation of a metal hydride, as outlined in reaction (1). In

$$M\text{-}H \xrightarrow{H^+} M\begin{matrix}\swarrow H^+ \\ \searrow H\end{matrix} \xrightarrow[+L]{-H_2} M\text{-}L^+ \qquad (1)$$

this context it was gratifying that the closely analogous *trans*-[FeH$_2$(dppe)$_2$] reacts with acid to yield *trans*-[FeH(η^2-H$_2$)(dppe)$_2$]$^+$, a species in which the reaction towards dihydrogen elimination is clearly well advanced.[1]

Although successful attempts have been made to bind (and activate) a range of small unsaturated molecules by the strategy described in reaction (1) at the robust Mo(dppe)$_2$ site,[2] in iron chemistry the iron–phosphorus bonds are so weak that chelate ring opening rapidly destroys the site. The kinetics of these ring-opening reactions have been studied in detail as described below. In addition, studies on the replacement of the chloro-group in *trans*-[FeH(Cl)(diphosphine)$_2$] by the nucleophiles CO, MeCN, or PhCN have shown that substitution reactions at this site are much slower than the phosphine ring-opening process.

Experimental

All manipulations in both the preparative and kinetic aspects of this work were routinely performed 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.

Anhydrous FeBr$_2$ (Aldrich Ltd.) was used as received and the complexes FeCl$_2$ (anhydrous),[3] and *trans*-[FeH(X)(depe)$_2$][4] were prepared by the literature methods, as was depe.[5] Attempts to prepare *trans*-[FeH(Cl)(dppe)$_2$] by the literature method[6] gave only poor yields of the product, highly contaminated with free dppe. A much better synthesis of this complex is outlined below.

Preparation of trans-*Bis*[1,2-*bis*(*diphenylphosphino*)*ethane*]-*chlorohydridoiron*(II).—To a stirred solution of *trans*-[FeH$_2$(dppe)$_2$][7] (0.5 g, 0.58 mmol) in dichloromethane (*ca.* 20 cm^3) was added methanol (0.028 cm^3, 0.87 mmol), then chlorotrimethylsilane (0.095 cm^3, 0.87 mmol). The solution was stirred for *ca.* 1 h during which time the solution turned dark red. It was concentrated *in vacuo* to *ca.* half its volume, and then methanol was added to crystallise the product. Yield 0.25 g (48%) (Found: C, 69.9; H, 5.9. $C_{52}H_{49}ClFeP_4$ requires C, 70.2; H, 5.5%). Visible absorption spectrum: $\lambda_{max.}$ = 465 nm, $\varepsilon_{max.}$ = 716.5 dm^3 mol^{-1} cm^{-1}.

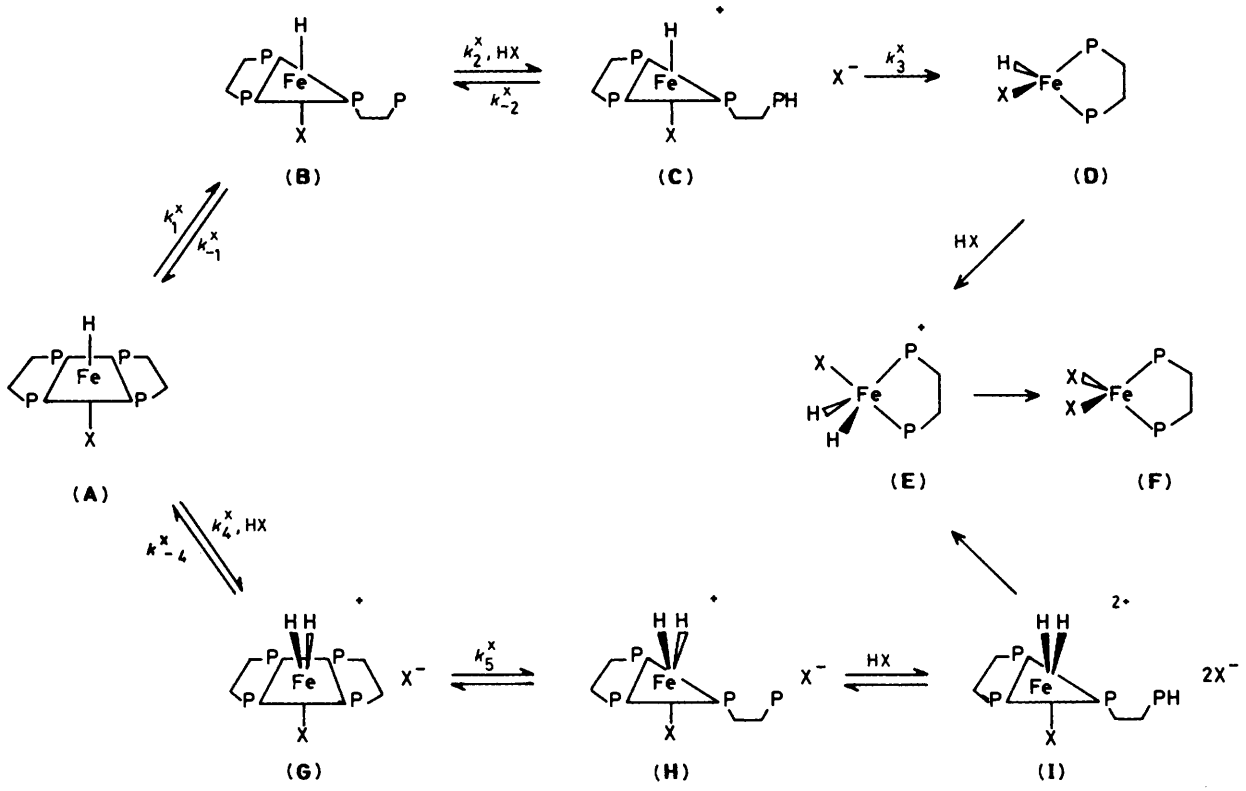
The bromo complex was prepared in an analogous fashion using bromotrimethylsilane. Yield *ca.* 40% (Found: C, 66.5; H, 5.0. $C_{52}H_{49}BrFeP_4$ requires C, 66.8; H, 5.2%). Visible absorption spectrum: $\lambda_{max.}$ = 475 nm, $\varepsilon_{max.}$ = 907.8 dm^3 mol^{-1} cm^{-1}.

