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The mechanism of displacement of dihydrogen and dinitrogen from iron, ruthenium and osmium hydrides and implications for models of nitrogenase action

Caroline A. Helleren,[a] Richard A. Henderson[b] and G. Jeffery Leigh*[a]

[a] *School of Chemistry, Physics and Environmental Science, University of Sussex, Brighton, UK BN1 9QJ*
[b] *Nitrogen Fixation Laboratory, John Innes Centre, Norwich Research Park, Colney, UK NR4 7UH*

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The substitution of dihydrogen in complexes $[FeH(H_2)(phosphine)_x]^+$ [phosphine = $R_2PCH_2CH_2PR_2$ (R = Et or Me) or $P(CH_2CH_2PR'_2)_3$ (R′ = Me or Ph)] by ligands L (MeCN, PhCN, or Cl^-) has been shown to be first order in the concentration of complex and zero order in the concentration of L, in both acetone and thf. Activation parameters have been determined, and the mechanism of substitution is proposed to involve rate-determining loss of H_2 from the parent complexes and subsequent rapid co-ordination of L. This mechanism differs from that recently proposed for an analogous complex of $Ph_2PCH_2CH_2PPh_2$, and the reasons for this are discussed. Less thorough studies of some related dinitrogen complexes, and of some homologous complexes of Ru and Os, are consistent with a similar loss of dinitrogen or dihydrogen being rate determining.

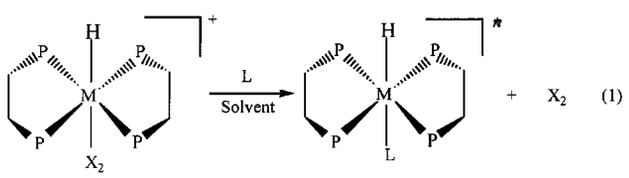
Introduction

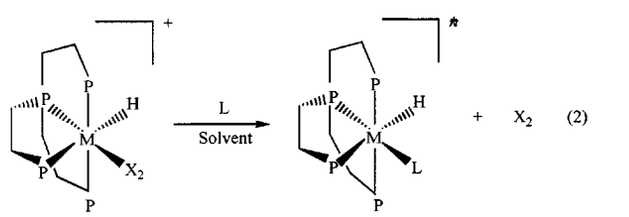
There is considerable circumstantial evidence that the dinitrogen-binding site of the molybdenum–iron nitrogenases is hydridic during at least part of the catalytic cycle.[1] In particular, the fixation of dinitrogen involves the obligatory evolution of at least one molecule of dihydrogen for each molecule of dinitrogen fixed, and dihydrogen is a competitive inhibitor of nitrogen fixation. Both features can be explained by dinitrogen binding involving displacement of dihydrogen.[2]

In a chemical context of models for dinitrogen binding, it has been recognised for some time that iron trihydrides such as *trans*-$[FeH(H_2)(dmpe)_2]^+$ (dmpe = $Me_2PCH_2CH_2PMe_2$) react with several donors (L), such as CO, N_2 and MeCN, losing H_2 and forming *trans*-$[FeH(L)(dmpe)_2]^+$.[3] The mechanism of these displacements has not been definitively determined. In order to extend this type of reaction, we originally attempted[4] to prepare complexes containing a dinitrogen molecule bridging between iron and molybdenum by a reaction of *trans*-$[FeH(H_2)(dmpe)_2]^+$ with *trans*-$[Mo(N_2)_2(dppe)_2]$(dppe = $Ph_2PCH_2CH_2PPh_2$), but all we were able to isolate was a mixture containing *trans*-$[MoH_4(dppe)_2]$ and *trans*-$[FeH(N_2)(dmpe)_2]^+$, although it is now evident[5] that there are also further products. A preliminary study[6] suggested that the rate of this surprising exchange exhibited a first-order dependence on the concentration of the iron complex, and this prompted us to pursue the work reported here on the kinetics of substitution reactions of a series of metal hydrides as generalised in the following equations (M = Fe, Ru, or Os; pp = dmpe or $Et_2PCH_2CH_2PEt_2$; depe or, less often, tetraphosphines; $x = 1$ or 2; $n = 1$ or 0; and L = MeCN, PhCN, or Cl^-).

$$trans\text{-}[MH(X_2)(pp)_x]^+ + L \longrightarrow trans\text{-}[MH(L)(pp)_x]^{n+} + X_2$$

Such studies should enable us to determine the influences of substituent, stereochemistry, incoming nucleophile, and solvent on the reaction. When this work had been completed some parallel studies on the reactions of *trans*-$[FeH(H_2)(dppe)_2]^+$ with nitriles were described.[7] We shall include these published data in our discussions, and show how a spectrum of mechanisms can





operate within the family of complexes of general formula *trans*-$[FeH(H)_2(pp)_2]^+$ (pp = dmpe, depe, or dppe).

Preliminary work in our group[4,6] has indicated that the reactions we are interested in are first order in the concentration of complex. Thus, in the substitution of dihydrogen by isocyanides and nitriles in *trans*-$[FeH(H_2)(pp)_2][BPh_4]$ (pp = dmpe or depe)[3,4,6] the rate of reaction exhibits a first-order dependence on the concentration of complex and is independent of the concentration of nitrile. The reaction of *trans*-$[FeH(H_2)(dmpe)_2][BPh_4]$ with MeCN in thf under argon was studied by following the intensity of the band assigned to the $\nu(N{\equiv}C)$ of the product in the IR spectrum and the first-order rate constant, k_{obs}, was found to be $(1.6 \pm 0.2) \times 10^{-3}$ s^{-1}, essentially identical to that for the formation of *trans*-$[FeH(N_2)(dmpe)_2][BPh_4]$ from *trans*-$[FeH(H_2)(dmpe)_2]^+$, $(1.2 \pm 0.1) \times 10^{-3}$ s^{-1} determined previously.[3,6] This measurement was performed at only one temperature, that of the IR beam, estimated to be 325 K. The reaction of *trans*-$[FeH(H_2)(depe)_2][BPh_4]$ with MeCN, eqn. (3),

$$trans\text{-}[FeH(H_2)(depe)_2]^+ + MeCN \xrightarrow{thf} trans\text{-}[FeH(MeCN)(depe)_2]^+ + H_2 \quad (3)$$

was studied[6] in thf by following the intensities of the

resonances of the starting material and product in their ^{31}P-$\{^1H\}$ NMR spectra. Under pseudo-first-order conditions, a rate constant $k_{obs} = (3.2 \pm 0.2) \times 10^{-4}$ s^{-1} at 296 K was determined. In some related work[8] the kinetics of the reactions of *trans*-$[FeH(N_2)(depe)_2]^+$ with several nucleophiles at 298 K has been studied. The reactions exhibit a first-order dependence on the concentration of *trans*-$[FeH(N_2)(depe)_2]^+$, with $k_{av} = 1.0 \times 10^{-3}$ s^{-1} for the reactions with CO, MeCN and PhCN.

