The Mechanism of Formation of Hydrazido(2—)- and Hydrido-complexes by the Reaction of Dinitrogen Complexes with Acids in Tetrahydrofuran

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The kinetics of the reactions of *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ or *trans*-$[M(N_2)_2(Et_2PCH_2CH_2PEt_2)_2]$ (M = Mo or W) with acids, HX (X = Cl, Br, or HSO_4), in tetrahydrofuran, to yield the corresponding hydrazido(2−)-complexes, *trans*-$[M(NNH_2)X(diphos)_2]^+$ (diphos = bidentate diphosphine), have been investigated. The mechanism proposed involves the initial rapid formation of an adduct between HX and the substrate, and protonation of a co-ordinated dinitrogen by another molecule of acid, prior to the rate-limiting dissociation of dinitrogen. The reaction between HCl and *trans*-$[M(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]$ yields the hydrido-complexes $[WH(N_2)_2(Ph_2PCH_2CH_2PPh_2)_2]^+$ and $[MoH_2Cl_2(Ph_2PCH_2CH_2PPh_2)_2]$. The kinetics of formation of these hydrides have also been studied and a rationalisation for their formation, rather than the hydrazido(2−)-complexes, is presented.

DESPITE the great variety of transition-metal dinitrogen complexes, only a few yield ammonia on treatment with acid, indeed often the most favoured site of protonation for mononuclear dinitrogen complexes is the metal.[1] The complexes $[M(N_2)_2(P)_4]$ [2] (M = Mo or W, P = monotertiary phosphine) and $[Mo(N_2)_2(PPh_3)(bdpp)]$ [3] [bdpp = $PPh(CH_2CH_2PPh_2)_2$] are unique in being the only mononuclear complexes which give ammonia in high yield. The presence of at least one unidentate phosphine ligand in these complexes is necessary before ammonia is obtained under ambient conditions.[4] The presence of two bidentate phosphine ligands results in the dinitrogen ligand being reduced only as far as the hydrazido(2—)-ligand, equation (1) (diphos = bidentate diphosphine, thf = tetrahydrofuran).

$$trans\text{-}[M(N_2)_2(diphos)_2] + 2HX \xrightarrow{thf} trans\text{-}[M(NNH_2)X(diphos)_2]X + N_2 \quad (1)$$

Although it was originally believed, on the basis of i.r. studies, that some of these complexes contained the diazene ligand (NH-NH), more recent information indicates that all of them are hydrazido(2—)-complexes.[2] The hydrazido(2—)-stage represents an intermediate on the pathway leading to ammonia and similar hydrazido(2—)-complexes can be produced from the $[M(N_2)_2(P)_4]$ series.[5]

Under certain, very specific, conditions the reactions of *trans*-$[M(N_2)_2(dppe)_2]$ [dppe = 1,2-bis(diphenylphosphino)ethane] with acid lead to metal hydrides,[6] which are not intermediates on the pathway leading to hydrazido(2—)-complexes. In order to understand more fully the factors which influence the position of protonation, a kinetic study of the formation of hydrazido(2—)- and hydrido-complexes derived from *trans*-$[M(N_2)_2(dppe)_2]$ and *trans*-$[M(N_2)_2(depe)_2]$ in thf is reported herein [depe = 1,2-bis(diethylphosphino)ethane].

The kinetics of formation of both the hydrido- and hydrazido(2—)-complexes are categorised, in the Results section, with respect to the acid used with the various dinitrogen complexes, rather than with respect to the product. This presentation is adopted in order to emphasise that it is predominantly the nature of the acid which influences which product is obtained, rather than a change of mechanism.

RESULTS

Kinetics of the Reactions with H_2SO_4 *and* HBr.—The kinetics of the reactions between *trans*-$[M(N_2)_2(depe)_2]$ and HX (X = Br or HSO_4) were monitored using stopped-flow spectrophotometry. These and all other reactions were monitored at 25 °C. The absorbance–time curves were exponential for at least three half-lives (provided [HX] > 20[complex]). The initial absorbance was identical to that of *trans*-$[M(N_2)_2(depe)_2]$ at all the wavelengths studied [λ(nm) = 380 (Mo and W), 490 (Mo and W), 450 (Mo), and 400 (W)]. The spectral characteristics of the analogous reactions of *trans*-$[M(N_2)_2(dppe)_2]$ were similar at all wavelengths in the range λ = 350—550 nm. The kinetics of all these reactions showed a first-order dependence on the concentration of complex ([complex] = 0.20—10.0 mmol dm^{-3}), but the dependence on the concentration of acid was a function both of the nature of the acid and of the complex. The small quantity of water which was introduced with the HBr and H_2SO_4 was shown to have a negligible effect on the kinetics, both by the deliberate introduction of small aliquots of water to the reaction mixture and by generating anhydrous HBr in thf by the reaction of $SiBrMe_3$ with an equimolar amount of MeOH.

Kinetics of the Reactions with HCl.—The kinetics of the reaction between *trans*-$[Mo(N_2)_2(dppe)_2]$ and HCl to yield $[MoH_2Cl_2(dppe)_2]$ were determined using visible absorption spectroscopy. The reaction of *trans*-$[W(N_2)_2(dppe)_2]$ with HCl yields a mixture of a metal hydride $[WH(N_2)_2(dppe)_2]^+$ and the hydrazido(2—)-complex *trans*-$[W(NNH_2)Cl(dppe)_2]^+$ at low concentration of acid ([HCl] < 500 mmol dm^{-3}). The kinetics of formation of both of these products were determined using a combination of visible absorption spectroscopy ([HCl] = 100—500 mmol dm^{-3}) and solution i.r. spectroscopy ([HCl] = 40—150 mmol dm^{-3}). The latter technique allowed the determination of the kinetics of formation of $[WH(N_2)_2(dppe)_2]^+$ by monitoring the characteristic dinitrogen stretch of the metal hydride at 2 005 cm^{-1}, and the ultimate concentration of the hydride in the mixture.

In these studies, anhydrous HCl was generated in thf by the reaction of $SiClMe_3$ with an equimolar amount of MeOH. The kinetics of the reaction between *trans*-$[W(N_2)_2(dppe)_2]$ and ^2HCl were also measured, generating the acid from reaction of $SiClMe_3$ with MeO^2H.

All reactions with HCl showed a first-order dependence on the concentration of complex ([complex] = 0.20—10.0 mmol dm^{-3}). The rate of formation of the metal hydrides was independent of the concentration of HCl, but the rate of formation of *trans*-$[W(NNH_2)Cl(dppe)_2]^+$ showed a first-order dependence on the concentration of HCl ([HCl] = 40—500 mmol dm^{-3}).