Product Analyses.—The product of the protonation of *trans*-[FeH(Cl)(diphosphine)$_2$] with HCl is [FeCl$_2$(diphosphine)] which can be prepared as described below.

[1,2-*Bis*(*diphenylphosphino*)*ethane*]*dichloroiron*(II). A solution of *trans*-[FeH(Cl)(dppe)$_2$] (0.2 g, 0.23 mmol) in the minimum volume of tetrahydrofuran (thf) was stirred rapidly while methanol (0.10 cm^3, 3.1 mmol) followed by chlorotrimethylsilane (0.34 cm^3, 3.1 mmol) was added. The red colour of the solution was rapidly discharged, and after several minutes a white solid was deposited, which was removed by filtration, washed with diethyl ether, and dried *in vacuo* (Found: C, 59.7; H, 4.5. $C_{26}H_{24}Cl_2FeP_2$ requires C, 59.4; H, 4.6%), $\mu_{eff.}$ = 5.0.

The complex [FeCl$_2$(depe)]was prepared in an analogous fashion (Found: C, 36.1; H, 7.8. $C_{10}H_{24}Cl_2FeP_2$ requires C, 35.8; H, 7.2%), $\mu_{eff.}$ = 5.1.

The products of the substitution reactions of *trans*-[FeH(Cl)(diphosphine)$_2$] with CO, MeCN, or PhCN were established using their characteristic visible absorption spectra, which were identical with those of authentic samples prepared



Scheme 1. Generalised mechanism of the reaction of *trans*-[FeH(X)(diphosphine)$_2$] (X = Cl or Br, diphosphine = dppe or depe) with HCl or HBr in thf

independently: *trans*-[FeH(CO)(dppe)$_2$]BPh$_4$[8] ($\lambda_{max.}$ = 450 nm, $\varepsilon_{max.}$ = 310.0 dm^3 mol^{-1} cm^{-1}), *trans*-[FeH(CO)(depe)$_2$]BPh$_4$[9] ($\lambda_{max.}$ = 450 nm, $\varepsilon_{max.}$ = 400.0 dm^3 mol^{-1} cm^{-1}); *trans*-[FeH(NCMe)(dppe)$_2$]BPh$_4$[8] ($\lambda_{max.}$ = 450 nm, $\varepsilon_{max.}$ = 760.5 dm^3 mol^{-1} cm^{-1}), *trans*-[FeH(NCMe)(depe)$_2$]BPh$_4$[9] ($\lambda_{max.}$ = 445 nm, $\varepsilon_{max.}$ = 840.0 dm^3 mol^{-1} cm^{-1}); *trans*-[FeH(NCPh)(dppe)$_2$]BPh$_4$[8] ($\lambda_{max.}$ = 405 nm, $\varepsilon_{max.}$ = 2.8 × 10^3 dm^3 mol^{-1} cm^{-1}), *trans*-[FeH(NCPh)(depe)$_2$]BPh$_4$[9] ($\lambda_{max.}$ = 410 nm, $\varepsilon_{max.}$ = 6.0 × 10^3 dm^3 mol^{-1} cm^{-1}).

Kinetic Studies.—All kinetic studies were performed in thf in the presence of 0.1 mol dm^{-3} [NBu$^n_4$][BF$_4$] at 25.0 °C.

The rapid reactions with acid were followed using a stopped-flow spectrophotometer (Aminco-Morrow) interfaced to a B.B.C. microcomputer as described previously.[10] The traces were analysed by a curve-fitting program to obtain the rate constants, together with the initial and final absorbance values. The values of the rate constants shown in the figures or in the tables are the averages of at least three independent determinations, all agreeing to within 5% of one another. The rate expressions described below were derived from a least-squares analysis of the data.