The present study is one of the *first comprehensive quantitative studies* to show the effect of changing the metal, ancillary ligands and nucleophile on the kinetics and mechanisms for the substitution of H_2 or N_2 in octahedral Group 8 phosphine complexes. We have also extended the studies to a limited number of homologous hydrides of ruthenium and osmium (Table 1). However, we were unable to complete this study to include all complexes *trans*-$[MH(X_2)(pp)_2][BPh_4]$ and *cis*-$[MH(X_2)\{P(CH_2CH_2PR_2)_3\}][BPh_4]$ (M = Fe, Ru or Os; X = H or N; pp = dmpe or depe; R = Me [pp_3Me] or Ph [pp_3]) because some of them are too kinetically stable or unstable in solution, whilst others have yet to be reported.

Experimental

All manipulations were carried out using standard Schlenk techniques under argon, unless otherwise stated. House dinitrogen was dried with potassium hydroxide and silica gel before use. Otherwise, pure dinitrogen (Air Products) was used directly from the cylinder. Solvents were dried by heating them to reflux over an appropriate drying agent under dinitrogen. Absolute ethanol was used as supplied and analytical grade acetone was dried over a succession of molecular sieves. The volatile solvents were degassed by freeze-thawing. Non-volatile solvents were purged of dioxygen by bubbling argon or dinitrogen through them.

The preparations of complexes $[FeH(H_2)(dmpe)_2][BPh_4]$,[3,5,9] $[FeH(N_2)(dmpe)_2][BPh_4]$,[3,9,10] $[FeH(H_2)(depe)_2][BPh_4]$,[3,5,9] $[FeH(N_2)(depe)_2][BPh_4]$,[3,9,10] $[FeH(H_2)(pp_3)][BPh_4]$,[11] $[FeH(N_2)(pp_3)][BPh_4]$,[11] $[FeH(H_2)(pp_3Me)][BPh_4]$,[12] $[FeH(N_2)(pp_3Me)][BPh_4]$,[12] $[RuH(H_2)(depe)_2][BPh_4]$,[9a,10,13] $[RuH(N_2)(depe)_2][BPh_4]$,[9a,10,13] and their ruthenium dmpe homologues, $[OsH(H_2)(depe)_2][BPh_4]$,[3,5,6,9,14,15] $[OsH(N_2)(depe)_2][BPh_4]$,[3,5,6,9,14,15] and the osmium dmpe homologues, and their derivatives $[MH(L)(phosphine)_n][BPh_4]$ (M = Fe, Ru or Os; L = MeCN, PhCN or Cl, as detailed in the text; $n = 1$ or 2 as required by the stoichiometry; phosphine = dmpe, depe, pp_3 or pp_3Me)[3,5,6,10] were attempted and most were characterised as described in the literature. Not all our attempts were successful, and only some of these complexes (see text) were found to be amenable to our kinetic experimental techniques.

Nuclear magnetic resonance (NMR) spectra were measured using either a Bruker ACP-250 (operating frequencies ^1H 250.2 MHz, ^{31}P 101.3 MHz) or a Bruker DPX-300 spectrometer (operating frequencies ^1H 300.1 MHz and ^{31}P 121.5 MHz), with ^1H referenced against the deuteriated solvent and 85% H_3PO_4 in D_2O (δ 0) used as the external ^{31}P reference. The NMR solvents were used as supplied from Cambridge Isotope Laboratory after they were transferred into dried Schlenk tubes and kept under argon. The decoupler frequency in ^{31}P-$\{^1H\}$ NMR spectroscopy was centred on the metal hydride resonances, which exhibit the strongest P–H coupling, as determined from the ^1H NMR spectra.

The UV-vis spectra were obtained on a UV-2101 PC scanning spectrophotometer and stopped-flow measurements were carried out using a Hi-Tech SF-51 spectrophotometer modified to enable manipulation of air-sensitive solutions. The temperature was maintained at 25 °C using a Grant LE8 thermostat bath and the spectrophotometer was interfaced to a computer *via* an A/D converter. Data were transferred directly to the computer and analysed by a computer program which fitted the exponential absorbance–time curves by use of single exponential functions.

Methods of kinetic measurement

(a) Iron and osmium dihydrogen and/or dinitrogen complexes. The intensity of the phosphorus resonances for the starting material and product was monitored by ^{31}P-$\{^1H\}$ NMR spectroscopy at 101.3 or 121.5 MHz on spectrometers with variable-temperature facilities.

An appropriate weight of *trans*-$[MH(X_2)(pp)_2][BPh_4]$ (M = Fe or Os; X = N or H) (*ca.* 0.1 mmol) was dissolved in either 0.5 cm^3 of a mixture of deuteriated and undeuteriated solvent (1 : 9 v/v) when the resonances were measured with a base frequency

Table 1 Summary of systems studied

Group 8 complex	Nucleophile
trans-$[FeH(N_2)(dmpe)_2][BPh_4]$	MeCN, PhCN and chloride
trans-$[FeH(X_2)(depe)_2][BPh_4]$	MeCN, PhCN and chloride
trans-$[RuH(H_2)(depe)_2][BPh_4]$	MeCN
trans-$[OsH(H_2)(dmpe)_2][BPh_4]$	MeCN and PhCN

Table 3 Rate constants for the reactions of *trans*-$[FeH(X_2)(pp)_2][BPh_4]$ in the concentration range 100–200 mmol dm^{-3} with $[^nBu_4N]Cl$ (7–10-fold excess) in acetone at 298.2 K

	k_{obs}/s^{-1} for	
Complex	Loss of X_2 from $[FeH(X_2)(pp)_2]^+$	Formation of $[FeH(Cl)(pp)_2]$
$[FeH(H_2)(depe)_2]^+$	$(3.5 \pm 0.1) \times 10^{-4}$	$(5.8 \pm 0.5) \times 10^{-4}$
$[FeH(N_2)(depe)_2]^+$	$(9.7 \pm 0.1) \times 10^{-4}$	$(11.1 \pm 0.7) \times 10^{-4}$
$[FeH(N_2)(dmpe)_2]^+$	$(2.1 \pm 0.1) \times 10^{-4}$	