The data for the reactions of acids with the molybdenum and tungsten complexes are collected in Tables 1 and 2

TABLE 1

Kinetic data for the reactions of *trans*-$[Mo(N_2)_2(dppe)_2]$ and *trans*-$[Mo(N_2)_2(depe)_2]$ with HX (X = Cl, Br, or HSO_4) in thf at 20 °C [a]

Complex	Acid	[HX]/ mmol dm^{-3}	$k_{obs.}/s^{-1}$
$[Mo(N_2)_2(dppe)_2]$ [b]	HCl	5.0	2.3×10^{-2}
		10.0	1.9×10^{-2}
		10.0 [c]	2.5×10^{-2}
		20.0	2.0×10^{-2}
		30.0	2.1×10^{-2}
		40.0	1.9×10^{-2}
$[Mo(N_2)_2(dppe)_2]$	HBr	25.0	0.91
		50.0	4.16
		50.0 [d]	4.30
		100.0	18.1
		100.0 [d]	17.6
		150.0	37.4
		200.0	68.8
		200.0 [d]	67.2
$[Mo(N_2)_2(depe)_2]$	HBr	4.0	51
		6.0	138
		8.0	220
		10.0	320
$[Mo(N_2)_2(dppe)_2]$	H_2SO_4	10.0	5.5×10^{-5}
		25.0	3.2×10^{-5}
		50.0	2.1×10^{-3}
		50.0 [d]	2.2×10^{-3}
		100.0	1.2×10^{-2}
		100.0 [d]	1.3×10^{-2}
		200.0	7.6×10^{-2}
		200.0 [d]	7.7×10^{-2}
		400.0	5.3×10^{-1}
$[Mo(N_2)_2(depe)_2]$	H_2SO_4	10.0	0.8
		15.0	1.9
		20.0	3.8
		20.0 [d]	3.6
		30.0	9.2
		40.0	21.5
		40.0 [d]	24.1
		50.0	36.0
		60.0	61.2
		60.0 [d]	57.0
		70.0	91.7
		80.0	137

[a] [Mo] = 0.2 mmol dm^{-3}, unless otherwise stated. [b] Formation of $[MoH_2Cl_2(dppe)_2]$, [Mo] = 1.0 mmol dm^{-3}. [c] [Mo] = 10 mmol dm^{-3}, reaction monitored using solution i.r. spectroscopy. [d] [Mo] = 1.0 mmol dm^{-3}.

TABLE 2

Kinetic data for the reactions of *trans*-$[W(N_2)_2(dppe)_2]$ and *trans*-$[W(N_2)_2(depe)_2]$ with HX (X = Cl, Br, or HSO_4) in thf at 25 °C [a]

Complex	Acid	[HX]/ mmol dm^{-3}	$k_{obs.}/s^{-1}$
$[W(N_2)_2(dppe)_2]$	HCl	40.0 [b]	3.3×10^{-3}
		60.0 [b]	4.3×10^{-3}
		80.0 [b]	5.1×10^{-3}
		100.0 [b]	6.2×10^{-3}
		100.0 [c]	6.1×10^{-3}
		200.0	9.0×10^{-3}
		200.0 [c]	9.2×10^{-3}
		300.0	1.2×10^{-2}
		400.0	1.5×10^{-2}
		400.0 [c]	1.6×10^{-2}
		500.0	1.8×10^{-2}
	HCl [d]	40.0 [b]	2.3×10^{-3}
		60.0 [b]	2.6×10^{-3}
		80.0 [b]	2.6×10^{-3}
		100.0 [b]	2.8×10^{-3}
		140.0 [b]	3.2×10^{-3}
	^{2}HCl	100.0	5.9×10^{-3}
		200.0	9.0×10^{-3}
		300.0	1.0×10^{-2}
		400.0	1.6×10^{-2}
$[W(N_2)_2(dppe)_2]$	HBr	5.0	2.5
		5.0 [c]	2.2
		10.0	14.2
		10.0 [c]	14.0
		15.0	40.8
		20.0	90.5
		20.0 [c]	92.1
		25.0	154
$[W(N_2)_2(dppe)_2]$	H_2SO_4	10.0	2.9×10^{-3}
		20.0	1.4×10^{-2}
		50.0	0.13
		100.0	0.76
		150.0	2.3
		200.0	5.1
$[W(N_2)_2(depe)_2]$	H_2SO_4	5.0	7.5
		5.0 [c]	9.2
		7.5	19.1
		10.0	33.2
		10.0 [c]	36.1
		12.5	55.3
		15.0	81.4
		17.5	125
		20.0	175
		20.0 [c]	184

[a] [W] = 0.2 mmol dm^{-3}, unless otherwise stated. [b] [W] = 10 mmol dm^{-3}, measured using solution i.r. spectroscopy. [c] [W] = 1.0 mmol dm^{-3}. [d] Formation of $[WH(N_2)_2(dppe)_2]^+$, measured using solution i.r. spectroscopy.

TABLE 3

Summary of the rate laws observed in the reactions of *trans*-$[M(N_2)_2(diphos)_2]$ with HX in thf at 25 °C

Acid	Complex	Rate law ($k_{obs.}$)	Ratio $(k_w/k_{Mo})_n$
HCl	$[W(N_2)_2(dppe)_2]$	$(3.2 \pm 0.2) \times 10^{-2}$ [HCl]	
		$(2.7 \pm 0.4) \times 10^{-3}$ [a]	
	$[Mo(N_2)_2(dppe)_2]$	$(2.1 \pm 0.4) \times 10^{-2}$ [b]	
HBr	$[Mo(N_2)_2(depe)_2]$	$(3.2 \pm 0.4) \times 10^{6}$ $[HBr]^2$	
	$[W(N_2)_2(depe)_2]$ [c]	$> (3 \times 10^{7})$ $[HBr]^2$	>10 ($n = 2$)
	$[Mo(N_2)_2(dppe)_2]$	$(1.7 \pm 0.3) \times 10^{3}$ $[HBr]^2$	34 ($n = 2$)
	$[W(N_2)_2(dppe)_2]$	$(5.7 \pm 0.2) \times 10^{4}$ $[HBr]^2$ + $(8.3 \pm 0.2) \times 10^{6}$ $[HBr]^3$	
H_2SO_4	$[Mo(N_2)_2(depe)_2]$	$(5.2 \pm 0.2) \times 10^{3}$ $[H_2SO_4]^2$ + $(2.0 \pm 0.1) \times 10^{5}$ $[H_2SO_4]^3$	29 ($n = 2$)
	$[W(N_2)_2(depe)_2]$	$(1.5 \pm 0.2) \times 10^{5}$ $[H_2SO_4]^2$ + $(1.7 \pm 0.2) \times 10^{7}$ $[H_2SO_4]^3$	85 ($n = 3$)
	$[Mo(N_2)_2(dppe)_2]$	$(4.8 \pm 0.3) \times 10^{-1}$ $[H_2SO_4]^2$ + (7.1 ± 0.2) $[H_2SO_4]^3$	50 ($n = 2$)
	$[W(N_2)_2(dppe)_2]$	$(2.4 \pm 0.1) \times 10^{1}$ $[H_2SO_4]^2$ + $(5.2 \pm 0.2) \times 10^{2}$ $[H_2SO_4]^3$	73 ($n = 3$)

[a] Formation of $[WH(N_2)_2(dppe)_2]^+$. [b] Formation of $[MoH_2Cl_2(dppe)_2]$. [c] Reaction too fast (even at [HBr] = 4 mmol dm^{-3}). Limit established assuming second-order dependence on [HBr].

respectively and a summary of the derived rate laws is shown in Table 3.