Solutions of anhydrous HCl or HBr were prepared, analysed, and used as described previously.[10]

The slow reactions with CO, MeCN, or PhCN were studied on a Pye-Unicam SP1800 spectrophotometer equipped with a thermostatted cell holder. The temperature was maintained at 25.0 ± 0.1 °C by recirculating water from a Grant SE10 thermostat tank. Spectra were recorded in the wavelength range λ = 350—800 nm. The data were analysed at the wavelength of maximum absorbance change, by the normal semilogarithmic plot,[11] and the straight line thus obtained was linear for at least three half-lives.

Results and Discussion

The studies on the reactions of *trans*-[FeH(X)(diphosphine)$_2$] (X = Cl or Br, diphosphine = depe or dppe) described herein fall naturally into two sections: the reactions with HX resulting in phosphine chelate loss, and the nucleophilic substitution of the co-ordinated halide. The complexity and diversity of the mathematical treatments of the kinetic results could detract from the relatively simple mechanistic conclusions derived from these studies and for this reason these conclusions are briefly summarised at the beginning.

The reactions of acid with *trans*-[FeH(X)(diphosphine)$_2$] proceed by the two pathways shown in Scheme 1. When diphosphine = dppe, the mechanism is that shown on the top line of the Scheme, involving phosphine chelate ring opening followed by protonation of the pendant phosphorus atom and subsequent loss of this phosphine from the co-ordination sphere of the metal. When diphosphine = depe, in addition to the pathway shown on the top line, a further pathway is detectable in which protonation of the metal in the parent molecule occurs prior to phosphine chelate ring-opening. Most importantly, neither of the two pathways involving rapid phosphine chelate ring-opening reactions generates an intermediate which is capable of permitting attack from CO, MeCN, or PhCN ('external' nucleophiles), and so nucleophilic substitution of *trans*-[FeH(X)(diphosphine)$_2$] (as shown in Scheme 2) has to await the slow dissociation of halide.

I will now explain in detail how the mechanistic conclusions were arrived at.

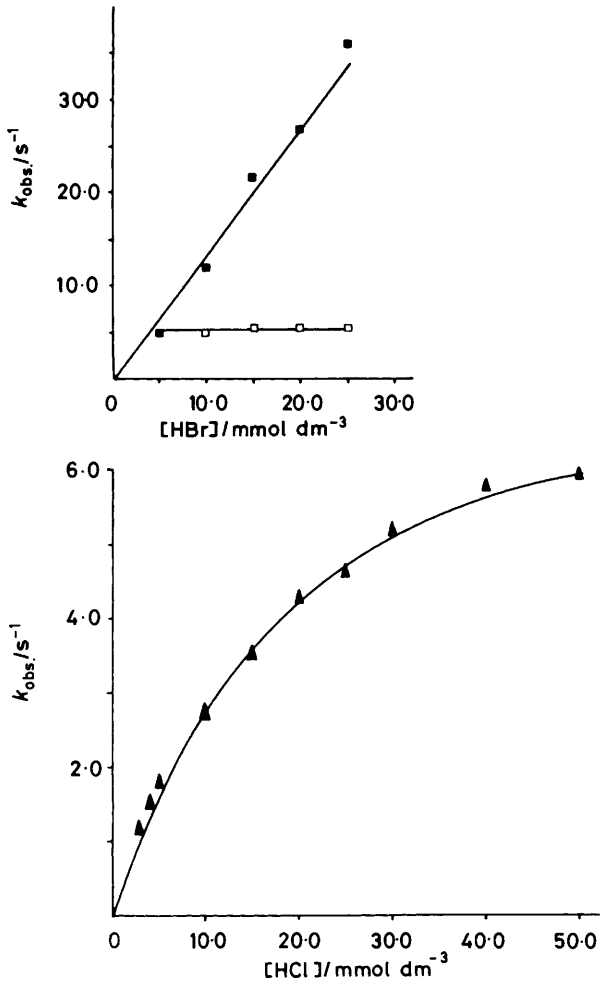


Figure 1. Dependence of $k_{obs.}$ on the concentrations of acid for the reactions of *trans*-[FeH(Cl)(dppe)$_2$] with HCl (▲), curve drawn is that defined by equation (3), or (insert) HBr. The data shown for the reaction with HBr illustrate both the acid-dependent (■) and acid-independent (□) phases

Reactions with Acids.—The reactions of an excess of acid (HCl or HBr) with *trans*-[FeH(X)(diphosphine)$_2$] result, even with the basic depe ligand, in the loss of a chelating phosphine as described by equation (2). However, kinetic analysis of these

$$trans\text{-}[FeH(X)(diphosphine)_2] + 2HX \longrightarrow [FeX_2(diphosphine)] + [Hdiphosphine]X + H_2 \quad (2)$$

reactions demonstrates that the mechanistic pathway depends upon the nature of the phosphine.