Table 2 Rate constants for the reactions of *trans*-$[MH(X_2)(pp)_2][BPh_4]$ (in the concentration ranges Fe 100–200, Ru *ca.* 0.2, Os 150–200 mmol dm^{-3}) with nitriles at 298.2 K

		k_{obs}/s^{-1} for	
Complex	Solvent	Loss of X_2 from $[MH(X_2)(pp)_2]^+$	Formation of $[MH(L)(pp)_2]^+$
$[FeH(H_2)(depe)_2]^+$	Acetone	$(4.0 \pm 0.3) \times 10^{-4}$	$(4.5 \pm 1.6) \times 10^{-4}$
	thf	$(2.7 \pm 0.2) \times 10^{-4}$	$(2.5 \pm 0.3) \times 10^{-4}$
$[FeH(N_2)(depe)_2]^+$	Acetone	$(12.5 \pm 0.8) \times 10^{-4}$	$(12.6 \pm 1.8) \times 10^{-4}$
	thf	$(10.6 \pm 0.6) \times 10^{-4}$	$(9.5 \pm 1.6) \times 10^{-4}$
$[FeH(N_2)(dmpe)_2]^+$	Acetone	$(2.5 \pm 0.2) \times 10^{-4}$	$(2.7 \pm 0.5) \times 10^{-4}$
	thf	$(1.7 \pm 0.3) \times 10^{-4}$	$(2.1 \pm 0.8) \times 10^{-4}$
$[RuH(H_2)(depe)_2]^+$	Acetone	$(2.8 \pm 0.2) \times 10^{-1}$	
$[OsH(H_2)(depe)_2]^+$	thf	$(3.5 \pm 0.2) \times 10^{-5}$ [a]	

[a] Taken at 323.2 K.

of 121.5 MHz (5 mm NMR tube), or 2 cm^3 of undeuteriated solvent when the spectra were measured with a base frequency of 101.3 MHz (10 mm tube with an insert containing D_2O as the lock solvent). The predried solvent was degassed prior to use and the reactions were carried out under argon, to prevent side reactions of the dihydrogen complexes with dinitrogen. It was assumed (reasonably) that the small percentage of deuteriated solvent would not significantly affect the rate constant of the reaction that would otherwise occur in the undeuteriated solvent.

The solution of starting material was transferred to an NMR tube and capped with an appropriately sized Subaseal. We assumed that the production of dihydrogen or dinitrogen would not exert undue pressure on the Subaseal of the argon-filled NMR tube.

The sample was equilibrated in the NMR probe to the required temperature for 20 to 30 min prior to the addition of nucleophile. The initial spectrum of starting material was taken with a number p of scans, p depending on the concentration of the complex. The tube was removed from the probe, an *excess* of nucleophile L was quickly added to the solution *via* a syringe, and the tube was then shaken and replaced in the probe. The same number p of scans was taken after set periods of time until the reaction was more than 75% complete.

Solutions of the starting materials, *trans*-$[MH(X_2)(pp)_2][BPh_4]$, had to be essentially stable in solution under argon to irreversible loss of X_2 in the absence of a nucleophile for the period of the experiment. They were placed in NMR tubes in a thermostatically controlled probe and spectra taken periodically. No concentration of any starting complex changed detectably over a period of up to 12 h.

(b) Ruthenium dihydrogen complex. The reactions of *trans*-$[RuH(H_2)(depe)_2][BPh_4]$ with nucleophiles are too rapid to be followed by the NMR spectroscopic methods outlined above. Therefore the reaction with MeCN was followed using stopped-flow spectrophotometry. At $\lambda = 420$ nm the reaction is characterised by a single exponential absorbance–time curve with an initial absorbance corresponding to that of *trans*-$[RuH(H_2)(depe)_2]^+$ and a final absorbance which is that of *trans*-$[RuH(NCMe)(depe)_2]^+$.

Results

Determination of rate constants

The kinetics of all the reactions studied was determined in the presence of a sufficient excess of nucleophile to ensure pseudo-first-order conditions. In the first instance (see later) the data were analysed in the usual way by plotting $\log_e\{[M(X_2)Ln_5]_t - [M(X_2)Ln_5]_0\}$ against t, where $[M(X_2)Ln_5]_t$ is the concentration of complex at time t, $[M(X_2)Ln_5]_0$ is its concentration at the beginning of the reaction and Ln_5 represents the remaining non-reactive ligands in the metal coordination sphere. The observed rate constant, k_{obs}, is the slope of this straight line. The kinetic data for the reaction between *trans*-$[RuH(H_2)(depe)_2]^+$ and MeCN determined on the stopped-flow apparatus were analysed by a computer curve-fitting program. The curve was a good fit to a single exponential for at least three half-lives.

Systematic variation of the concentration of the nucleophile (in the range 1.1- to 15-fold excess) led to no appreciable change in k_{obs}, demonstrating that the rate is independent of the concentration of the nucleophile. The average rate constants for the various complexes reacting in different solvents with MeCN or PhCN are summarised in Tables 2 and 3.

The data for the iron and osmium complexes, derived from the NMR spectroscopic studies, show rate constants obtained by analysing both the disappearance of the starting material and the appearance of the product. The latter type of study presented some problems, because the value of k_{obs} determined in this way was sometimes appreciably different from that determined by monitoring the disappearance of reactant. This is because the semi-logarithmic plot will only give accurate values reliably if the concentration of product at the end of the reaction is known reliably. We estimated $[M(X_2)Ln_5]_e$, the concentration at the end of the reaction, by extrapolating the data on the basis of an exponential increase in the intensity of the resonance in the ^{31}P-$\{^1H\}$ NMR spectrum. However, even small changes in the estimated value resulted in significantly different values of k_{obs}. To avoid this problem we used both the Guggenheim[16] and Kezdy–Swinbourne[17] methods of analysis that do not require the value of $[M(X_2)Ln_5]_e$. Unless data analysis was performed in this way we could not obtain accurate values of k_{obs}.

It has been claimed that both the Guggenheim[16] and Kezdy–Swinbourne[17] methods of analysis have similar orders of accuracy. Both give linear plots for first-order reactions. There is an evident advantage in the Guggenheim method when the order of reaction is not known, since this method relies principally on data obtained at the end of the reaction where there is a clear distinction between exponential (for reactions exhibiting a first-order dependence upon complex concentration) and hyperbolic (for reactions exhibiting a second-order dependence upon complex concentration) curves. However, in our case this distinction is not essential because the first-order dependence on the concentration of complex has been established by analysis of other data (see below). The average values of k_{obs} obtained by the Kezdy–Swinbourne[17] method of analysis are presented in Tables 2–4.