Influence of $[NBu_4]X$ *on the Kinetics of Formation of Hydrazido*(2−)*-complexes*.—The presence of tetra-n-butylammonium salts, $[NBu_4]X$ ($X = Br$ or HSO_4), did not affect the spectra observed in the reactions of HBr or H_2SO_4 with *trans*-$[M(N_2)_2(depe)_2]$ but did perturb the kinetics. The results are shown graphically for the reaction of HBr and H_2SO_4, in the presence of the respective salt, with *trans*-$[Mo(N_2)_2(depe)_2]$ in Figures 1 and 2 respectively; and for the reaction of H_2SO_4 with *trans*-$[W(N_2)_2(depe)_2]$ in Figure 3. Although the reaction rate is decreased by the addition of the salt, the extent of this inhibition is dependent on the concentration of acid. As is clearly shown in the inserts to Figures 1, 2, and 3, the order of the reaction with respect to acid changes with increasing $[NBu_4X]$. Studies with $[NBu_4][BF_4]$ showed that this salt had no effect on the rate of the reaction with HBr or H_2SO_4, demonstrating that the behaviour observed in the presence of $[NBu_4]X$ was not a salt effect.[7]

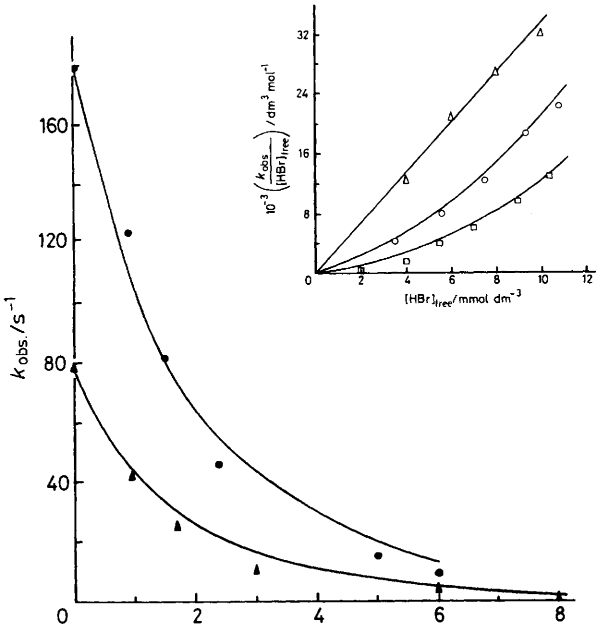


FIGURE 1 Inhibition of the reaction between HBr $\{[HBr]_{total} = 5$ (▲) and 7.5 mmol dm^{-3} (●)} and *trans*-$[Mo(N_2)_2(depe)_2]$ by $[NBu_4]Br$ $\{[NBu_4Br]_{total} = 0$—15 mmol dm^{-3}}. Insert: variation of $k_{obs.}/[HBr]_{free}$ with $[HBr]_{free}$ ($[HBr]_{total} = 0$—14 mmol dm^{-3}) in the presence of $[NBu_4]Br$ $\{[NBu_4Br]_{total} = 0$ (△), 2.5 (○), and 10 mmol dm^{-3} (□)}. Curves drawn are those predicted by equation (6)

The kinetic data for the reaction of HX, in the presence of $[NBu_4]X$, with *trans*-$[Mo(N_2)_2(depe)_2]$ and *trans*-$[W(N_2)_2(depe)_2]$ are collected in Tables 4 and 5 respectively.

DISCUSSION

Kinetics and Mechanism of the Formation of Hydrazido(2−)*-complexes*.—The rate of formation of the hydrazido(2−)-complexes from *trans*-$[M(N_2)_2(depe)_2]$ and *trans*-$[M(N_2)_2(dppe)_2]$ in thf shows a marked dependence on the concentration and the nature of the acid (Table 3). This contrasts with the kinetics of substitution[8] and alkylation[9] of these same substrates, the mechanism of which occurs with rate-limiting unimolecular dissociation of dinitrogen $\{[Mo(N_2)_2(depe)_2]$, $k = 3.7 \times 10^{-6}$ s^{-1};[10] $[Mo(N_2)_2(dppe)_2]$, $k = 1.3 \times 10^{-4}$ s^{-1};[9] 20 °C}.

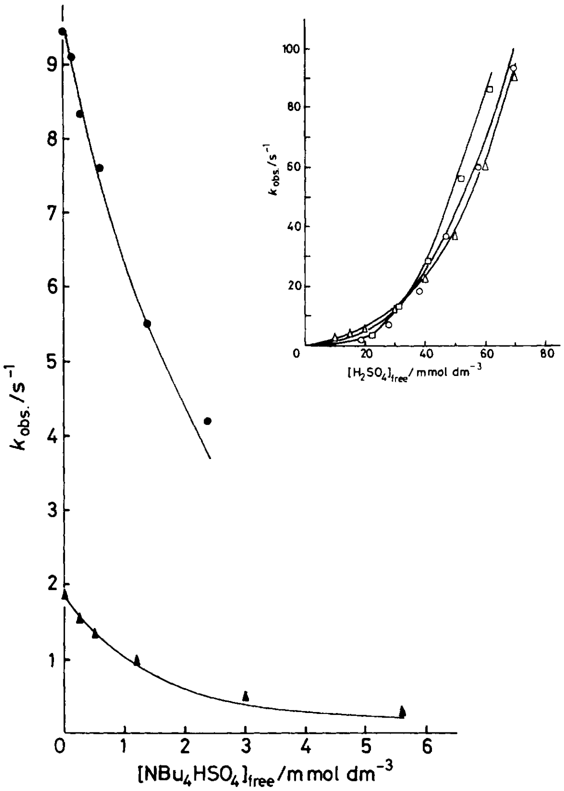


FIGURE 2 Inhibition of the reaction between H_2SO_4 $\{[H_2SO_4]_{total} = 15$ (▲) and 30 mmol dm^{-3} (●)} and *trans*-$[Mo(N_2)_2(depe)_2]$ by $[NBu_4]HSO_4$ $\{[NBu_4HSO_4]_{total} = 0$—15 mmol dm^{-3}}. Insert: variation of $k_{obs.}$ with $[H_2SO_4]_{free}$ ($[H_2SO_4]_{total} = 0$—20 mmol dm^{-3}) in the presence of $[NBu_4]HSO_4$ $\{[NBu_4HSO_4]_{total} = 0$ (△), 2.5 (○), and 10 mmol dm^{-3} (□)}. Curves drawn are those predicted by equation (11)