trans-[FeH(X)(dppe)$_2$]. The kinetics of the reaction between *trans*-[FeH(X)(dppe)$_2$] and HCl exhibits a first-order dependence on the concentration of the complex and (at low concentrations) acid. However, at high acid concentrations the reaction rate becomes independent of the acid as shown for the chloro-complex in Figure 1. The acid dependence of the reaction rate is described by the expression (3) where here, and

$$k_{obs.} = \frac{a[HCl]}{1 + b[HCl]} \quad (3)$$

in the rest of the paper, $k_{obs.}$ is the observed rate constant determined under pseudo-first-order conditions. When X = Cl, $a = (4.55 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1}, $b = (63.6 \pm 0.2)$ dm^3 mol^{-1}; X = Br, $a = 37.3 \pm 0.2$ dm^3 mol^{-1} s^{-1}, $b = 31.7 \pm 0.2$ dm^3 mol^{-1}. No intermediates are detectable in the reactions with HCl, since at all wavelengths in the range λ = 350—550 nm the initial absorbance observed in the stopped-flow traces is that corresponding to *trans*-[FeH(X)(dppe)$_2$]. Furthermore there is no rapid exchange of the halide *trans* to the hydrido group since the reaction between a large excess of HCl and a solution of *trans*-[FeH(Cl)(dppe)$_2$] in the presence of a twenty-fold excess of [NBu$^n_4$]Br occurred at a rate characteristic of the chloro-complex but quite different from that of the bromo-analogue.

Table 1. Kinetic data for the reactions of *trans*-[FeH(X)(dppe)$_2$] (X = Cl or Br) with HCl or HBr in thf at 25.0 °C (I = 0.1 mol dm^{-3}, [NBu$^n_4$][BF$_4$], λ = 520 nm)

		$k_{obs.}/s^{-1}$		
			With HBr	
X	[acid][a]/ mmol dm^{-3}	With HCl	fast phase	slow phase
Cl	3.0	1.15		
	4.0	1.50		
	5.0	1.74		5.00[b]
	10.0	2.70	13.30	5.00
	15.0	3.62	21.00	5.00
	20.0	4.00	29.85	5.50
	25.0	4.62	35.20	5.00
	30.0	5.15		
	40.0	5.50		
	50.0	5.65		
	5.0[c]	1.00		
	10.0[c]	2.35		
	20.0[c]	4.00		
	30.0[c]	4.80		
Br	5.0	0.16		1.25[b]
	10.0	0.28	3.52	1.05
	15.0	0.35	5.40	1.00
	20.0	0.44	7.82	1.10
	25.0	0.60	9.50	1.00
	30.0	0.68	11.90	1.10
	40.0	0.82		
	50.0	0.96		
	60.0	1.10		

[a] Data shown are those obtained with [Fe] = 1 × 10^{-4} mol dm^{-3}. In the concentration range [Fe] = (0.5—4.0) × 10^{-4} mol dm^{-3} the values of $k_{obs.}$ were independent of the complex concentration. [b] A single exponential absorbance–time trace was observed. [c] Studies in the presence of 2.0 × 10^{-3} mol dm^{-3} [NBu$^n_4$]Br.

The reaction of *trans*-[FeH(X)(dppe)$_2$] with an excess of HBr occurs in two phases when monitored at λ = 520 nm: an initial rapid absorbance decrease followed by an absorbance increase. Both phases are exponential, the initial phase exhibiting a first-order dependence on the concentrations of HBr as described by equation (4). When X = Cl, $c = (1.40 \pm 0.1) \times 10^3$ dm^3 mol^{-1}

$$k_{obs.} = c[HBr] \quad (4)$$

s^{-1}; X = Br, $c = (3.90 \pm 0.2) \times 10^2$ dm^3 mol^{-1} s^{-1}. The second phase is independent of the concentration of acid; X = Cl, $k_{obs.} = 5.10 \pm 0.2$ s^{-1}; X = Br, $k_{obs.} = 1.08 \pm 0.1$ s^{-1} as shown in Figure 1 (insert). The kinetic data for the reactions between *trans*-[FeH(X)(dppe)$_2$] and acid are summarised in Table 1.

The rather incongruous rate laws observed in the protonation reactions of *trans*-[FeH(X)(dppe)$_2$] with HCl or HBr can