Table 4 Rate constants for the reaction of *trans*-$[FeH(H_2)(depe)_2][BPh_4]$ in the concentration range 40–150 mmol dm^{-3} with MeCN in acetone at 298.2 K

Ratio Fe : MeCN or weight of iron complex (g)	$10^4\ k_{obs}/s^{-1}$ for Loss of H_2 from $[FeH(H_2)(depe)_2]^+$	$10^4\ k_{obs}/s^{-1}$ for Formation of $[FeH(MeCN)(depe)_2]^+$
1 : 1.1	3.9 ± 0.1	4.0 ± 0.3
0.015	4.3 ± 0.1	4.2 ± 0.3
0.029	4.3 ± 0.1	4.0 ± 0.3
0.050	4.2 ± 0.1	4.1 ± 0.3

Table 5 Rate constants for the reaction of *trans*-$[RuH(H_2)(depe)_2][BPh_4]$ at the concentration *ca.* 0.2 mmol dm^{-3} with MeCN in excess in acetone at 298.2 K

Ratio of Ru to MeCN	k_{obs}/s^{-1} for loss of H_2 from $[RuH(H_2)(depe)_2]^+$
1 : 50	0.260
1 : 25	0.285
1 : 12.5	0.285
1 : 6.3	0.285
1 : 6.3	0.275

Order of reaction in complex

The linearity of the semi-logarithmic plots described above is consistent with the reactions exhibiting a first-order dependence on the concentration of complex. This was confirmed by experiments in which the concentration of the complexes was varied whilst maintaining a constant concentration of nucleophile. Under these conditions k_{obs} did not change. Specimen data are shown in Tables 4 and 5.

Temperature dependence of rate constants

The reactions of the iron complexes were investigated at various temperatures to determine activation parameters for the

Table 6 Activation parameters for the reactions of *trans*-$[FeH(X_2)(pp)_2][BPh_4]$ with nitriles in the temperature range 291–313 K

Complex	Solvent	E_{act}/kJ mol^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}_{298.2\ K}$/kJ mol^{-1}
$[FeH(H_2)(depe)_2]^+$	Acetone	115.1 ± 4.7	112.4 ± 4.7	48 ± 15	98.1 ± 0.2
	thf	124.3 ± 4.2	121.7 ± 4.1	77 ± 14	98.9 ± 0.1
$[FeH(N_2)(depe)_2]^+$	Acetone	109.3 ± 4.7	107.2 ± 4.1	40 ± 14	95.2 ± 0.1
	thf	118.6 ± 3.4	115.9 ± 3.4	68 ± 12	95.6 ± 0.1
$[FeH(N_2)(dmpe)_2]^+$	Acetone	123.5 ± 3.7	120.8 ± 3.7	73 ± 13	99.2 ± 0.2
	thf	125.0 ± 1.4	122.3 ± 1.4	76 ± 5	99.8 ± 0.1

Table 7 Summary of the trends in rate constants and activation parameters for the reactions of *trans*-$[FeH(X_2)(pp)_2][BPh_4]$ with nucleophiles

Factor	k_{obs}	E_{act}, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$	$\Delta G^{\ddagger}$
Metal	Ru > Fe ⩾ Os		
X_2	$N_2 > H_2$	$N_2 < H_2$	$N_2 < H_2$
Ancillary ligand	depe > dmpe ⩾ pp_3	dmpe > depe	$N_2 < H_2$
Nucleophile	Independent of nucleophile	Independent of nucleophile	Independent of nucleophile
Solvent	Acetone > thf	thf > acetone	thf > acetone
Stereochemistry	*trans* ⩾ *cis*		
Temperature	Increases with increasing temperature		

dissociation of X_2 (X = H or N) from *trans*-$[FeH(X_2)(depe)_2]^+$. The complexes *trans*-$[RuH(H_2)(depe)_2]^+$ and *trans*-$[OsH(H_2)(depe)_2]^+$ were studied only at 298.2 and 323.2 K, respectively. Other structurally similar diphosphine or tetradentate tetraphosphine iron, osmium and ruthenium compounds were not amenable to study since they react either too rapidly or too slowly for an extensive temperature-dependence study to be possible.

Plots of $\log_e(k_{obs})$ against $1000/T$ give slopes of $-E_{act}/R$ from which the activation energies E_{act} were calculated (Table 6). The data are independent of the identity of the nitrile and are averaged. The errors reported are those for the data points about the line, as given by the least squares analysis. The temperature range employed (291–313 K) in these studies depended on the rate of reaction, the fastest reaction studied being complete within *ca*. 10 min. The activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated using the Eyring equation and the usual thermodynamic relationships.[17,18] A summary showing the main trends in the rate constants and activation parameters is given in Table 7.

Discussion

The mechanism of substitution of *trans*-$[MH(X_2)(pp)_2][BPh_4]$ (X = H or N)

In the studies with dmpe and depe complexes reported in this paper we have shown that: (i) the rate constants for the loss of *trans*-$[MH(X_2)(pp)_2][BPh_4]$ are equal to those for formation of *trans*-$[MH(L)(pp)_2][BPh_4]$ within experimental error and (ii) that the rates of reaction are strictly independent of the nature and concentration of nucleophile in both acetone and thf. Point (i) is consistent with the simple stoichiometries observed for these reactions and point (ii) dictates a mechanism involving a rate-limiting unimolecular reaction of *trans*-$[MH(X_2)(pp)_2][BPh_4]$. The possible mechanisms are discussed below, after an account of some solution properties of complexes *trans*-$[MH(H_2)(pp)_2]^+$.

At low temperatures in solution, complexes *trans*-$[MH(H_2)(pp)_2]^+$ show separate resonances for the hydride and dihydrogen ligands in the ^{1}H NMR spectra. As the temperature increases the hydride and dihydrogen atoms undergo intramolecular exchange,[3,9a] the rate of which increases with temperature. At the fast-exchange limit only a single broad resonance is observed in the ^{1}H NMR spectra of *trans*-$[MH(H_2)(pp)_2]^+$. This effectively scrambles all the hydrogen atoms. The question then arises as to which of the tautomers is the reactive species.

We studied the reactions of *trans*-$[FeH(H_2)(pp)_2][BPh_4]$ with nucleophiles at temperatures where this intramolecular exchange is rapid, and we assumed that the loss of dihydrogen occurred *via* $[MH(\eta^2\text{-}H_2)(pp)_2]^+$ derived from $[MH_3(pp)_2]^+$. However, intramolecular hydrogen-atom exchange in *trans*-$[RuH(H_2)(depe)_2][BPh_4]$ at 298.2 K is slow and the loss of H_2 upon reaction with a nitrile is almost certainly from the hydrido(dihydrogen) tautomer. Finally, $[OsH(H_2)(depe)_2][BPh_4]$ exists as two tautomers in rapid temperature-dependent equilibrium.[9a,14,19,20] We again assumed that at 323.2 K the loss of dihydrogen was *via* the hydrido(dihydrogen) tautomer. Indeed, it is difficult to conceive of any reasonable alternative.