The dependence of the rate of formation of the hydrazido(2−)-complexes on the nature of the acid in thf contrasts sharply with that observed in the only other reported study of the mechanism of formation of a hydrazido(2−)-complex. In methanol *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ reacts with acids at a rate which shows a second-order dependence on the acid concentration but is independent of the nature of the acid ($M = Mo$, $k = 3.9 \times 10^5[H^+]^2$ dm^6 mol^{-2} s^{-1}).[11] This different behaviour in the two solvents is a consequence of the fact that in methanol HCl, HBr, and H_2SO_4 are all strong monobasic acids, whereas the weakly basic nature of thf ($pK_a = -2.05$)[12] results in HCl, HBr, and H_2SO_4 not being 'levelled'. Although no quantitative information is available about the strengths of acids in thf, it is expected that the order of acid strengths is the same as in acetonitrile ($HBr > H_2SO_4 > HCl$).[13]

To accommodate all the rate laws shown in Table 3 the mechanism of formation of hydrazido(2−)-complexes in thf is as shown in Scheme 1. An adduct (B) is initially

TABLE 4

Kinetics of the reaction of *trans*-$[\mathrm{Mo(N_2)_2(depe)_2}]$ and HX in the presence of $[\mathrm{NBu_4}]$X in thf at 25 °C *

Acid	[HX]/ mmol dm^{-3}	X in $[\mathrm{NBu_4}]$X	$[\mathrm{NBu_4X}]$/ mmol dm^{-3}	$k_{obs.}$/s^{-1}
HBr	5.00	Br	0.00	79
			1.25	42
			2.50	23
			5.00	10
			10.0	2.0
			15.0	0.6
HBr	7.50	Br	0.00	180
			1.25	124
			2.50	83
			5.00	45
			10.0	15
			15.0	8
HBr	4.00	Br	2.50	15
	6.00			45
	8.00			93
	10.0			174
	12.0			240
HBr	4.00	Br	10.0	0.7
	6.00			5
	8.00			22.5
	10.0			43
	12.0			90
	14.0			126
HBr	5.00	$\mathrm{BF_4}$	0.00	79
			1.25	74
			2.50	79
			5.00	75
			10.0	74
			15.0	73
$\mathrm{H_2SO_4}$	15.0	$\mathrm{HSO_4}$	0.00	1.9
			1.25	1.5
			2.50	1.3
			5.00	1.0
			10.0	0.6
			15.0	0.3
$\mathrm{H_2SO_4}$	30.0	$\mathrm{HSO_4}$	0.00	9.5
			1.25	9.1
			2.50	8.3
			5.00	7.6
			10.0	5.5
			15.0	4.2
$\mathrm{H_2SO_4}$	10.0	$\mathrm{HSO_4}$	2.50	0.5
	20.0			2.6
	30.0			7.6
	40.0			15.9
	50.0			37.4
	70.0			93.4
$\mathrm{H_2SO_4}$	10.0	$\mathrm{HSO_4}$	10.0	0.4
	20.0			1.4
	30.0			5.0
	40.0			12.0
	50.0			29.3
	70.0			86.0
$\mathrm{H_2SO_4}$	15.0	$\mathrm{BF_4}$	0.00	2.1
			1.25	1.9
			2.50	1.9
			5.00	2.3
			10.0	2.0
			15.0	1.8

* $[\mathrm{Mo(N_2)_2(depe)_2}]$ = 0.2 mmol dm^{-3}.

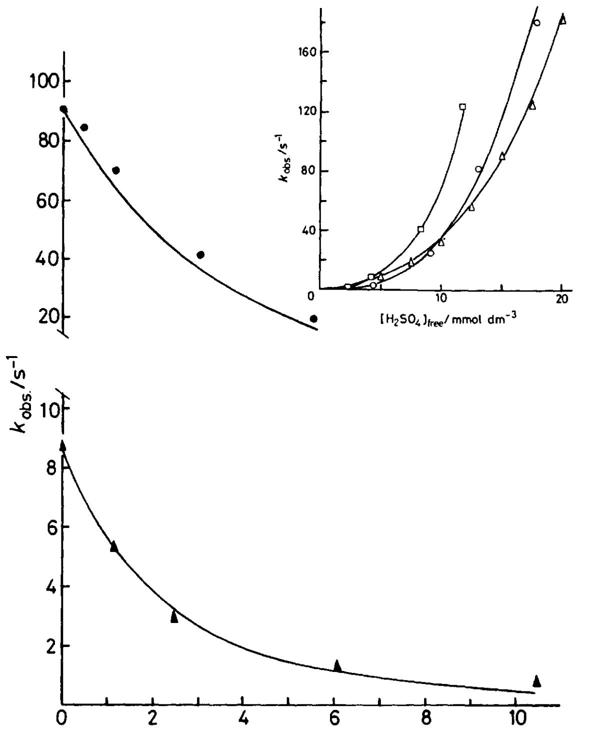


FIGURE 3 Inhibition of the reaction between $\mathrm{H_2SO_4}$ {$[\mathrm{H_2SO_4}]_{total}$ = 6 (▲) and 15 mmol dm^{-3} (●)} and *trans*-$[\mathrm{W(N_2)(depe)_2}]$ by $[\mathrm{NBu_4}]\mathrm{HSO_4}$ {$[\mathrm{NBu_4HSO_4}]_{total}$ = 0—15 mmol dm^{-3}}. Insert variation of $k_{obs.}$ with $[\mathrm{H_2SO_4}]_{,ee}$ ($[\mathrm{H_2SO_4}]_{total}$ = 0—20 mmol dm^{-3}) in the presence of $[\mathrm{NBu_4}]\mathrm{HSO_4}$ {$[\mathrm{NBu_4HSO_4}]_{total}$ = 0 (△), 2.5 (○), and 10 mmol dm^{-3} (□)}. Curves drawn are those predicted by equation (11)

TABLE 5

Kinetic data for the reaction between *trans*-$[\mathrm{W(N_2)_2(depe)_2}]$ and $\mathrm{H_2SO_4}$ in the presence of $[\mathrm{NBu_4}]\mathrm{HSO_4}$ in thf at 25 °C *