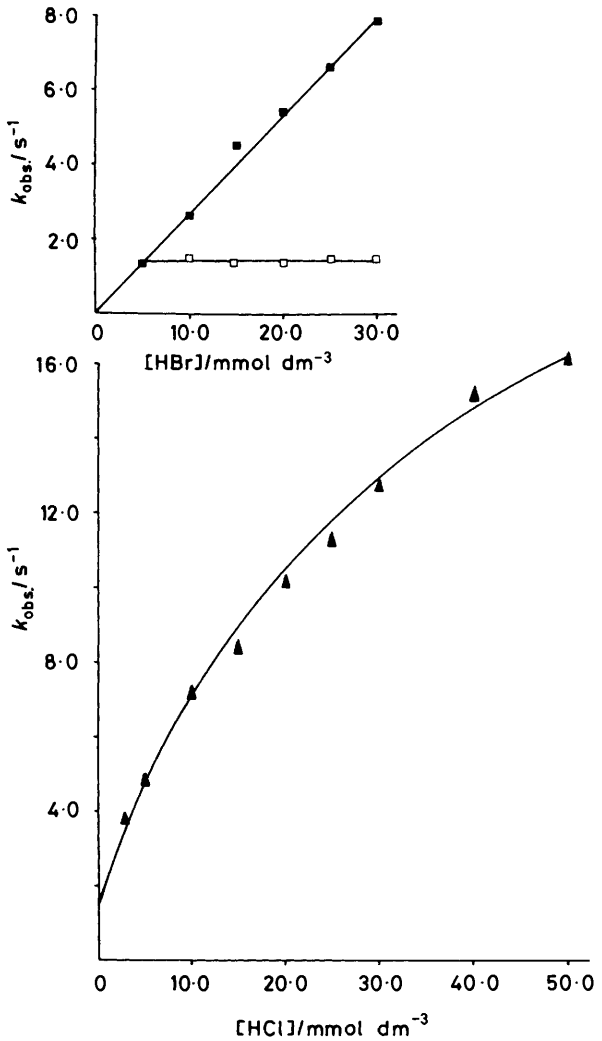


Figure 2. Dependence of $k_{obs.}$ on the concentrations of acid for the reactions of *trans*-[FeH(Cl)(depe)$_2$] with HCl (▲), curve drawn is that defined by equation (6), or (insert) HBr. The data shown for the reaction with HBr illustrate both the acid-dependent (■) and acid-independent (□) phases

Table 2. Kinetic data for the reactions of *trans*-[FeH(X)(depe)$_2$] (X = Cl or Br) with HCl or HBr in thf at 25.0 °C (I = 0.1 mol dm^{-3}, [NBu$^n_4$][BF$_4$], λ = 380 nm)

		$k_{obs.}/s^{-1}$		
			With HBr	
X	[acid]^a/mmol dm^{-3}	With HCl	fast phase	slow phase
Cl	3.0	3.70		
	5.0	4.85		1.40^b
	10.0	7.25	2.5	1.60
	15.0	9.00	4.52	1.60
	20.0	10.08	5.35	1.45
	25.0	11.00	6.50	1.50
	30.0	12.50	8.22	1.60
	40.0	15.18		
	50.0	16.80		
	5.0^c	2.22		
	10.0^c	3.10		
	20.0^c	4.65		
	30.0^c	6.20		
	40.0^c	7.90		
	50.0^c	9.95		
	10.0^d	7.50		
	20.0^d	10.32		
	30.0^d	12.30		
	50.0^d	15.35		
Br	3.0	2.50		
	5.0	2.85		2.10^b
	10.0	3.85	4.52	2.00
	15.0	4.90	8.00	2.32
	20.0	6.20	9.85	1.84
	25.0	6.72	12.28	1.90
	30.0	8.20	14.40	2.35
	40.0	9.50		

^{a} Data shown are those obtained with [Fe] = 1 × 10^{-4} mol dm^{-3}. The values of $k_{obs.}$ are independent of the complex concentration in the range [Fe] = (0.5—4.0) × 10^{-4} mol dm^{-3}. ^{b} Single exponential absorbance–time trace. ^{c} Studies using ^{2}HCl. ^{d} Studies in the presence of 2.0 × 10^{-3} mol dm^{-3} [NBu$^n_4$]Br.

be rationalised by the pathway shown on the top line of Scheme 1. In this route the rapid ring opening of a phosphine chelate from *trans*-[FeH(X)(dppe)$_2$] (**A**) yields the co-ordinatively unsaturated species (**B**) in which the chelate either can rebind to yield (**A**), or the acid can protonate the free phosphorus atom (hence prohibiting the chelation), to yield species (**C**). Subsequent dissociation of this protonated phosphine from the iron centre presumably results in the species (**D**), which reacts with further acid to yield the product [FeCl$_2$(dppe)] (**F**). The disparity between the rate laws observed with HCl and HBr and the detection of an intermediate with the latter acid, but not the former, is a consequence of the studies being performed in an aprotic solvent in which neither HCl or HBr is a strong acid.[12] With HCl the weaker of the two acids, the position of the equilibrium between species (**B**) and (**C**) lies towards (**B**) and no detectable concentration of (**C**) is attained. Treating the interconversions of species (**A**)—(**C**) as rapidly established equilibria, the rate equation (5) can be

$$k_{obs.} = \frac{k_3^X K_1^X K_2^X [HCl]}{1 + K_1^X + K_1^X K_2^X [HCl]} \quad (5)$$