The simplest (and most likely) mechanisms consistent with our data on the depe and dmpe complexes are the *dissociative mechanism* and the *dissociative interchange mechanism*.[17,18,21–23] For a dissociative mechanism as shown in eqn. (4) rate-limiting

$$[MH(X_2)Ln_m] \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [MHLn_m] + X_2 \xrightarrow[L]{k_2} [MH(L)Ln_m] \quad (4)$$

dissociation of X_2 generates the co-ordinatively unsaturated intermediate, $[MHLn_m]^+$, which is rapidly attacked by nucleophile (L) or solvent (solv) to form the product. Other work † has shown that, in the case of osmium, a five-co-ordinate species may actually be more stable than the dinitrogen adduct. The rate law associated with this mechanism is readily derived by treating $[MHLn_m]$ as a steady-state intermediate. The resulting expression is (5). If $k_2[L] > k_{-1}[X_2]$ (a condition that can be

$$\frac{-d[MH(X_2)Ln_m]}{dt} = \frac{k_1k_2[L][MH(X_2)Ln_m]}{k_{-1}[X_2] + k_2[L]} \quad (5)$$

fulfilled when there is a large excess of nucleophile present) eqn. (5) simplifies to (6). Eqn. (6) is consistent with our kinetic

$$-d[MH(X_2)Ln_m]/dt = k_1[MH(X_2)Ln_m] \quad (6)$$

data since it dictates that the rate of reaction is independent of the concentration of nucleophile and that k_1 is independent of the nature of the nucleophile.

However, in the dissociative interchange mechanism, eqn. (7),

$$[MH(X_2)Ln_m]^+ + L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} [MH(X_2)Ln_m]^+\cdot L \xrightarrow{k_4}$$
$$[MH(L)Ln_m]^+\cdot X_2 \xrightarrow{\text{fast}} [MH(L)Ln_m]^+ + X_2 \quad (7)$$

† As reported in ref. 10, for example, *trans*-$[OsH(N_2)(depe)_2]^+$ loses N_2 rapidly, even in the solid state.

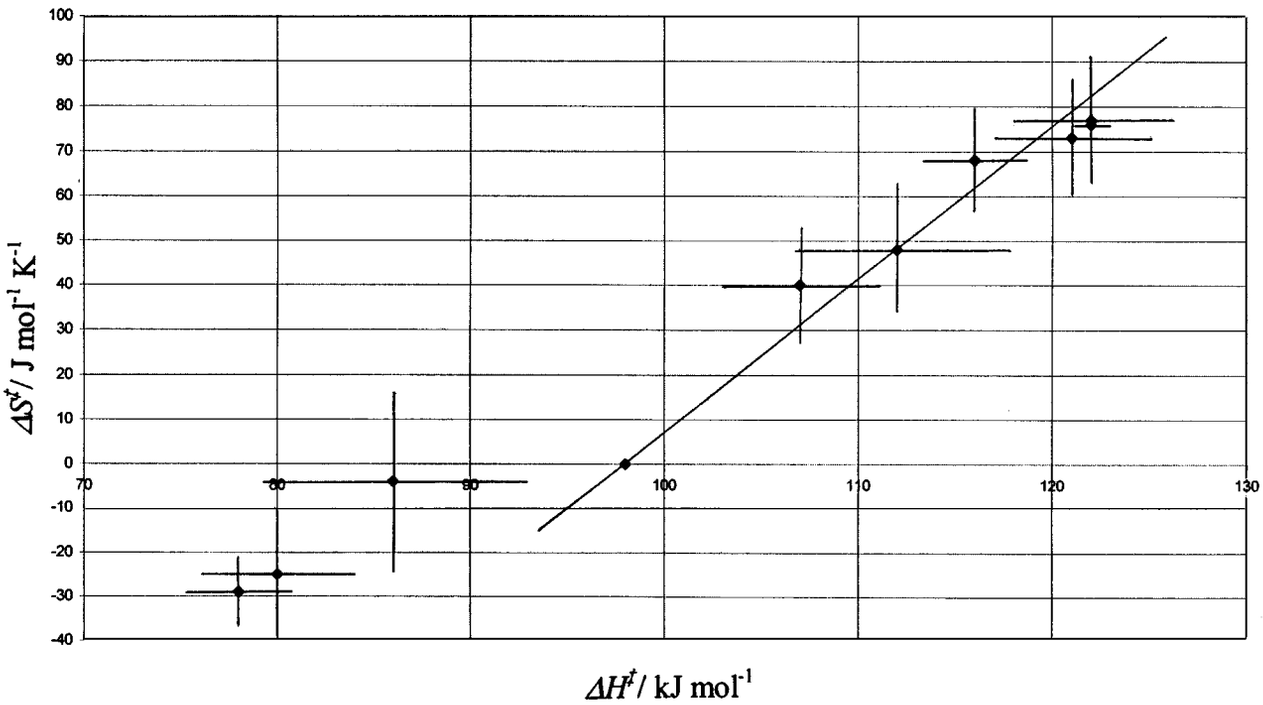


Fig. 1 The correlation of $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ for reactions of *trans*-$[FeH(X_2)(pp)_2]^+$ with nucleophiles.

outer-sphere association of the nucleophile with the complex occurs prior to dissociation of the leaving group. Upon dissociation of X_2 the nucleophile present in the first solvation sphere is advantageously positioned to bind to the vacant site. Assuming that association of L is a rapidly established equilibrium (K_3) and that k_4 represents the rate-limiting dissociation of M–X_2, the dissociative interchange mechanism gives the rate law (8). If $K_3[L] \gg 1$, eqn. (8) simplifies to (9), which is also

$$\frac{-d[MH(X_2)Ln_m]}{dt} = \frac{k_4K_3[MH(X_2)Ln_m][L]}{1 + K_3[L]} \quad (8)$$

$$-d[MH(X_2)Ln_m]/dt = k_4[MH(X_2)Ln_m] \quad (9)$$

consistent with the observed kinetics. Although the form of this rate law is identical to that observed experimentally, we consider this mechanism to be less likely than the dissociative mechanism for the following reasons. First, k_4 should be dependent to some degree on the nature of the nucleophile because of the presence of the nucleophile within the solvation sphere during this elementary reaction step, but we see no appreciable variation of the value of k_{obs} with a variety of nucleophiles. Secondly, in order for the limiting rate law to operate in the form of eqn. (9), $K_3[L] \gg 1$ even at the lowest concentration of nucleophile employed (1.0 mmol dm^{-3}). This allows us to calculate a limit of $K_3 \gg 1000$ dm^3 mol^{-1}. This is very tight binding for a neutral molecule such as MeCN to a monocation such as *trans*-$[FeH(X_2)(pp)_2]^+$, and seems unlikely.

Consistent with our proposed dissociative mechanism is the independence of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of the nature of L. Particularly significant are the large and positive values of $\Delta S^{\ddagger}$ that are entirely consistent with the dissociative mechanism. We discuss further aspects of the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ parameters in the next section.