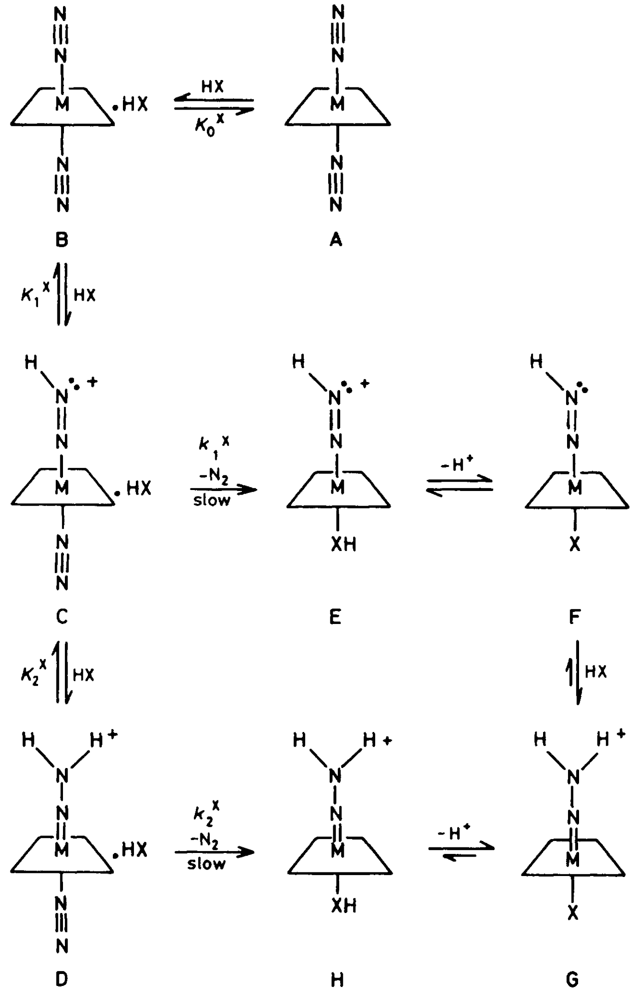
Acid	$[\mathrm{H_2SO_4}]$/ mmol dm^{-3}	X in $[\mathrm{NBu_4}]$X	$[\mathrm{NBu_4HSO_4}]$/ mmol dm^{-3}	$k_{obs.}$/s^{-1}
$\mathrm{H_2SO_4}$	6.00	$\mathrm{HSO_4}$	0.00	8.7
			2.50	5.3
			5.00	2.9
			10.0	1.4
			15.0	0.9
$\mathrm{H_2SO_4}$	15.0	$\mathrm{HSO_4}$	0.00	91
			2.50	85
			5.00	70
			10.0	43
			15.0	20
$\mathrm{H_2SO_4}$	5.00	$\mathrm{BF_4}$	0.00	7.0
			2.50	6.7
			5.00	6.7
			10.0	7.4
			15.0	7.9
$\mathrm{H_2SO_4}$	5.00	$\mathrm{HSO_4}$	2.50	5.0
	10.0			28.0
	15.0			81
	20.0			180
$\mathrm{H_2SO_4}$	5.00	$\mathrm{HSO_4}$	10.0	1.0
	10.00			8.7
	15.00			42
	20.0			123

* $[\mathrm{W(N_2)_2(depe)_2}]$ = 0.2 mmol dm^{-3}.

rapidly formed between the substrate A and HX. A dinitrogen group is then protonated by other molecules of HX and this labilises the remaining dinitrogen in C and D which is lost in the rate-limiting step. After the loss of the dinitrogen, the adduct molecule HX is now advantageously orientated to enter the co-ordination sphere, E and H. Subsequent rapid deprotonation of the co-ordinated HX (and, for E, rapid protonation of the diazenido-ligand) results in the hydrazido(2—)-complex (G).

The proposal that the loss of dinitrogen is rate-limiting is consistent with the absence of a primary isotope effect (Table 2) and the solution i.r. studies.

The mechanism in Scheme 1, and in particular the generation of the adduct B, rationalises some otherwise anomalous observations in this system. In particular the influence that $[NBu_4]X$ has on the kinetics, and the formation of metal hydrides under certain conditions, both of which will be discussed later. The third-order dependence on the concentration of acid in the reactions with H_2SO_4 is also indicative of this mechanism. It seems unlikely that this reflects a transition state involving the hydrazido(1—)-ligand ($N_2H_3^-$), since (from the stoicheiometry of the reaction) this would require that *trans*-$[M(N_2)_2(diphos)_2]$ is sufficiently basic to bind three protons, but upon substituting the *trans*-dinitrogen by the more electron-releasing hydrogensulphate anion a proton is released (!).



SCHEME 1 Phosphine ligands omitted for clarity

Assuming that the equilibria, prior to the rate-limiting dinitrogen dissociation, are rapidly established the rate law derived from the mechanism in Scheme 1 is given by equation (2).

$$k_{obs.} = \frac{K_0^X K_1^X k_1^X [HX]^2 + K_0^X K_1^X K_2^X k_2^X [HX]^3}{1 + K_0^X [HX] + K_0^X K_1^X [HX]^2 + K_0^X K_1^X K_2^X [HX]^3} \qquad (2)$$

Three limiting forms of equation (2) are of relevance to the discussion of the observed rate laws shown in Table 3. (*i*) If $K_0^X[HX]$, *etc.* <1 and K_2^X is negligible, $k_{obs.} = K_0^X K_1^X k_1^X [HX]^2$. This is the observed form when X = Br with *trans*-$[Mo(N_2)_2(depe)_2]$ and *trans*-$[Mo(N_2)_2(dppe)_2]$. (*ii*) If $K_0^X[HX]$, *etc.* <1 and K_2^X is detectable, $k_{obs.} = K_0^X K_1^X k_1^X [HX]^2 + K_0^X K_1^X K_2^X k_2^X [HX]^3$. This is the observed form when X = HSO_4 with all complexes and when X = Br with *trans*-$[W(N_2)_2(dppe)_2]$. (*iii*) If $K_0^X[HX] > 1$ and K_2^X is negligible; $k_{obs.} = K_1^X k_1^X [HX]$. This is the observed form when X = Cl with *trans*-$[W(N_2)_2(dppe)_2]$.

Influence of the Metal and Ligands on the Kinetics.—A clear feature of the data shown in Table 3 is that a given acid reacts with the tungsten complexes more rapidly than it does with the molybdenum analogues. Similar behaviour was observed in the study in methanol[11] ($k_W/k_{Mo} = 9 \times 10^2$). In thf this ratio is dependent both on the acid and the order of the reaction with respect to acid (n) $[(k_W/k_{Mo})_n = 29—85]$. This behaviour contrasts sharply with that observed in the alkylation and substitution reactions of *trans*-$[M(N_2)_2(dppe)_2]$ ($k_W/k_{Mo} \leqslant 0.01$)[8,9] and *cis*-$[M(N_2)_2(PMe_2Ph)_4]$ ($k_W/k_{Mo} = 0.021$).[10] The last two values reflect a decrease in lability to dissociation for dinitrogen on passing down Group 6. However, the larger ratio for the hydrazide-forming reaction is consistent with the mechanism shown in Scheme 1 but in which dinitrogen co-ordinated to tungsten is more basic than when it is co-ordinated to molybdenum $[K_1^X(W) > K_1^X(Mo)]$. The increased basicity of dinitrogen co-ordinated to tungsten is a consequence of the more electron-releasing nature of the heavier element.[14] This property is manifest in the rates of alkylation of *trans*-$[M(N_2R)X(dppe)_2]$ (R = alkyl)[10] and the observation that *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ can be protonated through to ammonia by methanol alone whereas the molybdenum analogue cannot.[15] Somewhat surprisingly the trimethylaluminium adduct of *trans*-$[M(N_2)_2(dppe)_2]$ is most extensively formed with the molybdenum complex;[16] however, this may reflect a stabilisation of the adducts by π donation to aluminium.