derived, where $K_1^X = k_1^X/k_{-1}^X$ *etc.* and the superscript designates the *trans* halide. This equation is of the same form as the experimentally determined one [equation (3)], and comparison of the two equations permits determination of the quotient $K_1^X K_2^X/(1 + K_1^X)$: X = Cl, 63.6 ± 0.5 dm^3 mol^{-1}; X = Br, 31.6 ± 0.5 dm^3 mol^{-1}. At high concentrations of HCl, dissociation of the protonated phosphine from (**C**) becomes rate-limiting, under which conditions $K_1^X K_2^X [HCl] > 1 + K_1^X$, and equation (5) simplifies to $k_{obs.} = k_3^X$: X = Cl, k_3^{Cl} = 7.15 ± 0.5 s^{-1}; X = Br, k_3^{Br} = 1.18 ± 0.2 s^{-1}. With the stronger acid, HBr, the value of k_{-2}^X is small, resulting in the biphasic behaviour. The two phases correspond to the formation of (**C**) [X = Cl, $k_1^{Cl}k_2^{Cl}/k_{-1}^{Cl}$ = (1.40 ± 0.1) × 10^3 dm^3 mol^{-1} s^{-1}; X = Br, $k_1^{Br}k_2^{Br}/k_{-1}^{Br}$ = (3.90 ± 0.2) × 10^2 dm^3 mol^{-1} s^{-1}] and then its decomposition (X = Cl, k_3^{Cl} = 5.10 ± 0.2 s^{-1}; X = Br, k_3^{Br} = 1.08 ± 0.1 s^{-1}]. This interpretation of the kinetic results with HCl and HBr is able to rationalise that (*i*) HBr reacts faster than HCl, (*ii*) intermediates are detected with HBr but not HCl, and (*iii*) the reaction rate independent of the concentration of acid is also independent of the nature of the acid.

It is important to stress that the initial phosphine chelate ring-opening step is not caused by the acid, but rather is a process that is occurring all the time in solution. It is only that the acid

Table 3. Elementary rate constants for the reactions of *trans*-[FeH(X)(depe)$_2$] (X = Cl or Br) with HCl or HBr in thf

X	Acid	k_1^X/s^{-1}	$10^{-2}k_4^X$/ dm^3 mol^{-1} s^{-1}	k_5^X/s^{-1}
Cl	HCl	1.50 ± 0.1	8.13 ± 0.05	22.2
	HBr	1.50 ± 0.1	2.60 ± 0.05	
Br	HCl	2.00 ± 0.1	1.95 ± 0.1	
	HBr	2.08 ± 0.1	4.93 ± 0.05	

'traps' the ring-opened species by protonating the pendant phosphorus atom. A further feature of note is that the iron–dppe bonds are so weak that the initial ring-opening reaction is rapid and never becomes rate-limiting in the reactions of *trans*-[FeH(X)(dppe)$_2$].

trans-[FeH(X)(depe)$_2$]. The kinetic behaviour of *trans*-[FeH(X)(depe)$_2$] is very similar to that observed with the dppe analogues, however analysis of the data shows, besides the previously described pathway, that an additional acid-dependent route operates with these more electron-rich complexes.

The kinetics of the reaction between *trans*-[FeH(X)(depe)$_2$] and an excess of HCl exhibits a first-order dependence on the concentration of the iron complex, but a complicated dependence on the concentration of acid, as shown in Figure 2. The data demonstrate that there are two product-forming pathways: one which occurs at a rate independent of the acid concentration, and another which exhibits saturation kinetics with respect to the concentration of HCl, as described by equation (6). When X = Cl, d = 1.50 ± 0.1 s^{-1}, e = (8.13 ±

$$k_{obs.} = d + \frac{e[HCl]}{1 + f[HCl]} \qquad (6)$$

0.05) × 10^2 dm^3 mol^{-1} s^{-1}, and f = 36.6 ± 0.1 dm^3 mol^{-1}; X = Br, d = 2.00 ± 0.1 s^{-1}, e = (1.95 ± 0.1) × 10^2 dm^3 mol^{-1} s^{-1}, and f < 2.5 dm^3 mol^{-1}.

The kinetic data were fitted by use of equation (6) and the value of d obtained from the studies with HBr. The values of e and f were determined from a plot of $1/(k_{obs} - d)$ against 1/[HCl].

The reactions of *trans*-[FeH(X)(depe)$_2$] with HBr occur in two phases, both involving an exponential increase in absorbance. The kinetics of the first phase exhibits a first-order dependence on the concentration of acid as described by equation (4): X = Cl, c = (2.60 ± 0.05) × 10^2 dm^3 mol^{-1} s^{-1}; X = Br, c = (4.93 ± 0.05) × 10^2 dm^3 mol^{-1} s^{-1}. The second phase is independent of acid with a rate identical to that of the pathway d in equation (6), and illustrated in Figure 2 (insert). The kinetic data for the protonations of *trans*-[FeH(X)(depe)$_2$] are presented in Table 2.

Experiments similar to those described for the dppe analogues demonstrated that no intermediate is detectable in the reactions of *trans*-[FeH(Cl)(depe)$_2$] with HCl and that the co-ordinated halide does not rapidly exchange.