Comparison with the reaction mechanism proposed for $[FeH(H_2)(dppe)_2]^+$

Recently the kinetics of the reactions of *trans*-$[FeH(H_2)(dppe)_2][BPh_4]$ with MeCN, PhCN, and Me_2SO has been studied in acetone and thf.[7] The results obtained differ from ours in two key respects. First, the rate of the reaction depends on the concentration and nature of the nucleophile. Secondly, $\Delta H^{\ddagger} = ca.$ 80 kJ mol^{-1} and $\Delta S^{\ddagger} = ca.$ −20 J K^{-1} mol^{-1}. This has been interpreted as indicating the mechanism shown in eqns. (10)–(12), in which one arm of a dppe ligand dissociates

$$[FeH(H_2)(dppe)_2]^+ \rightleftharpoons [FeH(H_2)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]^+ \quad (10)$$

$$[FeH(H_2)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]^+ + L \rightleftharpoons [FeH(H_2)(L)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]^+ \quad (11)$$

$$[FeH(H_2)(L)(dppe\text{-}\kappa^2P)(dppe\text{-}\kappa P)]^+ \longrightarrow [FeH(L)(dppe)_2]^+ + H_2 \quad (12)$$

and then solvent binds weakly to the vacant site. The rate-limiting step is proposed to be associative attack of the nucleophile on this intermediate. The activation volumes, $\Delta V^{\ddagger}$, for the reaction were found to be *ca.* −20 cm^3 mol^{-1}, consistent with an associative mechanism. Analogous lability of diphosphine ligands on iron(II) sites has been noted before[8,24] and suggested as the pathway for substitution reactions of other iron complexes. Clearly our rate data on the dmpe and depe analogues are not consistent with this mechanism. This conclusion is supported by the temperature-dependence data for these reactions.

Fig. 1 shows the correlation between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the substitution reactions of the complexes *trans*-$[FeH(X_2)(pp)_2]^+$, where pp = dmpe, depe, and dppe. The data points corresponding to the dmpe and depe complexes studied in this work cluster in the top right hand corner. The line presented is that defined by a least squares analysis of our data in Table 6 alone, together with the additional restriction that the intercept at $\Delta S^{\ddagger} = 0$ is $\Delta H^{\ddagger} = 98$ kJ mol^{-1} (the mean value of $\Delta G^{\ddagger}$ observed for all the depe and dmpe complexes, Table 6). Clearly our data on the dmpe and depe analogues are not consistent with the mechanism proposed for the dppe complexes. This conclusion is supported by the temperature-dependence studies.

The enthalpies of activation and entropies of activation for the reactions of the iron complexes apparently compensate to give an almost invariant $\Delta G^{\ddagger}$. When a reaction has a large value of $\Delta H^{\ddagger}$ then it is generally assumed that the M–X_2 bond dissociation energy is large. The tighter binding of X_2 may

mean that its mobility in the ground and excited states is restricted and therefore the associated value of $\Delta S^{\ddagger}$ is small. A weak M–X_2 bond should give rise to a larger value of $\Delta S^{\ddagger}$. Since $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ then balance to give similar $\Delta G^{\ddagger}$ values at the same temperature. There are no published data comparable to those for our iron complexes, nor for the corresponding ruthenium or osmium compounds, $[MH(X_2)(pp)_2]^+$, so we cannot assess whether changing metal would affect this generalisation. Observations of such compensatory effects are common in many areas of chemistry, both for kinetic and equilibrium data.[25]

The points in the bottom left hand corner of Fig. 1 correspond to the published data for *trans*-$[FeH(H_2)(dppe)_2]^+$. Clearly these points do not lie on the line defined by the dmpe and depe complexes. This is a further indication that a different mechanism operates for these analogues. The distinctly different behaviour between the dmpe or depe and the dppe analogues immediately poses the question of which factors control the mechanisms of substitution reactions in this family of compounds. In reactions operating by a dissociative mechanism the primary controlling factor must be the metal–ligand bond strengths. We infer that the Fe–P, Fe–H_2 and Fe–N_2 bond strengths are very similar in the family of complexes $[FeH(X_2)(pp)_2]^+$ and that, depending on the diphosphine, either Fe–P (pp = dppe) or Fe–X_2 cleavage (pp = depe or dmpe) can occur. The dppe is sterically quite demanding because of the bulky phenyl groups and this would favour dissociation of one arm of this ligand. In contrast, dmpe and depe are sterically less demanding and better electron donors due to their alkyl groups. This would make their dissociation less likely. In addition the increased electron density on Fe in the dmpe and depe complexes would make the site more electron-rich, facilitating Fe-to-X_2 back bonding.

Clearly, changing the electronic and steric properties of the phosphine co-ligands by varying the substituents on the phosphorus atoms will perturb the labilities of both the H_2 and phosphine ligands, with the result that in the family of complexes *trans*-$[FeH(X_2)(pp)_2]^+$ a change in mechanism of substitution may occur as the diphosphine ligand is changed.

Factors affecting the rate constants

In this and the remaining sections of the discussion we shall restrict consideration to the dmpe and depe complexes that undergo substitution by the dissociative mechanism depicted in eqn. (4). The largest change in rate constants (Table 7) occurs when the metal is changed. For example *trans*-$[RuH(H_2)(depe)_2]^+$ reacts 700 times faster than *trans*-$[FeH(H_2)(depe)_2]^+$ at 298.2 K. As *trans*-$[OsH(H_2)(depe)_2]^+$ is unreactive at 298.2 K the reactions with nitriles were carried out at 323.2 K. These results show a very large decrease in rate constant when iron or ruthenium is replaced by osmium in structurally analogous complexes. The reactions involving *trans*-$[OsH(H_2)(depe)_2]^+$ were studied only in thf, because 323.2 K is too close to the boiling point of acetone for measurements to be made in that solvent. Our conclusion that the rate constants for the loss of H_2 decrease in the sequence 4d ≫ 3d ≫ 5d is consistent with other studies of Group 8 complexes by Halpern *et al.*[26] (quantitative), by Amendola *et al.*[27] and by Morris and coworkers[9a,13,20] (qualitative). For example, Jessop and Morris[20] concluded that 5d dihydrogen complexes are always more stable to dihydrogen loss than the analogous 3d or 4d complexes. However, the relative lability of H_2 in 3d and 4d metal complexes (3d < 4d or 3d < 4d) depends on the ancillary ligands.[20]

We have now shown that compounds *trans*-$[MH(X_2)(depe)_2]^+$ are more labile to dissociation of X_2 when X = N than when X = H, but only by a factor of *ca.* 3.5 (see rate constants in Table 2). This trend in the lability is independent of temperature.