The increased reactivity of the complexes containing the depe ligand over their dppe analogues is a consequence of the greater basicity of the former ligand. Although the increased basicity results in a more tightly bound dinitrogen (decrease in k_1^X and k_2^X), it also increases the basicity of dinitrogen (increase in K_1^X and K_2^X). Clearly the latter effect dominates.

The Nature of the Adduct B.—Although the kinetic results strongly indicate the formation of the adduct B, there is no direct spectroscopic evidence for such an adduct. However, if B were an outer-sphere association of HX with the substrate A it would not be expected that the visible spectrum of the adduct should be very different to that of A. The outer-sphere association of electrophiles with neutral low-valent metal complexes has been observed before.[17] It seems most likely that the protic end of HX is most strongly attracted to either the electron-rich metal centre or one of the phosphorus atoms of the chelating diphosphine. However, it has previously been shown that van der Waals forces can be important in substitution reactions in methanol,[18] and certainly the lower dielectric constant of thf ($\varepsilon = 7.4$) [19] would encourage this association.

The formation of the adduct B may well assist the subsequent protonation(s) of dinitrogen by acids (which are rendered weak acids in thf), by attracting further HX molecules into close proximity with the substrate.

Although it is difficult to assess the influence that the associated molecule of HX has on the basicity of co-ordinated dinitrogen, the mechanism shown in Scheme 1 suggests that, for a given complex, increasing the acid strength will result in an increasingly dominant higher-order [HX] term. However, H_2SO_4 exhibits, a perhaps, anomalously dominant $[H_2SO_4]^3$ term. This may represent a contribution from an alternative pathway involving dissociation of dinitrogen from $\{[M(N_2H)(N_2)(depe)_2]\cdot 2H_2SO_4\}^+$ formed by the equilibria (3) and (4).

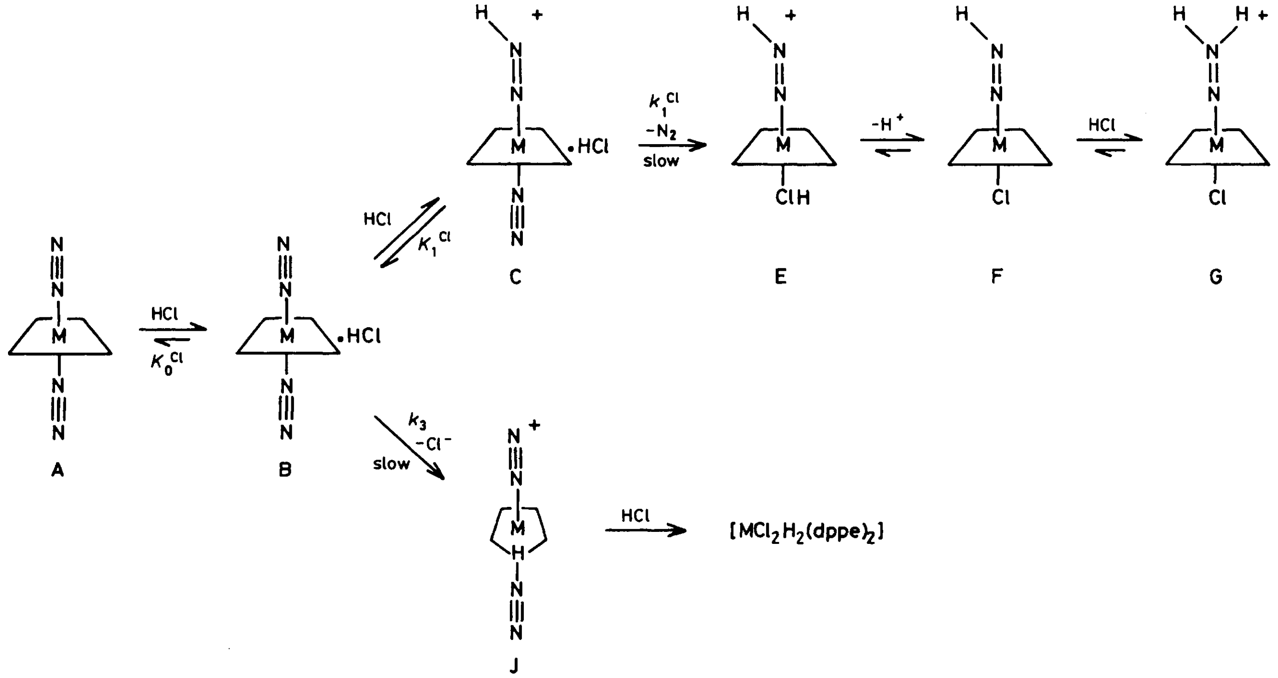
$$[M(N_2)_2(depe)_2]\cdot H_2SO_4 + H_2SO_4 \rightleftharpoons [M(N_2)_2(depe)_2]\cdot 2H_2SO_4 \quad (3)$$

$$[M(N_2)_2(depe)_2]\cdot 2H_2SO_4 + H_2SO_4 \rightleftharpoons \{[M(N_2H)(N_2)(depe)_2]\cdot 2H_2SO_4\}^+HSO_4^- \quad (4)$$

It is not possible, however, to assess the contributions from the various pathways.

Kinetics and Mechanism of Formation of Metal Hydrides.—It has previously been shown [6] that in thf the reaction of HCl with *trans*-$[M(N_2)_2(dppe)_2]$ can give rise to metal hydrides. In particular, there is the somewhat anomalous observation that, provided at least six equivalents of HCl are added to the tungsten complex, *trans*-$[W(NNH_2)Cl(dppe)_2]^+$ is obtained, but that if only two equivalents of HCl are added the seven-co-ordinate cation $[WH(N_2)_2(dppe)_2]^+$ is isolated. Treatment of this hydride with an excess of acid results in the loss of both dinitrogen ligands and formation of $[WH_2Cl_2(dppe)_2]$. These observations can now readily be rationalised in terms of the previously described mechanism.

As discussed above (and outlined again in the upper half of Scheme 2) the mechanism of formation of *trans*-$[W(NNH_2)Cl(dppe)_2]^+$ involves the extensive rapid formation of the adduct B, together with protonation of a dinitrogen prior to the rate-limiting dissociation of the remaining dinitrogen. This pathway exhibits a first-order dependence on [HCl] ($k_{obs.} = 3.2 \times 10^{-2}$ [HCl]). In contrast, the rate of formation of $[WH(N_2)_2(dppe)_2]^+$



SCHEME 2 Phosphine ligands omitted for clarity

[monitored by the solution i.r. band, ν(N–N) at 2 005 cm^{-1}] is independent of the concentration of acid ($k_{obs.} = 2.7 \times 10^{-3}$ s^{-1}) in the concentration range amenable to study ([HCl] = 40—150 mmol dm^{-3}). Thus, at low acid concentration the formation of [WH(N$_2$)$_2$(dppe)$_2$]$^+$, by intramolecular electrophilic attack of HX on the metal within the adduct B, is the faster of the two reactions. Upon increasing the concentration of acid, however, the reaction leading to *trans*-[W(NNH$_2$)Cl(dppe)$_2$]$^+$ soon becomes the dominant pathway. The observed concentrations of [WH(N$_2$)$_2$(dppe)$_2$]$^+$ (determined by solution i.r. spectroscopy) formed at various concentrations of HCl agree well with that calculated using the respective rate laws for the hydrazido(2—)- and hydrido-complexes (Table 6).