The mechanism for the reaction of acid with *trans*-[FeH(X)-(depe)$_2$] is that shown in Scheme 1. The top line of this Scheme is the pathway adopted by the dppe analogues whose kinetics we have discussed above. With the more basic depe ligand however this pathway exhibits a rate law different to that observed with *trans*-[FeH(X)(dppe)$_2$], because now the phosphine chelate ring-opening reaction is sufficiently slow to become rate-limiting: X = Cl, $k_1^{Cl} = d$ = 1.50 ± 0.1 s^{-1}; X = Br, k_1^{Br} = 2.00 ± 0.1 s^{-1}. Consistent with this interpretation, the reactions of *trans*-[FeCl$_2$(dppe)$_2$] with an excess of HCl or HBr ([HX] = 0—30 mmol dm^{-3}) also result in the loss of a phosphine ligand, at a rate independent of the concentration and nature of the acid, k_1 = 4.50 ± 0.2 s^{-1}. Here, too, phosphine chelate ring opening is rate-limiting.

The reactions of acid with *trans*-[FeH(X)(depe)$_2$] also proceed *via* a parallel pathway to that described above, in which protonation of the metal occurs prior to phosphine chelate ring opening, as shown in the bottom line of Scheme 1. This pathway is energetically available in these systems because of the greater electron-releasing ability, and smaller size, of the depe ligand compared to dppe. Protonation of the iron to generate (**G**) decreases the electron density at the metal centre, thus further weakening the iron–phosphorus bond and resulting in phosphine chelate ring opening to yield the co-ordinatively unsaturated species (**H**). Rapid protonation of the free phosphorus atom and subsequent phosphine dissociation yields (**E**) which, presumably, rapidly loses dihydrogen to produce [FeCl$_2$(depe)] (**F**). The saturation kinetics which are observed in the reaction of *trans*-[FeH(Cl)(depe)$_2$] with HCl [equation (6)] are consistent with the pathway described if, at low acid concentrations, protonation of the metal is rate-limiting, but at higher acid concentrations phosphine chelate ring opening from (**G**) becomes the slow step. This interpretation is consistent with the primary isotope effect measured for the reaction of HCl with the chloro-complex, k_H/k_D = 5.2 ± 0.2. Protonation of the Fe(diphosphine)$_2$ site has, of course, been observed before. As alluded to earlier, treatment of *trans*-[FeH$_2$(dppe)$_2$] with 1 mol equivalent of HBF$_4$ yields *trans*-[FeH(η^2-H$_2$)(dppe)$_2$]BF$_4$.[1] However I have shown that, in the presence of an excess of acid, loss of phosphine occurs presumably by mechanisms analogous to those described herein. Attempts to isolate the proposed intermediate, [FeH$_2$(Cl)(depe)$_2$]$^+$ (**G**) by the reaction of *trans*-[FeH(Cl)(depe)$_2$] with 1 mol equivalent of HCl in thf yielded only a mixture of unreacted starting material and [FeCl$_2$(depe)] (**F**).

It is only in the reaction of HCl with *trans*-[FeH(Cl)(depe)$_2$] that saturation kinetics have been observed (Figure 2), but the same limiting rate constant should be attained at high concentrations of HBr in its reaction with the chloro-complex. However the decomposition of the solvent, thf, by HBr prohibits the use of sufficiently concentrated acid to observe saturation kinetics.

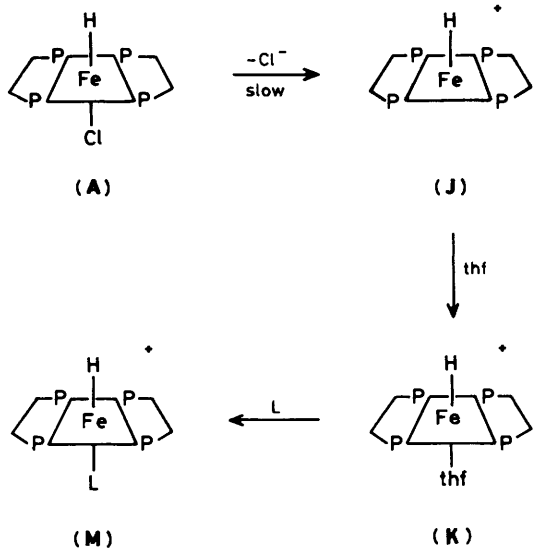
The values of the elementary rate constants for the reactions of acids with *trans*-[FeH(X)(depe)$_2$] are summarised in Table 3. Two features require further comment. The labilisation of the iron–phosphorus bond by protonation of the iron centre in *trans*-[FeH(Cl)(depe)$_2$] is given by k_5^{Cl}/k_1^{Cl} = 14.8 and reflects the relative electron densities at the metal site in (**A**) and (**G**). The second feature refers to the relative rates of protonation of *trans*-[FeH(X)(depe)$_2$] with HCl or HBr (k_4^X). In the aprotic solvent, thf, the reactivity of the acid is dominated by two factors: the size of the acid and the strength of the acid. In all the reactions summarised in Table 3 the values of k_4^X cover the narrow range 1.95 × 10^2 < k_4^X < 8.13 × 10^2 dm^3 mol^{-1} s^{-1}. However there is no particular trend in the rates of the acid reactions with either the chloro- or the bromo-complex. It would appear that there is a fine balance between the factors which define the rate of protonation of the metal by a molecule of HX.