The rate constants are also dependent upon the alkyl group of the diphosphine, increasing *ca.* 5-fold from dmpe to depe in *trans*-$[FeH(N_2)(pp)_2]^+$ (pp = dmpe or depe) in all solvents and for all nucleophiles. It has been reported[9a] that there is not much difference in the "stabilities" of *trans*-$[MH(H_2)(pp)_2]^+$ (M = Fe, Ru or Os; pp = depe or dppe) though whether they are kinetic or thermodynamic stabilities was not clarified. We rationalise the difference between the dmpe and depe complexes in the following terms. Kubas *et al.*[28] have stated that steric interactions are of much less consequence than electronic effects in stabilising H_2 (and presumably also N_2) bound to a metal. The ethyl group in depe makes it a better σ donor than the methyl group in dmpe. Consequently, less σ donation to the metal from dinitrogen may occur, although there may be more π acceptance into dinitrogen. This could weaken Fe-to-N_2 bonds more in the depe complex than in the dmpe complex. Arguments based upon steric interactions between the phosphine substituents and the dinitrogen in the ground state and in the transition state would lead to the opposite conclusion. We conclude that electronic effects appear to be more important than steric for our complexes.

Although there are no literature data available for a direct comparison with ours, it is instructive to extend our discussion to closely related compounds for which some information is available. For example, it has been shown qualitatively that *trans* ligands which compete effectively with dihydrogen for π-electron density weaken the back donation (M→H_2).[20] The *trans* effect influences both the kinetic and thermodynamic stability of dihydrogen complexes, and is shown clearly by Group 8 *trans*-$[MY(X_2)(pp)_2]^+$ complexes (Y = H or Cl; X = H or N; pp = diphosphine), where the complexes *trans*-$[MCl(H_2)(pp)_2]^+$ are generally more reactive than the analogous hydrido(dihydrogen) complexes. The strength of the metal-to-H_2 bond follows a different trend (3d < 4d < 5d) in Group 8 for a chloride *trans* to dihydrogen than for a hydride *trans* to dihydrogen (4d < 3d< 5d).[15,20,29,30] Ruthenium complexes containing a chloride *trans* to dihydrogen are relatively more stable than for the *trans* hydride series in *trans*-$[RuY(H_2)(pp)_2]^+$ (Y = H or Cl; pp = depe or dppe). For example *trans*-$[RuCl(H_2)(depe)_2]^+$ is stable to H_2 loss (although it can lose HCl through reductive elimination) but dihydrogen in *trans*-$[RuH(H_2)(depe)_2]^+$ is labile.[31] However, when pp = $Cy_2PCH_2CH_2PCy_2$ (Cy = cyclohexyl) the converse is true.[30] Therefore, the effect of the *trans* ligand on the lability of the dihydrogen also depends on the ancillary ligands.

Dinitrogen in *trans*-$[FeCl(N_2)(depe)_2]^+$ is very labile,[32] dissociating from the complex both in solution and in the solid state, whereas we have shown that the corresponding *trans*-hydride complexes are more stable to dinitrogen loss under the same conditions. We conclude that the rate constant for the loss of X_2 depends subtly on the metal and on all the ancillary ligands.

Our results (Table 6) show that changing the solvent from acetone to thf reduces the rate constants by a very small amount, *ca.* 15–35%. Similar small changes were observed in the reactions of *trans*-$[FeH(H_2)(dppe)_2]^+$. In these substitution reactions a similar degree of solvation is to be expected for the transition state and reactants since the solvents are of similar polarity. The observation that the rate constants for the substitution of X_2 in our complexes increase slightly from thf to acetone may be more to do with the donor power of the individual solvents than with any changes in polarity of species during the reaction.

Factors affecting the activation parameters

The values of E_{act}, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$ for *trans*-$[FeH(H_2)(pp)_2]^+$ are all larger than for *trans*-$[FeH(N_2)(pp)_2]^+$, although the values of $\Delta G^{\ddagger}$ are very similar. This implies that dihydrogen is more strongly bound to iron than dinitrogen in the same ancillary ligand environments. Dihydrogen complexes are there-

fore more thermodynamically stable than dinitrogen complexes, as well as being more kinetically stable.

Comparable values also increase from depe to dmpe, although again $\Delta G^{\ddagger}$ values are almost invariant. The increase of these activation parameters is associated with the *ca*. 5-fold decrease in rate constant when depe is replaced by dmpe. Changing the solvent has little effect on the activation parameters.

The mechanism of substitution reactions of $[MH(X_2)(tetraphos)]^+$

The tetraphosphines pp_3 and pp_3Me force a *cis* configuration on the associated X_2 and hydride ligands. The kinetics and thermodynamics for the loss of X_2 from *cis*-$[MH(X_2)\{P(CH_2CH_2PR_2)_3\}]^+$ were not studied because of the lack of reactivity or else the instability of these complexes in solution under argon. Several of the homologues of this kind have yet to be synthesized. Consequently we can make only qualitative comparisons between the complexes with two diphosphines and those with one tetraphosphine.

The differences in reactivity between *cis* and *trans* (hydride and X_2) complexes are pronounced for iron. The complex *cis*-$[FeH(H_2)(pp_3)]^+$ is kinetically stable to nucleophiles in solution[11a,b] under argon at room temperature, whereas *trans*-$[FeH(H_2)(pp)_2]^+$ react within a couple of hours under the same conditions.[3,9a] The faster rates of dissociation of N_2 from *cis*-$[FeH(N_2)(pp_3)]^+$ compared to that from *trans*-$[FeH(N_2)(pp)_2]^+$ are highlighted by the fact that the *cis* complex is unstable in potentially ligating solvents, even under dinitrogen. This made measurement of NMR spectra difficult, although no solvolysis products were detected spectroscopically.

The complex *cis*-$[FeH(H_2)(pp_3Me)]^+$[33] is more labile than *cis*-$[FeH(H_2)(pp_3)]^+$.[11a,b] It will react with nucleophiles to completion after several hours at room temperature, or after 30 min at 333 K, whereas *cis*-$[FeH(H_2)(pp_3)]^+$ takes several days to react at room temperature. The rates of reaction of ruthenium or osmium tetraphosphine complexes are not as well documented as of iron. Nevertheless, the trend in reactivity Ru ≫ Fe ≫ Os was found in *cis*-$[MH(X_2)(pp_3)]^+$, just as in *trans*-$[MH(X_2)(pp)_2]^+$. Bianchini *et al.*[34] stated that *cis*-$[MH(H_2)(pp_3)]^+$ is more stable than *trans*-$[MH(H_2)(pp)_2]^+$ because of the "attractive *cis*-effect" in the former. This effect is supposed to arise by incipient formation of an H_3 ligand due to the enforced *cis* arrangement of H and H_2, and it is reported to be significant for $X_2 = H_2$. There is no comparable effect for $X_2 = N_2$ or CO.[35] A *cis* interaction is obviously impossible in a *trans* arrangement of H and H_2.[11b,36] There is qualitative evidence that *cis*-$[RuH(H_2)(pp_3)]^+$[37] reacts with nucleophiles much faster than *cis*-$[FeH(H_2)(pp_3)]^+$,[11a,b] and that *cis*-$[OsH(H_2)(pp_3)]^+$ reacts much slower than the iron complex.[34] The hydride complex *cis*-$[RuH(H_2)(pp_3)]^+$ is unstable in solution unless under dihydrogen and it is therefore less kinetically stable than *trans*-$[RuH(H_2)(pp)_2]^+$.[9a,37] The complex *cis*-$[OsH(H_2)(pp_3)]^+$[35] reacts with nitriles only at high temperatures, which is similar to our observations for *trans*-$[OsH(H_2)(depe)_2]^+$. The compound *cis*-$[OsH(N_2)(pp_3)]^+$[34] reacts rapidly with nitriles, which is also consistent with our data because we had difficulty even isolating *trans*-$[OsH(N_2)(depe)_2]^+$ due to the lability of dinitrogen.[10] The complex *cis*-$[MH(X_2)(pp_3Me)]^+$ (M = Ru or Os) have not been described in the literature.