TABLE 6

Comparison of the spectroscopically measured [WH(N$_2$)$_2$(dppe)$_2$$^+$] with that calculated using the kinetic data

[W(N$_2$)$_2$(dppe)$_2$]/ mmol dm^{-3}	[HCl]/mmol dm^{-3}	[WH(N$_2$)$_2$(dppe)$_2$$^+$]/ mmol dm^{-3} Found	Calc.*
10	60	5.5	5.7
10	100	4.5	4.5
5	100	2.4	2.3
10	200	3.3	2.9
5	200	1.7	1.5
10	400	1.1	1.5
5	400	0.8	0.8

* Calculated using the rate laws: formation of hydride, $k_{obs.} = 2.7 \times 10^{-3}$ s^{-1}; formation of hydrazide, $k_{obs.} = 3.2 \times 10^{-2}$ [HCl] s^{-1}.

The reaction between *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] and HCl to yield [MoH$_2$Cl$_2$(dppe)$_2$] occurs at a rate independent of the concentration of acid ($k_{obs.} = 2.1 \times 10^{-2}$ s^{-1}) (provided [HCl] > 5[Mo]), but at a rate faster than the loss of dinitrogen dissociation from *trans*-[Mo(N$_2$)$_2$(dppe)$_2$] ($k_{obs.} = 1.3 \times 10^{-4}$ s^{-1}).[9] This behaviour is also consistent with rapid extensive formation of the adduct [Mo(N$_2$)$_2$(dppe)$_2$]·HCl (B) which then, like its tungsten analogue, undergoes intramolecular formation of [MoH(N$_2$)$_2$(dppe)$_2$]$^+$. The greater lability of the molybdenum complex results in the reaction proceeding rapidly through to [MoH$_2$Cl$_2$(dppe)$_2$].

The reasons why these hydrido-complexes are formed in the reactions of *trans*-[M(N$_2$)$_2$(dppe)$_2$] with HCl in thf, but not with other acids {no hydride could be detected by solution i.r. spectroscopy when two equivalents of HBr are added to *trans*-[W(N$_2$)$_2$(dppe)$_2$]}, is now readily rationalised. The adduct B is most extensively formed with HCl {*trans*-[W(N$_2$)$_2$(dppe)$_2$]; $K_0^{Cl} > 25$ dm^3 mol^{-1}, $K_0^{Br} < 20$ dm^3 mol^{-1}}, but protonation of the dinitrogen (K_1^{Cl}) is least extensive with this acid (HCl is the weakest acid of the three used in this study). Thus with HCl only, the alternative pathway involving electrophilic attack on the metal has the greatest opportunity to dominate, particularly at low concentration of acid. For *trans*-[W(N$_2$)$_2$(dppe)$_2$] the greater basicity of the dinitrogen ligands permits its protonation and the formation of the hydrazido(2—)-complex at high acid concentration.

Influence of [NBu$_4$]X *on the Kinetics of Formation of Hydrazido*(2—)*-complexes*.—The decreased rate observed upon the addition of [NBu$_4$]Br {[NBu$_4$Br]$_{total}$ = 1.25—15 mmol dm^{-3}} to the reaction between *trans*-[Mo(N$_2$)$_2$(depe)$_2$] (0.2 mmol dm^{-3}) and HBr ([HBr]$_{total}$ = 5 or 7.5 mmol dm^{-3}) (Table 4, Figure 1) is a consequence of the inhibition of the pathway(s) observed in the absence of [NBu$_4$]Br, and an additional slower, higher-order pathway catalysed by [NBu$_4$]Br. This dual role for the salt becomes more apparent when the effect of constant [NBu$_4$Br]$_{total}$ (2.5 or 10 mmol dm^{-3}) with varying [HBr]$_{total}$ (0—14 mmol dm^{-3}) on the rate is monitored (Figure 1, insert).

In solvents of low dielectric constant, such as thf, polar solutes tend to form aggregates, and a particular manifestation of this is the phenomenon of homoconjugation [equation (5)].[20] The data on the bromide

$$[NBu_4]X + HX \underset{}{\overset{K_3^X}{\rightleftharpoons}} [NBu_4]HX_2 \qquad (5)$$

system can be fitted by an iterative procedure to equation (6) where $S = 1 + K_3^{Br}[NBu_4Br]_{free} + K_3^{Br}$-

$$k_{obs.} = \frac{a[HBr]^2}{S^2} + \frac{b[HBr]^3[NBu_4Br]_{free}}{S^3} \qquad (6)$$

$K_4^{Br}[NBu_4Br]_{free}^2$, $a = 3.2 \times 10^6$ dm^6 mol^{-2} s^{-1} (obtained from the studies in the absence of [NBu$_4$]Br), $b = 1.2 \times 10^{11}$ dm^{12} mol^{-4} s^{-1}, $K_3^{Br} = 400$ dm^3 mol^{-1}, and $K_4^{Br} =$ 90 dm^3 mol^{-1}.

The first term of equation (6) describes the inhibition of the originally observed pathway by the homoconjugation equilibrium of equation (5), together with the additional association of equation (7). The second

$$[NBu_4]X + [NBu_4]HX_2 \overset{K_4^X}{\rightleftharpoons} [NBu_4]X\cdot[NBu_4]HX_2 \qquad (7)$$

term in equation (6) describes the new [NBu$_4$]Br catalysed pathway. The homoconjugation equilibrium will clearly lead to an inhibition of the original pathway(s) by effectively decreasing the concentration of HBr, and a new pathway is generated in which [NBu$_4$]HX$_2$ (RHX$_2$) associates with the substrate, *i.e.* equations (8)—(10).

$$[Mo(N_2)_2(depe)_2] + RHBr_2 \rightleftharpoons [M(N_2)_2(depe)_2]\cdot RHBr_2 \qquad (8)$$

$$[Mo(N_2)_2(depe)_2]\cdot RHBr_2 + HBr \rightleftharpoons \{[M(N_2H)(N_2)(depe)_2]\cdot RHBr_2\}^+Br^- \qquad (9)$$

$$\{[M(N_2H)(N_2)(depe)_2]\cdot RHBr_2\}^+Br^- + HBr \rightleftharpoons \{[M(N_2H_2)(N_2)(depe)_2]\cdot RHBr_2\}^{2+}\cdot 2Br^- \qquad (10)$$

The adduct of equation (8) gives rise to the higher-order pathway possibly by attracting more HBr into the solvation sphere of the substrate, equation (9), prior to the rate-limiting loss of dinitrogen from {[M(N$_2$H$_2$)(N$_2$)(depe)$_2$]·RHBr$_2$}$^{2+}$·2Br$^-$.