Previous studies on the mechanisms of chelate ring-opening reactions[13,14] have defined two pathways by which acids can influence this process: (*i*) protonation of the pendant ligand from acid in solution, and (*ii*) prior co-ordination or association of a weak acid adjacent to the ring-opening site. Although in the present system the first of these pathways has been observed, the second pathway is prohibited because of the co-ordinatively saturated nature of the complex. However the relatively high basicity of the Fe(diphosphine)$_2$ core permits the pathway involving protonation at the metal.

Table 4. Kinetic data for the reactions of *trans*-[FeH(Cl)(diphosphine)$_2$] (diphosphine = dppe or depe) with L = CO, MeCN, or PhCN in thf at 25.0 °C (I = 0.1 mol dm^{-3}, [NBu$^n_4$][BF$_4$])

		$10^5 k_{obs.}$*/s^{-1}		
Diphosphine	[L]/ mmol dm^{-3}	L = CO	MeCN	PhCN
dppe	2.06	8.10		
	10.00		8.55	8.65
	20.00		8.62	8.50
	50.00		8.50	8.92
	100.00		8.83	8.95
depe	2.06	7.95		
	10.00		8.10	8.00
	20.00		8.72	8.10
	50.00		8.70	7.90
	100.00		8.98	7.98

* Data shown are those with [Fe] = 4.0 × 10^{-4} mol dm^{-3}.



Scheme 2. Mechanism of the substitution reactions of *trans*-[FeH(Cl)(diphosphine)$_2$] (diphosphine = dppe or depe)

Substitution Reactions.—The substitution of the co-ordinated halide in *trans*-[FeH(Cl)(diphosphine)$_2$] by the nucleophiles CO, MeCN, or PhCN in thf occurs according to the stoicheiometry (7). For a given phosphine, the rate of substitution shows

$$trans\text{-}[FeH(Cl)(diphosphine)_2] + L \longrightarrow trans\text{-}[FeH(L)(diphosphine)_2]^+ + Cl^- \quad (7)$$

a first-order dependence on the concentration of the iron complex but is independent of both the concentration and nature of the nucleophile: 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}. This is consistent with the mechanism shown in Scheme 2 in which rate-limiting loss of chloride from *trans*-[FeH(Cl)(diphosphine)$_2$] (**A**) generates the co-ordinatively unsaturated, sixteen-electron species [FeH(diphosphine)$_2$]$^+$ (**J**). This complex can be isolated (as the tetraphenylborate salt) by the reaction of (**A**) with $NaBPh_4$ in thf under an atmosphere of argon.[8] In the presence of such a large excess of solvent molecules, (**J**) is almost certainly solvated by the weakly co-ordinating thf to yield (**K**). Subsequent rapid replacement of the co-ordinated thf by a molecule of the nucleophile yields the product, *trans*-[FeH(L)(diphosphine)$_2$]$^+$ (**M**).

The kinetic data for the substitution reactions are shown in Table 4.

The slow rates of substitution of *trans*-[FeH(Cl)(diphosphine)$_2$] contrast sharply with the rapid phosphine chelate ring-opening reactions which are occurring in these molecules. Clearly substitution is not proceeding *via* a pathway involving attack of the nucleophile at the vacant site in (**B**), generated by chelate ring opening. Rather, nucleophilic attack has to await the much slower dissociation of chloride from *trans*-[FeH(Cl)(diphosphine)$_2$]. Although not studied in detail, investigation of the substitution reaction of *trans*-[FeCl$_2$(depe)$_2$] with PhCN in thf indicates $k_{obs.} \leqslant 5 \times 10^{-4}$ s^{-1}, which again contrasts with the rapid ring-opening reaction ($k_1 = 4.50 \pm 0.2$ s^{-1}).

The reason for this inability of nucleophiles to accomplish substitution *via* phosphine chelate ring-opened species must be a consequence of the rapid ring-closure reaction (k^X_{-1}). The 'external' nucleophile, CO, MeCN, or PhCN, is unable to compete effectively [for the metal site in species (**B**)] with the rapid reaction of the 'internal' nucleophile (the pendant phosphorus atom). It must be remembered that the studies described herein have, in the most part, resulted in the determination of the rate of ring-opening reactions (k^X_1), but have not allowed calculation of the rate constant associated with the reverse process (k^X_{-1}).

In the following paper I will elaborate further on the pathways for phosphine chelate ring-opening and nucleophilic substitution at the Fe(diphosphine)$_2$ site, and outline the conditions under which substitution *can* proceed *via* chelate ring-opened species.

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