The strengths of the bonds between metals and the dihydrogen ligand,[20] as indicated by the magnitude of the thermodynamic parameter ($H°$ and by IR spectroscopy, increase in the order 4d < 3d < 5d. This order is common for many isostructural complexes of metals of Groups 6 and 8,[20] for example for *trans*-$[MH(H_2)(pp)_2]^+$.[9a] A less common order, 3d < 4d < 5d, has been noted[20] for *trans*-$[MCl(H_2)(depe)_2]$ and the order 3d, 4d < 5d has been reported for $[MH(H_2)\{PPh(OEt)_2\}_4]^+$ and for the restricted series $[MH_4(PPh_3)_4]$ (M = Ru or Os).[20] The steric crowding at the metal in the Group 8 complexes *cis*-$[MH(H_2)(pp_3)][BPh_4]$ decreases with increasing metal radius,[38] but the catalytic activity has been shown to relate to the strengths of the metal–dihydrogen bond, which changes in the order Os ≥ Fe ≫ Ru. Our data are clearly not inconsistent with these trends.

Possible implications for nitrogenase mechanism

The production of H_2 and the fixation of N_2 are two reactions which are intimately associated with one another in the action of the nitrogenases. In the absence of any other reducible substrate nitrogenases will reduce H^+ to H_2. Progressively introducing more N_2 results in a decrease in the amount of H_2 formed and a concomitant increase in the amount of NH_3 produced. However, even at high pressures of N_2 the production of H_2 cannot be suppressed entirely. Thus the limiting stoichiometry for the action of the molybdenum-containing nitrogenases is that shown in eqn. (13) (P_i represents inorganic

$$N_2 + 8H^+ + 16\,ATP + 8\,e \longrightarrow 2\,NH_3 + H_2 + 16\,ADP + 16\,P_i \quad (13)$$

phosphate), in which approximately one mole of H_2 is produced for every mole of N_2 reduced. With the vanadium-based nitrogenases the limiting stoichiometry involves proportionately even more H_2, *ca.* 3 H_2 per N_2 fixed.[2]

A variety of mononuclear chemical systems, and the work presented in this paper, clearly show that displacement of H_2 at a metal site by N_2 can occur. However, most studies (including our own) show that the mechanism is dissociative and hence that the H_2 dissociation is not facilitated by the attacking nucleophile, dinitrogen. It has been proposed that these complexes represent models for the N_2 binding in the enzyme.[39] However, when the reactions of nitrogenases with D_2 are studied it becomes clear that the enzyme is performing much more elaborate chemistry, which these simple complexes are not mimicking in any sense.

The formation of HD by conventional molybdenum–iron nitrogenases when they reduce N_2 in the presence of D_2 is one of the most intriguing phenomena associated with biological nitrogen fixation.[2] The stoichiometry is represented by eqn. (14). The most striking features of the HD formation are as

$$D_2 + 2\,H^+ + 2\,e \longrightarrow 2HD \quad (14)$$

follows. It is associated with no reducible substrate other than N_2, there is no indication that any of the deuterium ever passes into solution, and no D_2 is formed when fixing N_2 in the presence of HD. The clear implications are that the H and D which are eventually combined in HD come from different sources that do not mix their hydrogen atoms and, most important, that the reaction is facilitated only when N_2 is bound. This implies that the displacement of H_2 by N_2 at a single active site must be an associative process.

The most complete explanation put forward to explain this phenomenon in nitrogenase is that N_2 binds to a trihydride species, MH_3, with displacement of H_2. Subsequent loss of N_2 (by reaction with protons towards ammonia or by simple dissociation) followed by binding of D_2 would generate MHD_2, and this last species is a plausible source of HD.[40] This scheme is made more attractive by the Lowe–Thorneley[41] model of nitrogenase mechanism, that has been interpreted to mean that a trihydride species is indeed generated before dinitrogen is bound, and that some dihydrogen is released when that process occurs. Further, there are model chemical compounds, such as $[CoH_3(PPh_3)_3]$,[42] that apparently exhibit similar N_2/H_2 displacement reactivity.

However, this model does not explain why, in the comparable experiment performed under HD, no D_2 is ever formed. Nor does it explain why substrates other than dinitrogen do not also stimulate HD formation. After all, those substrates may also

be imagined to bind at the nitrogenase active site. Finally, if dihydrogen is also able to interact with the active site, why is any substrate at all necessary to promote HD formation?

Chemical models and the work presented above clearly show that displacement of dihydrogen is not a necessity for binding dinitrogen. The formation of a considerable proportion of the dihydrogen generated by nitrogenases during turnover does not require the presence of an incoming group to provoke it. Consequently, why is HD formation observed only when dinitrogen is being reduced?

Chemical systems have been developed in which binding of N_2 can occur before the release of H_2. These involve dissociation of a carboxylate group from the co-ordination sphere of molybdenum hydrido species.[43] This also has the additional merit of being consistent with the sequence of events presented by the Lowe–Thorneley model.[41] However, the specific reactivity of the enzyme as described above has yet to be successfully mimicked in a chemical system.

The simplest rationalisation is that HD formation and dinitrogen binding (and perhaps, by extension, ordinary dihydrogen evolution) occur at different places. The active site of these nitrogenases is the iron–molybdenum cofactor, an Fe–S-based cluster with the stoichiometry $MoFe_7S_9$.[2] It is not unreasonable to assume that different substrates bind and are transformed at different parts of this large cluster. More data are required. For example, dinitrogen is a ligand that, like CO, should stabilise low oxidation states of metals in complexes. Carbon monoxide inhibits nitrogen fixation in nitrogenases, but not dihydrogen evolution. It should also be able to facilitate HD formation, though we know of no attempts to check this. However, evidence is now accumulating that the nitrogenase cluster promotes multi-site processes, and chemical models for nitrogenase function must begin to take account of this.

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