The reaction of *trans*-[Mo(N$_2$)$_2$(depe)$_2$] with H$_2$SO$_4$ is similarly affected by [NBu$_4$]HSO$_4$ and the data can be fitted to equation (11) (Table 4, Figure 2) where $T = 1 +$

$$k_{\text{obs.}} = \frac{a[H_2SO_4]^2}{T^2} + \frac{b[H_2SO_4]^3}{T^3} + \frac{c[H_2SO_4]^3[NBu_4HSO_4]_{\text{free}}}{T^3} \tag{11}$$

$K_3^{HSO_4}[NBu_4HSO_4]_{\text{free}}$, $a = 5.2 \times 10^3$ dm^6 mol^{-2} s^{-1}, $b = 2.0 \times 10^5$ dm^9 mol^{-3} s^{-1} (obtained from the studies in the absence of $[NBu_4]HSO_4$), $c = 7.8 \times 10^7$ dm^{12} mol^{-4} s^{-1}, and $K_3^{HSO_4} = 300$ dm^3 mol^{-1}. The first two terms of equation (11) represent the inhibition afforded to the originally observed pathways by the homoconjugation equilibrium and the last term represents the new $[NBu_4]HSO_4$ catalysed pathway.

Consistent with the inhibition being merely an association between H_2SO_4 and $[NBu_4]HSO_4$, and independent of the complex, the data for the analogous reaction with *trans*-$[W(N_2)_2(depe)_2]$ give an excellent fit (Table 4, Figure 3) using the same value of $K_3^{HSO_4}$. Equation (11) fitted using $a = 1.5 \times 10^5$ dm^6 mol^{-2} s^{-1}, $b = 1.7 \times 10^7$ dm^9 mol^{-3} s^{-1} (obtained from the studies in the absence of $[NBu_4]HSO_4$), and $c = 1.2 \times 10^{10}$ dm^{12} mol^{-4} s^{-1}.

Conclusions.—The mechanism of formation of hydrazido(2−)-complexes from the reaction between *trans*-$[M(N_2)_2(diphos)_2]$ and acid (Scheme 1) involves the formation of an adduct (B) and protonation(s) of a co-ordinated dinitrogen group (C and D) prior to the rate-limiting dissociation of the remaining dinitrogen.

The formation of metal hydrides in the reactions with HCl in thf is readily explained in terms of this mechanism. The fact that adduct B is most extensively formed with HCl, together with the weak acidity of HCl (inextensive protonation of dinitrogen), permits the competitive electrophilic attack on the metal to dominate, particularly at low concentrations of acid (Scheme 2).

EXPERIMENTAL

All manipulations in both the preparative and kinetic aspects of this work were routinely performed under dry dinitrogen, using standard Schlenk-tube and syringe techniques as appropriate.

Kinetic Measurements.—All kinetic measurements for fast reactions ($t_{\frac{1}{2}} < 10$ s) were made on an Aminco–Morrow stopped-flow apparatus, in conjunction with a linear logarithmic photometer and a Tektronix 549 oscilloscope. For the study of air-sensitive solutions the following modifications to the basic apparatus were necessary. (*i*) In order to stop aerial oxidation of the solutions in the drive syringes the drive-syringe pistons were modified so that a stream of dinitrogen gas flowed down a hole in the centre, and emerged from four holes drilled just behind the PTFE O ring. (*ii*) The compartment containing the Teflon tubing which connects the drive and stopping syringes to the mixing chamber was permanently flushed with dinitrogen.

The relatively slow reactions were monitored both by solution i.r. [monitoring the disappearance of $\nu(N_2)$ or appearance of ν(M–H)] on a Pye–Unicam SP2000 and by visible spectrophotometry on a Pye–Unicam SP1800 instrument.

All reactions were performed under pseudo-first-order conditions. The stopped-flow traces were photographed and curve-fitted by the method of Thorneley.[21] The rate constants were obtained from the slow reactions by the normal semi-logarithmic plot.[22]

Materials.—Hydrobromic acid (Reagent Grade, Hopkins and Williams) was redistilled under dinitrogen from barium bromide immediately prior to kinetic studies. Hydrochloric and sulphuric acids (A.R., B.D.H.) were used as received, as was $[N(C_4H_9)_4]Br$ (Lancaster Synthesis) and $[N(C_4H_9)_4]HSO_4$(Aldrich).

All solvents were dried and distilled immediately prior to use.

Preparation and Analysis of Solutions.—Stock solutions of acids were prepared in thf and these were used to make the more dilute solutions for the kinetic studies. However, it was found that HBr rapidly attacked thf, and thus solutions of this acid were prepared by the addition of a small aliquot to a known volume of thf. Stock solutions of anhydrous HCl were prepared by mixing equimolar amounts of trimethylsilyl chloride and methanol in thf. All acid solutions were used within 1 h of their preparation. The stock solutions of acids in thf were analysed by diluting an aliquot with water and then titrating against standard sodium hydroxide using phenolphthalein as indicator.

Preparation of Complexes.—The complexes *trans*-$[M(N_2)_2(dppe)_2]$,[23] *trans*-$[M(NNH_2)X(dppe)_2]X$ [X = Br, HSO_4, or Cl (W only)],[6] $[WH(N_2)_2(dppe)_2]HCl_2$,[6] and $[MoH_2Cl_2(dppe)_2]$ [6] were prepared by literature methods.

1,2-Bis(diethylphosphino)ethane (depe) was prepared by the method of Burt *et al.*[24] and *trans*-$[M(N_2)_2(depe)_2]$ by a modification of that of George and Noble [25] in which magnesium was used as the reductant {Found: C, 42.6; H, 8.8; N, 9.7. Calc. for $[Mo(N_2)_2(C_{20}H_{48}P_4)]$: C, 42.6; H, 8.5; N, 9.9%. Found: C, 37.0; H, 7.8; N, 8.5. Calc. for $[W(N_2)_2(C_{20}H_{48}P_4)]$: C, 36.8; H, 7.4; N, 8.6%}.

The complexes *trans*-$[M(NNH_2)Br(depe)_2]Br$ were prepared by the method of Chatt *et al.*[5] {Found: C, 34.6; H, 7.5; N, 4.1. Calc. for $[Mo(NNH_2)Br_2(C_{20}H_{48}P_4)]$: C, 34.3; H, 7.1; N, 4.2%. Found: C, 30.5; H, 6.0; N, 3.8. Calc. for $[W(NNH_2)Br_2(C_{20}H_{48}P_4)]$: C, 30.4; H, 6.3; N, 3.5%}.

Attempts to prepare *trans*-$[M(NNH_2)(HSO_4)(depe)_2]^+$ salts resulted only in the formation of oils. **CAUTION:** an attempt to isolate these complexes as the perchlorate salt resulted in a crystalline material which detonated upon mechanical shock.

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